Determination of the composition of kalsilites by an X-ray method.

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Summary.—Three new analyses of kalsilite are given, with optical and X-ray data; two $(K/(K+Na) = 0.95, 0.98)$ are from rocks where it is closely associated with nepheline. An analysis of one of the nephelines is also given $(K/(K+Na) = 0.31)$. The cell dimensions vary appreciably with sodium content, and the composition of kalsilite may be determined from the equation:

$$100 \, K/(K+Na) = 100 - 227.27(\Delta - 6.264),$$

where Δ is the difference, in degrees, between the diffraction angles 2θ for $10\bar{1}2$ and $10\bar{1}1$, using Cu-$K\alpha$ radiation.

THE variation of optical properties with chemical composition in the nepheline and kalsilite series is very slight. Accordingly, for determining the nepheline composition in petrographic rock description, optical methods will fail. On the other hand, a change in the ratio of potassium to sodium in nepheline is accompanied by a considerable change in the unit-cell dimensions. This fact offers a possibility for rapid determination of the nepheline composition by measuring the spacings of suitable powder diffraction lines. Such an X-ray method was successfully developed by Smith (1956) for synthetic materials and was later applied by Smith and Sahama (1954) to natural nephelines. This method allows a fairly accurate determination of the potassium content, expressed in atomic per cent, $100 \, K/(K+Na+Ca)$.

As in nepheline, powder diffraction data may be used for determining the ratio of potassium to sodium in kalsilite. In his paper mentioned above, Smith (loc. cit.) gives the difference in 2θ angle between the kalsilite lines $10\bar{1}2$ and $10\bar{1}1$. The measurements were made using copper radiation. No internal standard is needed. The difference, Δ, is

thus defined as follows: $\Delta = 2\theta_{(10\bar{1}2)} - 2\theta_{(10\bar{1}1)}$. The Δ-values were given by Smith for two synthetic kalsilite preparations that contained 90 and 100 % by weight $KAlSiO_4$, respectively. Assuming that the Δ-value varies linearly with the composition, these data may be used for determining the composition of kalsilite.

For natural kalsilite, the rarity of the mineral has, so far, made systematic measurements of Δ-values impossible. In literature, only three localities are known from which kalsilite has been studied physically and chemically: San Venanzo in Italy (Bannister, Sahama, and Wiik, 1953), Mafuru-Kyambogo crater in Uganda (Bannister and Hey, 1942; Sahama, 1954), and Nyiragongo area in the Belgian Congo (Sahama, 1953).

The last-mentioned area was visited by the authors in 1952. Kalsilite was found in one single flow that was later called the Kabfumu lava. In 1954 two of the authors (Th. G. S. and K. H.) paid a new visit to the Nyiragongo area and found several new localities with lavas containing kalsilite. Especially important in this connexion are the lavas of the extinct crater of Baruta, the great northern tributary of the active main crater of Mt. Nyiragongo. In Baruta several kalsilite-bearing rocks were found. Among the lavas collected, two specimens were selected from which kalsilite could be separated with heavy liquids, &c.

The availability of these two new kalsilite specimens made it possible to test the applicability of Smith's data for synthetic materials to natural kalsilite. For the petrology of the rare kalsilite-bearing lavas, like those of the Nyiragongo area, such a test is of a certain importance. The mode of occurrence of kalsilite in the Nyiragongo area will be described later by one of the authors (Th. G. S.) in the papers published by the Institut des Parcs Nationaux du Congo Belge in Brussels. In this paper only some physical and chemical data for kalsilite will be given.

The specimens.

The following specimens were available for the present study:

1. Synthetic kalsilite from blast-furnace lining. Original specimen investigated by Rigby and Richardson (1947) and Jay and Andrews (1947). The specimen, placed at the authors' disposal by Dr. G. R. Rigby, of the British Refractories Research Association, Stoke-on-Trent, was subjected to a heavy liquid separation with Clerici's solution and centrifuge. Of the purified material, virtually free of any contamination, a new chemical analysis was made by Dr. H. B. Wiik, of the Geological Survey of Finland, Helsinki. The result of the analysis (table

I) shows the material to be a pure kalsilite without any sodium component. The powder pattern[1] shows no foreign lines.

2. Specimen numbered S. 88. South-eastern part of the outer rim of Baruta crater, Nyiragongo area, Belgian Congo. The rock contains complex phenocrysts with kalsilite kernel and nepheline margin (fig. 1,
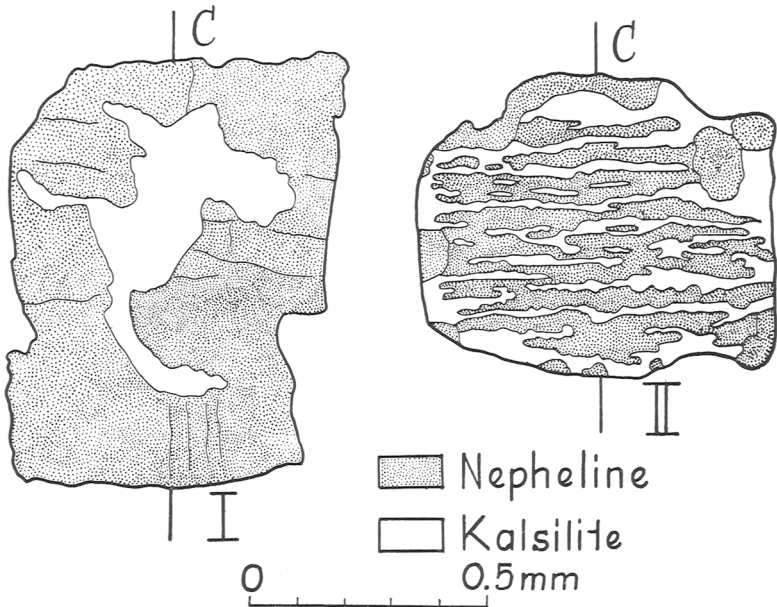

FIG. 1. Complex phenocrysts of nepheline and kalsilite in the lavas of Baruta crater, Nyiragongo area, Belgian Congo. I. Specimen S. 88. Kalsilite kernel surrounded by a nepheline margin. No sign of perthitic exsolution. II. Specimen S. 96 = M. 25. Perthitic exsolution of nepheline in kalsilite.

I). No sign of perthitic exsolution is visible. By a heavy liquid (Clerici's solution and centrifuge) and magnetic (Frantz-type isodynamic separator) separation, the complex phenocrysts were isolated from the rock, ground down to a grain size of c. 0·01 mm., and subjected to a final heavy liquid separation.

In the powder pattern of the best nepheline fraction the very sensitive kalsilite line $10\bar{1}2$ could not be traced. Accordingly, the kalsilite content of the material must be less than c. 1 % by weight. This nepheline material was analysed by Mr. Pentti Ojanperä of the Geological Survey

[1] The powder patterns used in this work were recorded with a Philips X-ray diffractometer ('Norelco') and copper radiation.

of Finland, Helsinki, with the following result: SiO_2 41·08, TiO_2 0·07, Al_2O_3 33·41, Fe_2O_3 0·96, FeO 0·18, MnO 0·01, MgO 0·13, CaO 0·18, Na_2O 14·02, K_2O 9·70, CO_2 0·00, H_2O+ 0·26, H_2O- 0·02, total 100·02. The analysis gives a composition of 31·1 atomic % K/(K+Na+Ca). Of the powder pattern, the lines $20\bar{2}2$ and $21\bar{3}0$ were measured. The results, $2\theta_{(20\bar{2}2)} = 29\cdot550°$ and $2\theta_{(21\bar{3}0)} = 27\cdot130°$, indicate a composition of 31·5 and 30·7 atomic % K/(K+Na+Ca), respectively. The composition deduced from the X-ray measurements is virtually identical with that calculated from the analysis. This fact represents a further proof of the purity of the nepheline analysed.

The powder pattern of the kalsilite fraction obtained in the separation showed the presence of the strongest nepheline lines. According to preliminary tests, 4 % by weight of nepheline in kalsilite could still be qualitatively detected with the apparatus used. The absence of all the nepheline lines from a powder pattern of kalsilite would, therefore, only indicate the nepheline contamination to be less than that amount. The amount of contamination in the low nepheline contents could, accordingly, not be accurately determined. For this reason, no attempt was made to remove nepheline from the kalsilite fraction completely. In the kalsilite material, intended for chemical analysis, enough nepheline was left behind to ensure accurate determination of its amount. It was found that, if more than 7 % nepheline is present in kalsilite, the intensities of the strongest nepheline lines are sufficient for a quantitative determination of the amount of nepheline contamination.

For quantitative determination of the amount of nepheline contamination in kalsilite, a series of standard mixtures was prepared of pure nepheline and pure kalsilite. The mixtures contained 7·0, 11·1, 15·0, 20·0, and 30·3 % by weight nepheline in kalsilite, respectively. All mixtures were thoroughly homogenized. Of each mixture, powder patterns were recorded six times. Between two runs the slide was slightly shifted so that a new spot came into the reflecting position. The intensities of nepheline $20\bar{2}2$ and of kalsilite $10\bar{1}3$ and $11\bar{2}1$ were measured in the chart. The intensities of all these lines were found to fall within the linear range of the recorder. The following intensity ratios were calculated and plotted against weight % nepheline in kalsilite: $I_{Ne(20\bar{2}2)}/$ $(I_{Ks(10\bar{1}3)}+I_{Ne(20\bar{2}2)})$ and $I_{Ne(20\bar{2}2)}/(I_{Ks(11\bar{2}1)}+I_{Ne(20\bar{2}2)})$. Six runs were made of the kalsilite material from specimen S. 88 as prepared for analysis; the averages of the above intensity ratios were calculated and the corresponding nepheline content read from the standard diagram. The results indicated a nepheline content of 9·2 and 10·8 % by weight,

respectively. The average, 10·0 % by weight, is believed to be correct within +1 %. Chemical analysis of the fraction made by Mr. Ojanperä gave the following results: SiO_2 38·68, TiO_2 0·06, Al_2O_3 31·20, Fe_2O_3 (total iron) 1·13, MnO 0·01, MgO 0·00, CaO 0·05, Na_2O 1·67, K_2O 26·42, CO_2 0·00, H_2O+ 0·63, H_2O- 0·07, total 99·92.

Now, knowing the composition and amount of nepheline in the kalsilite fraction of specimen S. 88 as well as the total composition of this fraction, the composition of the pure kalsilite phase may be calculated. The result is given in table I and is believed to be of an accuracy not far behind a direct chemical analysis.

3. Specimen numbered S. 96 = M. 25. Fallen block on the bottom of the Baruta crater, Nyiragongo area, Belgian Congo. The rock contains phenocrysts of kalsilite perthite (fig. 1, II) in which the perthitic structure is unusually coarse thus making a heavy liquid separation possible. As in the case of the previous specimen (S. 88), kalsilite could not be obtained in a pure fraction from specimen S. 96. Therefore, the amount and composition of the nepheline contamination was determined in the final material that had been accepted for chemical analysis and the result of the analysis was corrected for this nepheline contamination. The result of the chemical analysis made by Mr. Ojanperä is as follows: SiO_2 38·70, TiO_2 0·06, Al_2O_3 32·12, Fe_2O_3 (total iron) 0·98, MnO 0·01, MgO 0·00, CaO 0·03, Na_2O 3·85, K_2O 23·85, CO_2 0·00, H_2O+ 0·37, H_2O- 0·03, total 100·00. The intensity ratios of the powder lines of nepheline and kalsilite mentioned above in connexion with the previous specimen were calculated. The results indicate a nepheline content of 22·2 and 23·2 % by weight, respectively. The average, 22·7 % by weight, is again believed to be correct within ± 1 %. The 2θ angles of the nepheline lines $20\bar{2}2$ and $21\bar{3}0$ are: $2\theta_{(20\bar{2}2)} = 29\cdot560°$ and $2\theta_{(21\bar{3}0)} = 27\cdot145°$. These values correspond to 30·7 and 29·6 atomic % K/(K+Na+Ca) in nepheline. The average, 30·2 atomic % K/(K+Na+Ca), was adopted. According to these X-ray data, the composition of the nepheline contamination in the analysed kalsilite material of specimen S. 96 is very close to the composition of nepheline of specimen S. 88. Therefore, in correcting the analysis of the kalsilite material given above for the nepheline contamination, the nepheline phase was assumed to have a composition that is shown by the nepheline analysis of specimen S. 88. The composition of the kalsilite phase of specimen S. 96, corrected for nepheline contamination, is given in table I.

4. San Venanzo, Italy. Original specimen investigated by Bannister, Sahama, and Wiik (1953). Analysis reproduced in table I.

5. Kyambogo crater, Bunyaruguru field, Uganda. Original specimen investigated by Sahama (1954). Analysis reproduced in table I.

TABLE I. Chemical analyses of kalsilite.

	1. Synthetic.	2. Baruta S. 88.	3. Baruta S. 96.	4. San Venanzo.	5. Kyambogo FEAE 41.
SiO_2	37·89	38·48	37·98	38·47	38·50
TiO_2	0·19	0·05	0·05	0·00	0·09
Al_2O_3	32·60	31·01	31·73	30·81	26·27
Fe_2O_3	1·26	1·12*	0·98*	1·63	5·07
FeO	0·00	n.d.	n.d.	0·26	0·53
MnO	0·01	0·01	0·01	0·00	0·02
MgO	0·29	0·00	0·00	0·63	0·87
CaO	0·21	0·03	0·00	0·20	0·44
Na_2O	0·00	0·30	0·87	2·09	2·07
K_2O	27·88	28·33	27·99	25·65	24·85
H_2O+	0·00	0·67	0·40	0·20	1·04
H_2O-	0·00	—	—	0·00	0·05
Total	100·33	100·00	100·01	99·94	99·80

* Total iron as Fe_2O_3.

Physical properties.

The physical properties of the kalsilite specimens have been collected in table II. The unit-cell dimensions have all been converted from kX to Å. For the values of a and c not previously published, the uncertainties are given as estimated. The Δ-values are expressed in degrees. Each

TABLE II. Physical properties of kalsilite.

$\Delta = 2\theta_{(10\bar{1}2)} - 2\theta_{(10\bar{1}1)}$, using Cu-$K\alpha$ radiation.

	1. Synthetic.	2. Baruta S. 88.	3. Baruta S. 96.	4. San Venanzo.	5. Kyambogo FEAE 41.
Sp. gr.	n.d.	n.d.	n.d.	2·625	2·663
ϵ	1·532	1·533	1·534	1·537	1·550
ω	1·538	1·539	1·539	1·543	1·554
a	5·161*	5·161±0·004	5·160±0·002	5·151	5·165±0·003
c	8·702*	8·693±0·005	8·689±0·002	8·673	8·668±0·004
Δ	6·264°	6·274°	6·284°	6·317°	6·313°
$\dfrac{100\ K}{K+Na+Ca}$	100·0	98·3	95·0	88·5	87·6

* Determined by Jay and Andrews (1947).

Δ-value represents an average of six runs. With the same apparatus and following exactly the same procedure, the accuracy of the Δ-values is believed to be better than ±0·01°, probably of the order of ±0·005°.

This would correspond to an accuracy of 1 atomic % $K/(K+Na+Ca)$.

The unit-cell dimensions and the Δ-values of table II have been plotted against the composition in fig. 2. This figure includes also the following data for synthetic kalsilite given by Smith (1955): Ks_{100}, $a\ 5\cdot160\pm0\cdot002$,
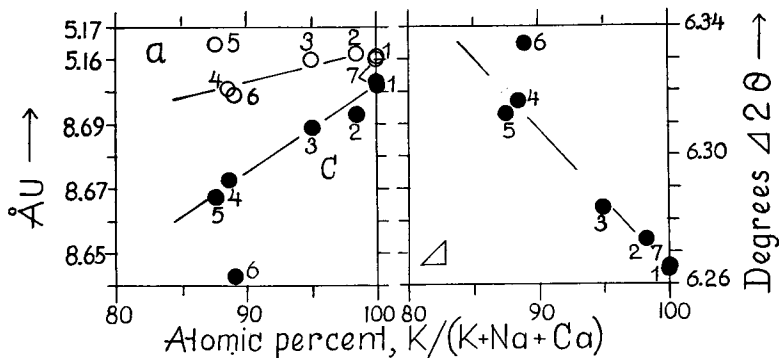

FIG. 2. Unit-cell dimensions and Δ-values for kalsilite plotted against composition. The numbers correspond to the specimens in table I. No. 6 denotes the synthetic kalsilite $Ks_{89\cdot0}$ and no. 7 the pure kalsilite Ks_{100} investigated by Smith.

$c\ 8\cdot703\pm0\cdot002$ Å., $\Delta\ 6\cdot265°$; $Ks_{89\cdot0}$,[1] $a\ 5\cdot149\pm0\cdot002$, $c\ 8\cdot643\pm0\cdot002$ Å., $\Delta\ 6\cdot335°$.

With a reasonable accuracy, the unit-cell dimensions vary linearly with the composition. There are, however, two exceptions. First, the a for the Kyambogo kalsilite is larger than presupposed by the linear relationship between a and composition. This deviation might be explained by the fact that the Kyambogo kalsilite has about 5 % Fe_2O_3 replacing Al_2O_3. Second, the value for c of the synthetic kalsilite $Ks_{89\cdot0}$ is low.

Dr. J. V. Smith informs us that there is some doubt about the purity of the two synthetic kalsilites. They were prepared from charges that had been originally crystallized at a high temperature. Recrystallization under hydrothermal conditions by Professor O. F. Tuttle gave a mixture of kalsilite and subordinate leucite. The presence of leucite shows that there has been loss of potassium in the charge. Loss of potassium would not change the K_2O/Na_2O ratio of the kalsilite prepared from a charge of original composition $Ks_{100}Ne_0$. Differential loss of potassium with respect to sodium could decrease the K_2O/Na_2O ratio of the kalsilite prepared from the charge of original composition $Ks_{90}Ne_{10}$. In accordance with this, the values of a and c obtained by Smith for the

[1] Corresponding to 90 % Ks (= $KAlSiO_4$) by weight.

soda-free kalsilite agree very closely with the other values obtained in this work whereas the value for the soda-containing synthetic kalsilite deviates in the direction of higher soda-content. There is no need to suppose that this deviation is a result of a difference in structure between natural and synthetic kalsilites, though this is a theoretical possibility, especially as there may be an order–disorder effect between the Si and Al atoms similar to that found in felspars.

Being the difference in reflection angles of the lines $10\bar{1}2$ and $10\bar{1}1$ for Cu-$K\alpha$ radiation, the Δ-value depends only on c. Accordingly, the Δ-value for synthetic kalsilite of composition $Ks_{89\cdot0}$ is off the straight line indicated in fig. 2. This straight line satisfies the equation $Ks = 100 - 227\cdot27\ (\Delta - 6\cdot264)$. In this equation, Ks denotes the atomic % K/ (K+Na+Ca) and Δ denotes the Δ-value measured for the kalsilite the composition of which is to be determined. This equation is recommended for determining the composition of kalsilite by X-rays. The scarcity of the data for natural kalsilite does not allow a statistical estimation of the accuracy of the method.

ADDENDUM.

Since this paper was written, Dr. J. V. Smith has very kindly tested the two soda-rich kalsilites, no. 4 (San Venanzo) and no. 5 (Kyambogo), for a possible nepheline contamination. The tests were made by step-counting on a diffractometer, counting for 5 minutes at angular spacings of $0\cdot025°$ in 2θ across the position of the strong nepheline peaks. To reduce the background scatter, a rotating specimen holder was used. Kalsilite no. 4 showed small peaks at 29·5, 27·0, and 22·9° which indicated the presence of small amounts of nepheline. On the other hand, kalsilite no. 5 was found to be free of nepheline. Dr. Smith also calculated the possible effect of iron on the lattice parameters. Taking the distances Si–O $= 1\cdot60$ Å., Al–O $= 1\cdot78$ Å., and Fe–O $= 1\cdot90$ Å., and assuming that all tetrahedral sites are filled and that the variation of the lattice parameters a and c is proportional to the size of the tetrahedra, he transformed our observed lattice parameters to calculated values for compositions with Si/Al $= 1$ and Fe $= 0$. He found the following calculated values:

	a	c	a^2c
Kalsilite no. 1.	5·158	8·697	231·39
2.	5·161	8·693	231·54
3.	5·157	8·684	230·95
4.	5·145	8·663	229·32
5.	5·153	8·648	229·63
Ks synthetic 100 %	5·160	8·703	231·72
Ks synthetic 89 %	5·149	8·643	229·15

The most accurate comparison should be with the values of a^2c. If these are plotted against atomic % $K/(K+Na+Ca)$, quite a good straight line may be drawn through the points; kalsilite no. 5 is a little high and Ks synthetic 89 % is a little low. It seems that the discrepancy between some of the data for kalsilites nos. 4 and 5 and, on the other hand, Ks synthetic 89 % may be resolved by invoking the operation of the three factors: change of composition of the synthetic preparation, iron content, or presence of nepheline. Accordingly, the equation for calculating the kalsilite composition given above might yield slightly too low values for the atomic % $K/(K+Na+Ca)$ in the range around 90 %. The authors are very grateful to Dr. Smith for this additional information.

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