STUDIES ON CANCRINITES: II—STABILITY FIELDS AND CELL DIMENSIONS OF CALCIUM AND POTASSIUM-RICH CANCRINITES

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ABSTRACT

Cancrinites of compositions $3NaAlSiO_4.CaCO_3$, $3NaAlSiO_4.Ca(OH)_2$, and $3NaAlSiO_4.K_2CO_3$ have been synthesized in the temperature range 200° C. to 800° C. at water vapour pressures of 10,000 p.s.i. to 30,000 p.s.i. Calcium-rich cancrinites are stable at the upper temperature and pressure limits of this study but potassium-rich cancrinites dissociate to nepheline and probably K_2CO_3 at 425–475° C. at these water vapour pressures. In addition the calcium-rich varieties have slightly smaller cell volumes than those of the potassium-rich type. These results are interpreted in terms of the inferred structure of cancrinites. Analcite ($NaAlSi_2O_6.H_2O$) was detected at low temperatures when synthesized from the calcium cancrinite starting materials and its presence is discussed in terms of three possible equations. The results obtained from the synthetic minerals are compared with those from three natural cancrinites.

INTRODUCTION

Compositions of the cancrinite family may be expressed by the general formula of $3NaAlSiO_4.R(CO_3,SO_4,Cl,OH).nH_2O$, where R = K, Na and Ca. In a previous paper, (Edgar & Burley, 1963) the sodium carbonate-rich cancrinite, termed by the authors natrodavyne, was discussed. This paper will be devoted to a discussion of the potassium carbonate, calcium carbonate and calcium hydroxide varieties of synthetic cancrinite. Table 1 gives the names and compositions of these cancrinite end-members. Slight modifications of both nomenclature and composition have been made from those given in Winchell & Winchell (1951). For example, the

TABLE 1. NAMES AND COMPOSITIONS OF CANCRINITE END-MEMBERS USED IN THE PRESENT STUDY

Name	Composition (after Winchell & Winchell, 1951)	Composition (Used in the present study)
Cancrinite proper	$3NaAlSiO_4.CaCO_3.(OH)_2$	$3NaAlSiO_4.CaCO_3$
Hydroxy cancrinite	—	$3NaAlSiO_4.Ca(OH)_2$
Davyne	$3NaAlSiO_4.(HKCO_3.KOH)$	$3NaAlSiO_4.K_2CO_3$ and $3NaAlSiO_4.KHCO_3$
Natrodavyne	$3NaAlSiO_4.(HNaCO_3.NaOH)$	$3NaAlSiO_4.Na_2CO_3$ and $3NaAlSiO_4.NaHCO_3$ and $3NaAlSiO_4.NaOH$

composition given by Winchell & Winchell for cancrinite proper has been divided into two separate end-members, one carbonate-rich and the other hydroxide-rich. These have been called cancrinite proper and hydroxy cancrinite, respectively. For the potassium carbonate-rich cancrinite, Winchell & Winchell's term "davyne" has been retained, although some authors, notably Hey (1955), claim that davynes always contain chlorine.

HISTORICAL INTRODUCTION

(a) Cancrinite

The name cancrinite was first used by Rose (1839) to describe a mineral from Miask in the Ural mountains. Analysis of this mineral showed its constituents to be SiO_2, Al_2O_3, CaO, Na_2O, K_2O and CO_2. During the following century, no fewer than twenty-one different compositions were termed cancrinite. Although there is very little agreement as to the formula of this mineral, the majority of analyses indicate that the mineral is rich in carbonate and contains sodium and calcium in excess of that required by the alumino-silicates. The amount of water which cancrinites can accommodate in their structures is also unknown, and most analyses of natural material show variable amounts (Deer, Howie & Zussman, 1963).

Thugutt (1892) analyzed a cancrinite from Brevig, Norway and concluded that the formula could be approximately written as $8Na_2Al_2Si_3O_{10}.3Na_2Al_3O_4.5CaCO_3.9H_2O$. In 1926, Larsen & Foshag reported an approximate formula of $3NaAlSiO_4.CaCO_3$ for a cancrinite from Iron Hill, Colorado and gave refractive indices of $\omega = 1.524$, $\epsilon = 1.501$. Gossner & Mussgnug (1930) examined cancrinite from the Miask locality and quoted the same formula as Larsen & Foshag. From x-ray measurements, these authors concluded that there were two molecules per unit with dimensions $a = 12.60$ Å, $c = 5.18$ Å.

Borgstrom (1930), reviewing the chemistry of the sodalite and cancrinite groups from the available analyses, concluded that the variable compositions of the cancrinite group were caused by isomorphous mixtures of calcium-rich cancrinite ($3Na_2Al_2Si_2O_8.2CaCO_3$) and sodium-rich cancrinite ($3Na_2Al_2Si_2O_8.Na_2CO_3$). A combination of the two molecules of the former to one of the latter produces the characteristic ratio $4Al_2O_3$:$8SiO_2$:$2CO_2$ found in many analyzed cancrinites.

Between 1931 and 1933 Kozu and co-workers published a series of papers on Korean cancrinite. Kozu (1931), describing a primary cancrinite in a sodalite nepheline syenite from Dodo, Korea, reported $\omega = 1.5238$, $\epsilon = 1.5015$: and cell dimensions of $a = 12.72$ Å, $c = 5.18$ Å. In a later paper, Kozu, Seto & Tsurumi (1932), the analysis of this cancrinite was shown to correspond to a formula of $2Na_2Al_2Si_2O_8.CaCO_3.H_2O$, based on one and one half molecules per unit cell. Kozu & Takane (1933) deduced the structure of this cancrinite and showed that sodium and calcium were probably not mutually replaceable as these atoms were on non-equivalent sites. Further work by Kozu, Ueda & Tsurumi (1933), using differential thermal analysis and thermo-balance techniques, indicated that around 900° C. internal deformation of the crystal took place due to loss of CO_2 and resulting in a transformation to a nepheline-type structure. Their experiments also indicated that the essential volatile constituents of this specimen were $-H_2O$, $+H_2O$ and CO_2.

Although Berman (1937) considered calcium to be a constituent of cancrinites, he believed that the cancrinite end-member did not contain this element and wrote its formula as $(Na,K)_{6-8}Al_6Si_6O_{24}(CO_3)_{1-2}.2—3H_2O$. From the most reliable analyses in the literature Berman suggested that there was a tendency for calcium to increase as sodium decreased, and also for the carbonate ion to increase with an increase in calcium.

Phoenix & Nuffield (1949) investigated a yellow cancrinite crystal from the Blue Mountain nepheline deposit, Methuen township, Ontario. Cell dimensions obtained from Weissenberg photographs gave $a = 12.60$ kX, $c = 5.12$ kX, and optical measurements gave $\omega = 1.515$, $\epsilon = 1.496$. The general formula computed from eight analyses and based on 24 oxygen atoms was:

$$(Na,K,Ca,Al)^{10}_{6-8}Si_6Al_6O^{6-}_{24}(SO_4,CO_3)^{4-}_{1-2}.1-5H_2O.$$

The present author investigated two cancrinite samples from the same locality, one a lemon-yellow, the other purplish-pink. The results of cell dimensions obtained on these samples are presented in a later section of this paper.

(*b*) *Davyne*

The name davyne was first used by Rauff in 1878 for a mineral from Vesuvius that contained a combination of calcium, sodium and potassium aluminosilicates together with calcium sulphate and sodium chloride. A survey of the literature shows that the formula of this mineral is extremely variable. Gossner (1925) gave the formula as $3[SiO_2.Na_2SiO_3.Al_2O_3].CaSO_4.CaCl_2$ and concluded that it was a double compound between hauyne and a hypothetical calcium sodalite. Niggli (1926) considered that davyne and microsommite were a combination of minerals similar to those of the hauyne group; the principal constituent of davyne being $3NaAlSiO_4.CaCl_2$ with substitution of $NaCl$ and Na_2SO_4 for $CaCl_2$. Gossner & Mussgnug (1930) determined cell dimensions of $a = 12.80$ Å, $c = 5.35$ Å from a davyne crystal from Monte Somma of unknown composition.

The literature of davyne and microsommite indicates that these minerals are varieties of cancrinite in which part or all of the carbonate has been replaced by chloride and sulphate. The substitution of sulphate for carbonate also suggests that these minerals may resemble the sulphatic cancrinites and wischnewites whose chemistry has been discussed by Beljankin (1931, 1944) and Stewart (1941). Although some authors trace a relationship between davyne and members of the sodalite family, particularly hauyne, no clear evidence has been cited as to whether this relationship occurs as solid solution or merely as a compositional similarity.

(*c*) *Synthetic cancrinites*

Eitel (1922), investigating the system $NaAlSiO_4 - CaCO_3$ under a carbon dioxide pressure of approximately 110 kg/cm^2, found that cancrinite of composition $3NaAlSiO_4 . CaCO_3$ melted incongruently at 1253° C.

To the author's knowledge, no synthetic work has been carried out on potassium carbonate or calcium hydroxide-rich cancrinites. Previous experimental work on sodium carbonate and sodium hydroxide-rich cancrinites has been summarized by Edgar & Burley (1963).

(*d*) *Summary of historical review*

Largely as a result of the multitude of published analyses, the name cancrinite has been applied to aluminosilicates, generally having the Al:Si ratios of 1:1, and containing varying amounts of the cations potassium, sodium and calcium; the acid radicals, carbonate, sulphate, chloride and water. In nature, the cancrinite end-member is often rich in carbonate, whereas davyne is rich in sulphate and chloride. Despite the fact that potassium carbonate-rich cancrinites are very uncommon in nature, the term davyne is being used in the present work for these varieties of cancrinite. This is in accordance with the terminology of Winchell & Winchell (1951), but does not agree with the nomenclature of other authors.

EXPERIMENTAL METHODS

Mixtures of the required compositions were prepared using "Analar" grade α-cristobalite, γ-alumina, Na_2SiO_3, and the necessary carbonates and hydroxides. The cancrinites were synthesized directly from the starting materials in pressure vessels of the type described by Tuttle (1949) and using the sealed tube technique of Goranson (1931). Temperatures were controlled by chromel-alumel thermocouples located near the lower ends of the pressure vessels, and are believed to be accurate to ±15° C. of the stated values. Pressure was maintained by a hand-operated hydraulic pump and measured by a Bourdon gauge, and is accurate to within ±500 p.s.i. of the stated values, during the duration of the experiments and to within ±1000 p.s.i. during the quenching of the sample.

All samples were run on a Philips *x*-ray diffractometer using filtered Cu radiation. Quartz was used as an internal standard for all determinations of lattice parameters. Full details of experimental methods are given in the first paper of this series (Edgar & Burley, 1963).

EXPERIMENTAL RESULTS

(a) Cancrinite proper ($3NaAlSiO_4.CaCO_3$)

Cancrinite proper failed to dissociate within the temperature and pressure limits of this study. At temperatures lower than 250° C., at water vapour pressures of 10,000 to 25,000 p.s.i., cancrinite, analcite and calcite were synthesized directly from starting material of cancrinite proper composition; and at temperatures lower than 450° C., in the pressure range 10,000 to 20,000 p.s.i., cancrinite, analcite and $Ca(OH)_2$ were synthesized directly from the hydroxy cancrinite starting material. These phases were not detected in runs made with the davyne composition. At higher temperatures, these additional phases were not found, and it is presumed that some of them form metastably at the lower temperatures. However, increasing the duration of the experiment by a factor of three, failed to eliminate any of the additional phases; thus it cannot be determined which phases are metastable.

The indexed *d* spacings of synthetic cancrinite proper are given in Table 2. The cell dimensions of this variety of cancrinite are $a = 12.59 \pm .02$ Å, $c = 5.17 \pm .02$ Å and a resulting cell volume of 710 ± 5 Å^3.

TABLE 2. INDEXED "*d*" SPACINGS OF SYNTHETIC CANCRINITE
Radiation = Cu$K\alpha$, Filter = Ni, Internal Standard = Quartz

Cancrinite proper			Hydroxy cancrinite		
d	*I*(visual)	*h k.l*	*d*	*I*(visual)	*h k.l*
6.35	35	11.0	4.63	40	10.1
4.65	65	10.1	3.641	25	30.0
3.649	40	30.0	3.211	100	21.1
3.217	100	21.1	2.999	15	31.0
3.035	15	31.0	2.731	40	40.0
2.923	7	30.1?	2.603	25	31.1
2.735	20	40.0	2.571	40	00.2
2.611	15	31.1	2.411	20	40.1
2.564	15	00.2	2.101	15	33.0
2.503	5d	32.0	1.867	5d	40.2
2.411	12	40.1	1.747	5d	41.2
2.162	5d	41.1	1.504	5d	44.1
2.101	12	33.0	1.492	7d	53.1
1.870	5	40.2	1.319	5d	42.3
1.791	5d	43.0	1.152	5d	53.3
1.745	5	52.0			
1.582	5d	61.1			
1.562	5	51.2			
1.492	5vd	53.1			
1.082	1	54.3			

d, diffuse
vd, very diffuse

(b) Hydroxy cancrinite $3NaAlSiO_4.Ca(OH)_2$

Cancrinite of this composition also failed to dissociate at the upper temperature limit of this study (800° C.). Although the composition of this cancrinite is represented as containing no carbonate ion, it is almost certain that minor $CaCO_3$ is present in the starting material, and hence in the synthesized phase, due to reaction of the calcium ion with CO_2 in the atmosphere.

The indexed *d* spacings of this cancrinite end-member are given in Table 2. Cell dimensions are $a = 12.60 \pm .02$ Å, $c = 5.14 \pm .02$ Å and a cell volume of 707 ± 5 Å^3. These results are not significantly different from those of cancrinite proper.

(c) Davyne ($3NaAlSiO_4.K_2CO_3$)

Davyne dissociates into nepheline and possibly K_2CO_3 between 450° C. and 500° C. in the water vapour pressure range of 15,000 p.s.i. to 30,000 p.s.i.; and between 425° C. and 450° C. at a water vapour pressure of 10,000 p.s.i. Because of the large temperature deviation from the stated values, no attempt was made to narrow these temperature limits. The experimental data are given in Table 3 and plotted in Figure 1. Both

TABLE 3. EXPERIMENTAL DATA FOR DAVYNE ($3NaAlSiO_4.K_2CO_3$)

Run No.	Water Vapour Pressure (in p.s.i.)	Temperature (°C.)	Time (hrs)	Phases
D14X	10,000	500	232	Nepheline
D21X	25,000	450	186	Davyne
D24X	15,000	400	100	Davyne
D28X	15,000	600	100	Nepheline
D33X	20,000	450	50	Davyne
D36X	15,000	600 for 400 for	68 76	Nepheline and minor Davyne?
D47X	10,000	500	190	Nepheline
D49X	20,000	500	122	Davyne and Nepheline
D51X	20,000	250	162	Davyne
D57X	10,000	450	188	Nepheline
D58X	10,000	400	188	Davyne
D62X	30,000	500	95	Nepheline
D46X	30,000	400	95	Davyne
D65X	20,000	550	148	Nepheline
D68X	15,000	550	144	Nepheline
D69X	10,000	425	195	Davyne and very minor Nepheline
D71X	15,000	500	145	Nepheline
D73X	20,000	650 for 575 for 500 for 400 for	72 13 11 70	Nepheline
D84X	25,000	500	126	Nepheline
D85X	25,000	550	126	Nepheline

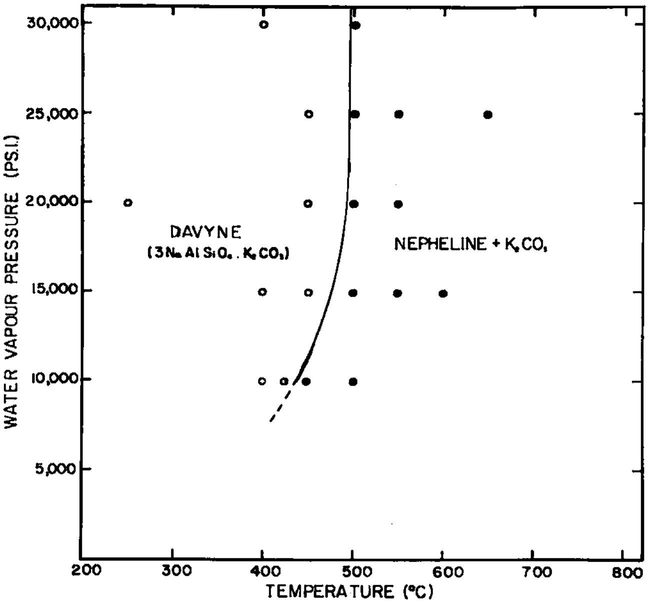

FIG. 1. Dissociation curve for davyne between 10,000 p.s.i.–30,000 p.s.i. water vapour pressure.

optical and *x*-ray examinations indicate that nepheline is the only phase present. The absence of K_2CO_3 is explained in a later section.

The *d* spacings of davyne are given in Table 4. The cell dimensions are $a = 12.73 \pm .02$ Å, $c = 5.18 \pm .02$ Å and a cell volume of 727 ± 5 Å^3.

TABLE 4. INDEXED "d" SPACINGS OF SYNTHETIC DAVYNE
Radiation = Cu*K*α, Filter = Ni, Internal Standard = Quartz

d	*I*(visual)	*h k.l*	*d*	*I* (visual)	*h k.l*
4.70	50	10.1	2.436	15	40.1
3.979	50	11.1	2.353	15	20.2
3.672	35	30.0	2.178	10d	41.1
3.251	70	21.1	2.033	5	50.1
3.115	100	31.0	1.931	5d	42.1
2.997	10	30.1	1.621	7	42.2
2.754	20	40.0	1.572	7d	53.0
2.579	40	00.2	1.489	10	43.2

The substitution of $KHCO_3$ for K_2CO_3 in this composition produces a phase with almost identical *d* spacings and stability.

Discussion of Results

The results presented here and in the previous paper (Edgar & Burley, 1963) show that the stability fields and cell parameters of the synthetic cancrinites investigated vary in a systematic manner. If the end-members proposed by Winchell & Winchell (1951) are taken as approximations of the compositions found in natural cancrinites, the results indicate that the dissociation (and transformation) temperatures and cell parameters of these mineral molecules depend largely on the cations in the non-silicate portion of the formula. The influence of composition on the cancrinite stability fields and cell parameters is more fully discussed below.

The presence of analcite at low temperatures in some of the cancrinite compositions is also discussed in terms of three postulated equations. It is not known whether the analcite or cancrinite is metastable, as runs of fairly long duration failed to promote the disappearance of either phase.

Although no exhaustive attempts were made, reversibility of reaction across the boundary curve was attained only in the sodium carbonate-rich cancrinite composition, discussed in the previous paper. In view of this, it is not known whether the curves represent equilibrium conditions.

(a) Influence of composition on stability fields

The dissociation or transformation temperatures of the six cancrinites synthesized are given in Table 5. Potassium-rich cancrinites dissociate at approximately 150° C. lower than the polymorphic transformation temperature of the sodium-rich cancrinites under the same water vapour pressure conditions; and at a temperature of at least 325° C. lower than the calcium-rich cancrinites may dissociate or melt. It is not known, from

Table 5. Cell Dimensions and Dissociation Temperature of Synthetic Cancrinites

		Cell dimensions			
Name	Composition	a(Å)	c(Å)	Vol(Å)^3	Temperature at P_{H_2O} = 20,000psi
Cancrinite proper	$3NaAlSiO_4.CaCO_3$	12.59	5.17	710	Greater than 800°C
Hydroxy cancrinite	$3NaAlSiO_4.Ca(OH)_2$	12.60	5.14	707	Greater than 800°C
Natrodavyne	$3NaAlSiO_4.Na_2CO_3$	12.67	5.18	720	polymorphic transformation to a cubic nosean type mineral at 600°C.–650°C.
	$3NaAlSiO_4.NaHCO_3$	12.67	5.16	717	
Davyne	$3NaAlSiO_4.K_2CO_3$	12.73	5.18	727	450°C.–500°C.
	$3NaAlSiO_4.KHCO_3$	12.73	5.20	728	450°C.–500°C.

Note: Cell dimensions are believed to have an accuracy of ±0.02Å and cell volumes of ±5Å^3.

the present investigation, whether calcium-rich cancrinites dissociate to nepheline and calcite or melt directly to a liquid. The substitution of the carbonate radical in cancrinite proper by the hydroxyl radical in hydroxy cancrinite does not promote dissociation of the calcium-rich cancrinite, nor does the substitution of the bicarbonate radical for the carbonate radical in potassium and sodium-rich cancrinites alter their stability fields.

Cancrinite proper and hydroxy cancrinite failed to dissociate even at the upper temperature limit of this investigation (800° C.). Several unsuccessful attempts were made to promote dissociation of cancrinite proper by adding small amounts of potassium, as KOH. The upper temperature limit of cancrinite proper, synthesized under water vapour pressure, is not known. However, Eitel (1922), in his investigation of the system nepheline-calcite using a CO_2 pressure of approximately 110 kg/cm^2, gives the incongruent melting temperature of cancrinite as 1253° C., but it is probably lower than this under higher water vapour pressure and CO_2 pressure conditions. Kozu, Ueda & Tsurumi (1933) using differential thermal analysis techniques at atmospheric pressure on a natural specimen of similar composition to the synthetic cancrinite proper, suggested that the dissociation temperature is around 900° C. The difference in dissociation temperature between calcium carbonate cancrinite and potassium carbonate cancrinite may be as low as 400° C. or as high as 700° C.

(b) Influence of composition on cell parameters

The cell parameters and cell volumes of the various synthesized cancrinites are given in Table 5. These results indicate a definite variation cell dimensions with composition. Of the carbonate varieties, the potassium-rich davyne has the largest cell volume; the sodium-rich natrodavyne, an intermediate cell volume; and the calcium-rich cancrinite proper, the smallest cell volume. Substitution of the bicarbonate radical for the carbonate radical in davyne and natrodavyne produces only very minor changes in the cell parameters. Substitution of the hydroxyl radical for the carbonate radical in hydroxy cancrinite produces no significant change in cell volume. However it is considered justifiable to separate the hydroxide end-member from the calcium carbonate end-member, as both compositions produce a cancrinite-type mineral. There is good evidence that synthetic sodium hydroxide cancrinites exist (Barrer & White, 1952), and there is a strong possibility that potassium hydroxide cancrinites can also be synthesized.

The major changes in cell volumes are produced by variation in the cations rather than by the carbonate, bicarbonate and hydroxyl radicals. If the cancrinites have a framework type structure, with open voids capable of accommodating the potassium, sodium and calcium that are combined with the acid radicals, it is reasonable that potassium-rich cancrinites have the largest cell volumes as the ionic radius of potassium is larger than that of sodium and calcium. This, however, does not explain why sodium-rich cancrinites have larger cell volumes than calcium-rich cancrinites as these elements have very similar ionic radii. One possible explanation is that the sodium carbonate variety has a slightly different structure from the other varieties or that the sodium atoms occupy different sized sites as is the case in nepheline (Smith & Tuttle, 1957). A complete explanation of cell volume variation with composition cannot be given until the structure of cancrinite is more definitely established.

(c) Presence of analcite at low temperatures

At low temperatures, analcite, a cancrinite, and the appropriate carbonate or hydroxide, were synthesized from starting minerals of both cancrinite proper and hydroxy cancrinite compositions. Considerations of the phase rule indicate that one or more of the solid phases must be metastable as it is impossible that three stable solid phases can form from the stoichiometric composition of a third phase when that phase is also present. For the cancrinite proper composition, ($3NaAlSiO_4 . CaCO_3$), the following theoretical equations can be postulated to explain this analcite:

(1) 1 cancrinite proper mix + $nH_2O \rightarrow$ 1 analcite + 1 nepheline + $\frac{1}{2}$ ($Na_2O . Al_2O_3$) + 1 calcite $\xrightarrow{\text{ca. } 250^\circ \text{ C.}}$ 1 cancrinite proper, i.e. ($1\frac{1}{2}\ Na_2O + 1\frac{1}{2}\ Al_2O_3 + 3SiO_2 + CaCO_3) + nH_2O \rightarrow (NaAlSi_2O_6 . H_2O) + (NaAlSiO_4) + \frac{1}{2}\ (Na_2O . Al_2O_3) + CaCO_3 \xrightarrow{\text{ca. } 250^\circ \text{ C.}} 3NaAlSiO_4 . CaCO_3$

(2) 1 cancrinite proper mix + $nH_2O \rightarrow$ 1 analcite + $\frac{1}{3}$ cancrinite proper + $\frac{2}{3}$ calcite + $\frac{1}{2}$ ($Na_2O . Al_2O_3$) $\xrightarrow{\text{ca. } 250^\circ \text{ C.}}$ 1 cancrinite proper, i.e. ($1\frac{1}{2}\ Na_2O + 1\frac{1}{2}\ Al_2O_3 + 3SiO_2 + CaCO_3) + nH_2O \rightarrow (NaAlSi_2O_6 . H_2O) + \frac{1}{3}(3NaAlSiO_4 . CaCO_3) + \frac{1}{2}\ (Na_2O . Al_2O_3) \xrightarrow{\text{ca. } 250^\circ \text{ C.}} 3NaAlSiO_4 . CaCO_3$

(3) 1 cancrinite proper mix + $nH_2O \rightarrow$ 1 analcite + 1 nepheline + $\frac{1}{2}$ ($CaAl_2O_4$) + $\frac{1}{2}$ (Na_2CO_3) + $\frac{1}{2}$ calcite $\xrightarrow{\text{ca. } 250^\circ \text{ C.}}$ 1 cancrinite proper, i.e. ($1\frac{1}{2}\ Na_2O + 1\frac{1}{2}\ Al_2O_3 + 3SiO_2 + CaCO_3) + nH_2O \rightarrow (NaAlSi_2O_6 . H_2O) + (NaAlSiO_4) + \frac{1}{2}\ (CaAl_2O_4) + \frac{1}{2}\ (Na_2CO_3) + \frac{1}{2}\ (CaCO_3) \xrightarrow{\text{ca. } 250^\circ \text{ C.}} 3NaAlSiO_4 . CaCO_3$.

Of these three equations, the second one would appear to fit more closely the experimental reaction as no nepheline was detected in the x-ray patterns containing analcite. In the cancrinite proper compositions analcite, cancrinite and calcite were detected. The compound $Na_2O . Al_2O_3$ (sodium aluminate) was not observed and it is likely that this material, being very soluble in water, is removed in solution when the capsules are opened. Even in dried charges, in which the sodium aluminate should precipitate, the relatively minor amounts could not be detected by x-ray diffraction methods. Corresponding equations can be written for the hydroxy cancrinite compositions.

(d) Identification of products

In hydrothermal experiments, there is often an uncertainty in the composition of the phases produced. This problem is one that cannot be readily solved as analysis of the small amounts of synthesized products is not usually feasible. In this study all products were examined by *x*-ray diffraction methods and representative samples by optical methods.

In potassium carbonate and bicarbonate cancrinites, the dissociation products consisted of only nepheline, even in experiments that had taken place in sealed capsules. There are several possible explanations of this. First, the K_2CO_3 and $KHCO_3$, both being soluble in water, may be removed in solution on opening the capsule, but would precipitate in the dried charge and be detected by both methods. Second, the K_2CO_3 and $KHCO_3$, being in rather minor amounts compared to the nepheline, might not appear on the *x*-ray patterns. Third, the potassium of the K_2CO_3 and $KHCO_3$ might enter the nepheline structure and the CO_2 escape as a gas when the capsule is opened. Fourth, the carbonate and bicarbonate dissociation products may be present as glasses and therefore not appear on the *x*-ray patterns. Potassium bicarbonate melts at 200° C. at atmospheric pressure and K_2CO_3 is one of the few carbonates that can be quenched to a glass (Dr. J. Gittins—personal communication).

Each of these possibilities was examined experimentally. A mixture of nepheline and K_2CO_3, in the same proportions as found in the cancrinite, was *x*-rayed and it was found that the resulting *x*-ray pattern contained both nepheline and K_2CO_3 peaks, suggesting that the first and second hypotheses are unlikely. The possibility of potassium entering into the nepheline structure is unlikely as the *x*-ray patterns of the nepheline product were the same as those of pure synthetic nepheline, and it is known that the presence of potassium in nephelines causes a measurable shift in *d* spacings (Smith & Tuttle, 1957). Optical examination of the dissociation products of the potassium-rich cancrinites showed the presence of some glass. Therefore, the most likely explanation for the absence of K_2CO_3 and $KHCO_3$ in the dissociation products of potassium carbonate cancrinites is that they are present as glasses.

(e) Geological implications

Cancrinites of seven different compositions have been synthesized during the course of this investigation. These are:—$3NaAlSiO_4.CaCO_3$ (cancrinite proper), $3NaAlSiO_4.Ca(OH)_2$ (hydroxy cancrinite), $3NaAlSiO_4.K_2CO_3$ and $3NaAlSiO_4.KHCO_3$ (davyne), $3NaAlSiO_4.Na_2CO_3$ and $3NaAlSiO_4$.

$NaHCO_3$ (natrodavyne), and $NaAlSiO_4.xNaOH$. The latter three compositions have been reported in the first part of this study (Edgar & Burley, 1963). These results are in agreement with the analyses of natural cancrinites which have a wide range of composition.

The stability data indicate that the common varieties of cancrinite, namely the calcium carbonate and the sodium carbonate end-members are moderately high temperature minerals. The calcium carbonate and potassium carbonate varieties are reaction products of nepheline and the appropriate carbonate. This was verified for the calcium carbonate cancrinite in one experiment in which natural nepheline and calcite were found to synthesize cancrinite at 600° C. and 15,000 p.s.i. water vapour pressure. Natural cancrinites are commonly found in close association with nepheline and carbonate bearing rocks, and cancrinites have been reported by many investigators as forming "reaction rims" around nepheline grains (c.f. Pirsson & Washington, 1907; Larsen & Foshag, 1926). The possibility of using the compositions of natural cancrinites as a basis for a geological thermometer would require extensive experimental work, as the cancrinite compositions used in the present study are only theoretical end-members and probably never occur in nature with these simple compositions.

Although analcite and cancrinite are often found in close association to the author's knowledge, no relationship between these minerals has been recorded. Analcite has been reported as a possible secondary mineral after sodalite by Labuntzov (1927) who proposes the reaction:—

$$2\ \text{sodalite} + nH_2O \rightarrow 3\ \text{analcite} + 3(Al_2O_3.nH_2O) + 4\ \text{halite} + 6\ NaOH$$

This mechanism differs from that proposed for the presence of analcite in the synthetic cancrinite systems.

RESULTS OBTAINED FROM NATURAL CANCRINITES

In conjunction with the studies of the synthetic minerals, four specimens of natural cancrinite were examined. Unfortunately, none of these specimens had been analyzed and consequently their compositions are unknown.

Three cancrinites and a sulphatic cancrinite were investigated. The first specimen was a lemon-yellow cancrinite from the alkaline complex of Red Hill, New Hampshire. Cancrinite from this locality has been described as an alteration product of sodalite by Quinn (1937). The second and third specimens are from the Blue Mountain nepheline syenite of Methuen Township, Ontario. One of the specimens from this locality is yellow, the other a purplish-pink. Phoenix & Nuffield (1949) have described a cancrinite from the same locality. The fourth specimen was a sulphatic cancrinite from the Allt a' Mhuillin pegmatites, Loch Borolan, Scotland. Stewart (1941) has described this specimen and has shown that it has quite different chemical and optical properties from the common carbonate cancrinites.

Unsuccessful attempts were made to dissociate the New Hampshire specimens within the temperature and pressure limits of this study. The cell parameters of this specimen, obtained by powder methods, were $a = 12.60 \pm .02$ Å, $c = 5.12 \pm .02$ Å. These values are very similar to those of the synthetic calcium carbonate cancrinite.

Both of the Ontario cancrinites have the same cell parameters ($a = 12.60 \pm .02$ Å, $c = 5.14 \pm .02$ Å) and these are similar to the New Hampshire specimen. They agree closely with the parameters obtained from single crystal studies by Phoenix & Nuffield (1949). It was thought that the difference in colour between the two Ontario samples from the same locality might be caused by a difference in trace element content. A semi-quantitative spectographic analysis showed that, with the exception of manganese, the trace element content of both specimens was similar.

The sulphatic cancrinite gave slightly larger cell dimensions than the other varieties with $a = 12.68 \pm .02$ Å, and $c = 5.18 \pm .02$ Å.

CONCLUSIONS

A number of different cancrinite compositions have been synthesized and their cell parameters determined in the temperature range 200° C. to 800° C. and at water vapour pressure of 10,000 p.s.i. to 30,000 p.s.i. Of five carbonate and bicarbonate-rich varieties, the potassium-rich cancrinites (davynes) dissociate at the lowest temperatures, whereas the calcium-rich cancrinite (cancrinite proper) is stable at the upper temperature limit of this investigation. Sodium-rich cancrinites (natrodavynes) undergo a polymorphic transition into a cubic form similar in structure to the nosean-hauyne group at a temperature about 100° C. higher than the dissociation temperature of potassium-rich cancrinites. Replacement of the carbonate radical by the hydroxide radical in calcium-rich cancrinites does not promote dissociation. Analcite and a carbonate or hydroxide, in addition to cancrinite, are also present at low temperatures in some of the cancrinite compositions, but one or more of these phases are almost certainly metastable.

The cell parameters of the synthetic minerals seem to indicate that the cation of the non-silicate portion of the formula controls the cell size of these minerals. Of the carbonate and bicarbonate varieties, the potassium rich cancrinites (davynes) have the largest cell volume and the calcium rich cancrinites (cancrinites proper) have the smallest. The sodium rich cancrinites (natrodavynes) have a cell volume intermediate between davynes and cancrinite proper. Replacement of the carbonate radical by the hydroxide radical in calcium-rich cancrinites does not significantly affect the cell volume.

This investigation confirms that possible substitutions in cancrinites are numerous and that there is an apparent wide range of temperature stability of cancrinite minerals depending on their compositions. The chemistry of cancrinites also affects their breakdown products, under hydrothermal conditions, potassium-rich cancrinites dissociate to nepheline and a potassium carbonate glass; sodium-rich cancrinites undergo a polymorphic transition; and calcium-rich cancrinites may melt incongruently (Eitel, 1922) or dissociate to nepheline and calcite. The cell dimensions determined from the synthetic minerals are in good agreement both with those reported in the literature and with those determined from four specimens of natural cancrinite investigated in this study.

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REFERENCES

BARRER, R. M. & WHITE, E. A. (1952): The hydrothermal chemistry of silicates. Part II, synthetic crystalline alumino-silicates. *J. Chem. Soc.*, **286**, 1561–1571.

BELJANKIN, D. S. (1931): Zur Mineralogie und Chemie eines Feldspatvertreters aus der "Wischnewy Gory" (Ural). *Zbl. Min. Abt.* A., 190–196. (*Min. Abst.*, 4, 499).

——— (1944): Vischnevite, and not sulphatic cancrinite. *Compt. Rend.* (*Doklady*) *Acad. Sci. URSS*, **42**, 304–306.

BERMAN, H. (1937): Constitution and classification of the natural silicates. *Am. Min.*, **22**, 342–408.

BORGSTROM, L. H. (1940): Chemisus der Mineralien der Sodalith und der cancrinitigruppe. *Zeit. Krist.*, **74**, 113–130.

DEER, W. A., HOWIE, R. A. & ZUSSMAN, J. (1963): *Rock forming minerals.* **4**, Longmans Green, London.

EDGAR, A. D. & BURLEY, B. J. (1963): Studies on Cancrinites I—Polymorphism in sodium carbonate rich cancrinite-natrodavyne. *Can. Mineral.*, **7**, 631–642.

EITEL, W. (1922): Uber das system $CaCO_3$-$NaAlSiO_4$ (Calcit-Nephelin) und den Cancrinit. *N. J. Min.* **2**, 45–61.

GORANSON, R. W. (1931): The solubility of water in granite magmas. *Am. J. Sci.*, **22**, 481–502.

GOSSNER, B. (1925): Die Beziehungen von Davyne zu Hauyn. *Zbl. Min.*, *Abt.* A, 169–177 (*Min. Abst.*, 4, 203).

——— & MUSSGNUG, F. (1930): Uber Davyn und seine Beziehungen zu Hauyn und Cancrinit. *Zeit. Krist.*, **73**, 52–60 (*Min. Abst.* 4, 279).

HEY, M. H. (1955): *An index of mineral species and varieties arranged chemically.* British Museum (Natural History).

KOZU, S. (1931): Preliminary note on studies of cancrinite from Korea. *Japan. Jour. Geol. and Geogr.* **9**, 1–2.

———, SETO, K. & TSURUMI, S. (1932): Chemical composition of cancrinite from Dodo, Korea. *Proc. Imp. Acad. Tokyo*, **8**, 432–435.

——— & TAKANE, K. (1933): Crystal structure of cancrinite from Dodo, Korea. *Proc. Imp. Acad. Tokyo*, **9**, 13–16.

LABUNTZOV, A. N. (1927): Les zeolithes des Montes Chibinas et Lajawrurt en Laponie russe. *Trav. Musee. Min. Acad. Sci. URSS*, **2**, 91–100. (*Min. Abst.*, **4**, p. 373).

LARSEN, E. S. & FOSHAG, W. F. (1926): Cancrinite as a high temperature hydrothermal mineral from Colorado. *Am. Min.*, **11**, 300–303.

NIGGLI, P. (1926): Lehrbuch der Mineralogie, II, Berlin, 208 p. (quoted by Borgstrom (1930)).

PHOENIX, R. & NUFFIELD, E. W. (1949): Cancrinite from Blue Mountain, Ontario. *Am. Min.*, **34**, 452–455.

PIRSSON, L. V. & WASHINGTON, H. S. (1907): Contributions to the geology of New Hampshire, III on Red Hill, Moultonboro. *Am. J. Sci.*, **23**, 257–276, 433–447.

QUINN, A. (1937): Petrology of the alkaline rocks at Red Hill, New Hampshire. *Geol. Soc. Am. Bull.*, **48**, 373–402.

RAUFF, H. (1878): Über die chemische Zusammensetzung des Nephelin, Cancrinits und Mikrosommits. *Zeit. Krist.*, **2**, 445–459.

ROSE, G. (1839): Beschreiben einiger neu mineral vom Ural. *Pogg. Ann.*, **48**, (quoted by Borgstrom (1930)).

SMITH, J. V. & TUTTLE, O. F. (1957): The nepheline-kalsilite system I—x-ray data for the crystalline phases. *Am. J. Sci.*, **255**, 282–305.

STEWART, F. H. (1941): On sulphatic cancrinite and analcime from Loch Borolan, Assynt. *Mineral. Mag.*, **26**, 1–8.

THUGUTT, S. J. (1892): Mineralchemische Studien. *Zeit. anorg. Chemie.*, **2**, 64–107, 113–156. (Abstract in *Econ. Geol.*, **32**, 658).

TUTTLE, O. F. (1949): Two pressure vessels for silicate-water studies. *Geol. Soc. Am. Bull.*, **60**, 1727–1729.

WINCHELL, A. N. & WINCHELL, H. (1951): *Elements of optical mineralogy, Part II—descriptions of minerals.* 4th Ed. Wiley, New York.

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