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MINERAL CHEMISTRY

OF SOME SYNTHETIC

CANCRINITES

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By

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SCOPE AND CONTENTS: An experimental and X-ray investigation was made of the fields of synthesis and cell parameters of eight different cancrinites, at temperatures between 200° and 800°C. and water pressures between 10,000 and 30,000 psi. Variations in fields of synthesis and unit cell dimensions were observed with compositional changes in the cancrinites. Analcite appeared as a second phase in some of the systems. Polymorphism was observed in two of the cancrinite compositions. A comparison between these synthetic cancrinites and four natural cancrinites is attempted. The extent of solid solution between end-members of some of the cancrinites was studied. Discussions of equilibrium criteria, identification of products, analcite formation and solid solution phenomena are given. A revised nomenclature for cancrinites is suggested.

ABSTRACT

A survey of the literature shows that the cancrinites have a complex chemistry and a confusing nomenclature. The approximate composition of these minerals can be expressed as $3NaAlSiO_4 \cdot R(CO_3,SO_4,Cl,OH)$ nH_2O, where $R = Na,Ca,K$.

Using the terminology and approximate compositions proposed by Winchell and Winchell (1951) for the various end-members of this mineral, the fields of synthesis and cell parameters of eight different cancrinites have been determined in the temperature range 200° to 800°C. and at water pressures of 10,000 to 30,000 psi. Some of the compositions proposed by Winchell and Winchell (1951) failed to synthesize cancrinites, but instead synthesized sodalite type minerals. As a result the nomenclature of the cancrinites has been revised.

A consideration of the temperature limits of syntheses of cancrinites possibly indicates that the controlling factor in their fields of syntheses is the cation attached to the carbonate, hydroxide, sulphate and chloride radicals, rather than the anionic radicals themselves. A similar type of control seems to effect the size of the unit cell volumes of these minerals.

At low temperatures analcite appears as a second phase in many of the cancrinite compositions. Several possible explanations of this low temperature analcite are discussed.

The sodium carbonate and bicarbonate cancrinites undergo a polymorphic transition to a hauyne-nosean type of mineral. A similar polymorphism exist in sodium hydroxide cancrinites.

The experimentally determined curves possibly represent metastable equilibrium. A discussion of the general conditions of equilibrium, the identification of the synthetic products and their applications to the cancrinites is given.

Preliminary investigation of the extent of solid solution between some end-members of the cancrinites indicates that complete solid solution between these end-members may not exist.

Results of cell parameter determinations of some of the synthetic cancrinites show good agreement with four natural cancrinites investigated in this thesis.

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I. INTRODUCTION

The term cancrinite applies to a family of minerals of approximate composition $3NaAlSiO_4.R(CO_3,SO_4,Cl,OH)nH_2O$ where R = Na,Ca,K. This family is a member of the feldspathoidal group and occurs, usually in minor amounts, in silica deficient igneous rocks. The relationships between cancrinite and other feldspathoidal minerals, as well as their origin, are imperfectly understood. In addition the chemistry and, as a result, the nomenclature of this family are not well established.

According to Winchell and Winchell (1951) cancrinite belongs to the hexagonal pyramidal class, with space group $C6_3$ and cell dimensions a = 12.75Å, c = 5.18Å. Although these authors note that the composition of cancrinite is variable, they suggest six names that seem to apply to end-members. These are as follows:-

Cancrinite proper	$3NaAlSiO_4.Ca[CO_3,(OH)_2]$
Microsommite	$3NaAlSiO_4.Ca(Cl,OH)_2$
Wischnewite	$3NaAlSiO_4.(HNaSO_4,NaOH)$
Davyne	$3NaAlSiO_4.(HKCO_3,KOH)$
Natrodavyne	$3NaAlSiO_4.(HNaCO_3,NaOH)$
Sulphatic cancrinite	$3NaAlSiO_4,\ Ca[SO_4,(OH)_2]$

The names applied to some of these end-members are either simplified or do not agree with the names used in the literature. However, in the present thesis, this terminology and composition was used as a starting basis for all syntheses.

Because of the difficulties in preparing synthetic mixtures containing sodium and potassium hydroxides, the compositions given above were slightly modified as follows:-

Cancrinite proper	$3NaAlSiO_4 \cdot CaCO_3$
Microsommite	$3NaAlSiO_4 \cdot CaCl_2$ and $3NaAlSiO_4Ca(OH)_2$
Wischnewite	$3NaAlSiO_4 \cdot (HNaSO_4)$ and $3NaAlSiO_4 \cdot Na_2SO_4$
Davyne	$3NaAlSiO_4 \cdot HKCO_3$ and $3NaAlSiO_4 \cdot K_2CO_3$
Natrodavyne	$3NaAlSiO_4 \cdot HNaCO_3$ and $3NaAlSiO_4 \cdot Na_2CO_3$
Sulphatic cancrinite	$3NaAlSiO_4CaSO_4$

Six of the above ten compositions were easily synthesized to a cancrinite-type mineral, while the other four synthesized a mineral of the sodalite group. It was found desirable to revise the nomenclature of some of these synthetic cancrinites in order to correlate them with the nomenclature found in the literature. The compositions and revised nomenclature are shown in Table 1.1. Of the eight cancrinite-type minerals synthesized, five are pure carbonate or bicarbonate end-members, two end-members contain carbonate and sulphate and one has all of the carbonate replaced by the hydroxide radical. All these syntheses were carried out in the presence of water. In addition, a cancrinite proper was synthesized using carbon dioxide and no water.

The objectives of the present thesis were fouffold. First, the stability fields of the various synthetic cancrinite minerals were determined in the pressure range ten thousand to thirty thousand pounds per square inch, and at temperatures between 200° and 800°C., the lower temperature representing the approximate limit of synthesis of the cancrinite, the upper temperature being the approximate temperature of failure of the pressure vessel. It was hoped that this would give some indication of the behaviour of these minerals with depth, and hence indicate their possible genesis. Second, the variation in lattice parameters between the different types of cancrinite was determined. Third, an attempt was made to measure, by X-ray methods, the extent of solid solution(1) between some of the end-members of the cancrinites. Fourth, the extent of solid solution between some of the cancrinite end-members and nosean was measured.

The results of this investigation show that three of the cancrinites are stable up to the upper temperature limit, two of the end-members dissociate into nepheline and liquid, and two undergo a polymorphic transformation at high temperatures. Determinations of the cell parameters agree well with those quoted in the literature for natural cancrinites. Solid solution measurements show that solid solution takes place to a limited extent between some of the cancrinite end-members and that there is a relationship between the cancrinite and the sodalite group.

Although this investigation shows the possible varieties of cancrinite minerals, it is unlikely that these pure end-members will ever be found in nature. The results of this investigation therefore, cannot be applied to natural cancrinites without further modification.

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(1) Positional-substitutional solid solution, where sites are replaced by another ion.

TABLE 1.1

Suggested Revisions in the Nomenclature of the Cancrinites

Winchell's Name	Composition (after Winchell)	Composition Used in Present Study	Revised Name	Remarks
Cancrinite proper	$3NaAlSiO_4Ca[CO_3(OH)_2]$	$3NaAlSiO_4 \cdot CaCO_3$	Cancrinite proper	-
Cancrinite proper	"	$3NaAlSiO_4 \cdot Ca(OH)_2$	Hydroxy cancrinite	-
Microsommite	$3NaAlSiO_4Ca(Cl,OH)_2$	$3NaAlSiO_4CaCl_2$	-	Synthesizes to sodalite + nepheline + anorthite
Microsommite	"	$4[3NaAlSiO_4 \cdot Ca(OH)_2] + 1[3NaAlSiO_4 \cdot CaCl_2]$	Microsommite	-
Wischnewite	$3NaAlSiO_4 (HNaSO_4,NaOH)$	$3NaAlSiO_4 \cdot HNaSO_4$	-	Synthesizes to nosean at temperatures greater than 500°C.
Davyne	$3NaAlSiO_4 \cdot (HKCO_3,KOH)$	$3NaAlSiO_4 \cdot KHCO_3$	Bicarbonate Davyne	-
Davyne	"	$3NaAlSiO_4 \cdot K_2CO_3$	Davyne proper	-

<u>Table 1.1 (contd.)</u>

Winchell's Name	Composition (after Winchell)	Composition Used in Present Study	Revised Name	Remarks
Natrodavyne	$3NaAlSiO_4 \cdot (HNaCO_3 \cdot NaOH)$	$3NaAlSiO_4 HNaCO_3$	Bicarbonate natrodavyne	-
Natrodavyne	"	$3NaAlSiO_4 Na_2CO_3$	Natrodavyne proper	-
Sulphatic cancrinite	$3NaAlSiO_4\ Ca[SO_4, (OH)_2]$	$3NaAlSiO_4 \cdot CaSO_4$	-	Synthesizes to hauyne
Sulphatic cancrinite	"	$7[3NaAlSiO_4 \cdot CaCO_3] + 1[3NaAlSiO_4 \cdot NaHSO_4]$	Sulphatic cancrinite	-

II. REVIEW OF PREVIOUS CANCRINITE STUDIES

In order to provide a general background for readers of this thesis, and to indicate the complexity of the chemistry and nomenclature of the cancrinite group, a review of previous studies is presented. Chemical composition and optical studies on each of the minerals comprising the cancrinite group is given; each member of the group being dealt with in turn. In addition, there is a discussion of the experimental work and field relationship reported in the literature.

1. Cancrinite

Rose (1839) first discovered cancrinite in a nepheline syenite from Miask in the Ural Mountains. Analyses of this mineral showed the constituents to be SiO_2, Al_2O_3, CaO, Na_2O, K_2O and CO_2. Later analyses indicated that H_2O was often present in considerable amounts, and that there were traces of manganese and sulphate.

Prior to 1900, at least four different formulae, with varying ratios of Al_2O_3, SiO_2, and CO_2 had been proposed for cancrinite. In 1878 Rauff gave the formula as $Na_8Al_8Si_9O_{24}2(Ca,Na_2)CO_3\cdot 3H_2O$. Clarke (1886) described and analyzed three specimens of cancrinite from Litchfield, Maine, and suggested the formula be written $Al_8(SiO_4)_8(CO_4)_2CaNa_8H_6$. He also stressed the similarity of cancrinite to sodalite and hydronephelite, both in origin and in structure. Yet another formula, $(Na_2Ca)_4H_6Si_9O_{36}Al_8(NaCO_3)_2$, was proposed by Groth (1889). In 1892 Thugutt suggested the formula should be written $8Na_2Al_2Si_3O_{10}\cdot 3Na_2Al_2O_4\cdot 5CaCO_3\cdot 9H_2O$. The presence of sodium and calcium in these formulae suggests that both of these elements are present in natural cancrinites.

Zambonini (1908) proposed a general formula $-mNa_2Al_2Si_2O_8\cdot nNa_4(AlNaCO_3)Si_2O_8\cdot pNa_2Al_2Si_3O_{10}$, which indicated that calcium was unnecessary. In 1912, Mauritz included manganese in the cancrinite formula, which he wrote as $H_4(Na_2K_2CaMn)_3Al_4Si_4O_{21}C$. Cesaro (1917), in a discussion of the analyses of cancrinite listed by Dana (1892), concluded that cancrinite was a combination of a diorthosilicate and a carbonate corresponding to the formula $[Al(AlOH)_2]_5(Na_2,Ca)_{6\frac{1}{2}}(Si_2O_7)_8 + 4Na_2CO_3$. Because this formula did not correspond with the kalk-cancrinite of Lemberg (1883, 1887), or the davyne of Rammelsberg (1860), Cesaro concluded that neither cancrinite nor calciocancrinite existed at Monte Somma, Vesuvius. Cesaro also reported birefringence of cancrinite from Miask Urals as 0.0222 - 0.0230. In a reply to this paper Zambonini (1918) suggested that Lemberg's calciocancrinite was identical to the carbonate-meionite of Borgström (1915). In this paper Borgström had shown that Lemberg's calciocancrinite closely resembled the composition of meionite $3CaAl_2Si_2O_8\cdot CaCO_3$. It seems likely from this evidence that Lemberg's calciocancrinite was actually a member of the scapolite family.

In 1920 Jakob, in a highly speculative and theoretical paper on the constitutional formulae of mineral silicates, deduced the formula of cancrinite as $Al(SiO_4)_3Al_2Na_3(CaNa_2)CO_3$. Gossner (1922) suggested two possible formulas, $3NaAlSiO_4\cdot CaCO_3$ or $3Na_2Al_2Si_2O_8\cdot Ca(HCO_2)_2$. Eitel (1922) in experimental work on the feldspathoids, gave the composition of synthetic cancrinite as $3NaAlSiO_4\cdot CaCO_3$ with $3NaAlSiO_4\cdot Na_2CO_3$, although no analyses were given. Biswas (1922) analyzed a cancrinite from Kishengarh, Rajputana, India, from which he deduced the formula $11(Na,K)_2O$.

$7CaO.11Al_2O_3.25SiO_2.7CO_2.10H_2O$. The analysis quoted by him also contained 0.26% MgO. Walker and Parsons (1925), describing cancrinite from Dungannon Township, Ontario, gave the general formula as $CaO.3R_2O.2Al_2O_3.4SiO_2CO_2$. From the analysis quoted in their paper R_2O represents mainly Na_2O although a small amount of K_2O (0.78%) is present. In a further paper Walker and Parsons (1926) analyzed cancrinite from French River, Ontario, with a higher $Na_2O:CaO$ ratio than the Dungannon specimen, but approximately the same amount of CO_2. This might suggest that both the $CaCO_3$ and Na_2CO_3 types of cancrinite were present in the French River specimen.

Larsen and Foshag (1926), describing several genetic types of cancrinite from the Iron Hill area, Colorado, give the refractive indices of the white to colourless cancrinite as $n_\omega = 1.524$, $n_\epsilon = 1.501$. Analysis of this cancrinite agrees approximately with the formula $3NaAlSiO_4.CaCO_3$, but a better agreement is given by a mixture of nepheline ($NaAlSiO_4$), echellite ($Na_2Al_4Si_3O_{13}$), $CaCO_3$ and H_2O.

In 1930, Gossner and Mussgnug reported the cell dimensions of Miask cancrinite as $a = 12.60Å$, $c = 5.18Å$ based on a hexagonal unit cell. The unit rhomb based cells have a maximum molecular weight of 1060, corresponding to two molecules of $3NaAlSiO_4.CaCO_3$ per unit cell. Zambonini and Ferrari (1930), using the rotating crystal X-ray method, gave the cell dimensions of a cancrinite from Monte Somma as $a = 12.73Å$, $c = 5.10Å$. The formula of one molecule per unit cell was given as $3(Na_2,Ca)Al_2Si_2O_8.1\frac{1}{2}(Na_2,Ca)CO_3.nH_2O$ where n varies from 0.75 to 5.4. These latter formulae were based on X-ray measurements and not on chemical analyses.

Borgström (1930), reviewing the chemistry of the sodalite and cancrinite groups, concluded that the variable compositions of the cancrinite group were caused by isomorphous mixtures of calcium cancrinite ($3Na_2Al_2Si_2O_8.2CaCO_3$) and sodium cancrinite ($3Na_2Al_2Si_2O_8.Na_2CO_3$). A combination of two molecules of calcium-cancrinite to one molecule of sodium cancrinite produces the characteristic ratio $4Al_2O_3:8SiO_2:2CO_2$ found in many of the analyses of natural cancrinites. Borgström also believed that the calcium does not have to be associated with the CO_2 but could be combined with the silicate. Thus $CaAl_2Si_2O_8$ and $K_2Al_2Si_2O_8$ could replace $Na_2Al_2Si_2O_8$. Replacement of $Na_2Al_2Si_2O_8$ by $CaAl_2Si_2O_8$ in the cancrinite formula however, would produce meionite, not cancrinite. The $CaCO_3$ could also be replaced by Na_2CO_3, $CaSO_4$, or $CaCl_2$. No suggestion was made by Borgström that K_2CO_3 can replace the $CaCO_3$ portion of the cancrinite.

Pauling (1930) proposed that minerals of the cancrinite group had a framework type of structure, based on a motif of rings of six tetrahedra. Such a configuration obeys the requirements of the space group and forms a unit cell with a = 12.8Å and c = 5.4Å. The position of the cations, acid radicals and water molecules were not however determined.

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 a n_ω of 1.5238, n_ϵ of 1.5015 using sodium light. The cell dimensions of this specimen are a = 12.72Å and c = 5.18Å; the specific gravity being 2.44. In a later paper Kozu, Seto and Tsurumi (1932) showed that the analysis of this cancrinite corresponds to a formula $2Na_2Al_2Si_2O_8.CaCO_3.H_2O$, and that the unit cell contained one and a half molecules. In two further papers, Kozu and Takane (1933) and Kozu, Ueda and Tsurumi (1933), the structure of the Korean cancrinite was deduced. The space group was determined as $C_6^6 = P6_3$ and from considerations of Pauling's principle, unit cell measurements and ionic radii, it was shown that sodium atoms were placed in the space between the $(Si,Al)_6O_{18}$ groups, whereas the $CaCO_3$ group was placed in the position of the three fold rotation axis. Thus sodium atoms are unlikely to replace calcium atoms because these atoms were on non-equivalent sites.

Berman (1937), in a paper discussing the constitution and classification of natural silicates, gave the structural formula of the cancrinite family as $W_{6-8}Z_{12}O_{24}N_{1-2}.2\text{-}3H_2O$ where $W = Ca,Na,K$; $Z = Si,Al$; $N = S,Cl^-,CO_3^=,SO_4^=$. He considered however, that the cancrinite end-member of this group did not contain calcium, and wrote its formula as $(Na,K)_{6-8}Al_6Si_6O_{24}(CO_3)_{1-2}2\text{-}3H_2O$. He also stressed the variability in composition of the group within the limits indicated by the group formula. From the most reliable analyses in the literature Berman suggested that there was a tendency for calcium to increase as sodium and potassium decreased and also for the carbonate ion to increase with an increase in calcium. The water content, as indicated by these analyses, varied between 2 and 3 molecules per 24 oxygen atoms. Finally, the Al:Si ratio was fairly constant at 1:1.

Matossi (1938) measured infrared characteristic features to show that the structure of cancrinite was similar to the nepheline structure. This wide-framework structure is built up from $[SiO_4]$ hexagonal rings that follow one another alternately in layers parallel to the hexagonal basal pinacoid. The sodium and calcium ions are contained in the wide spaces of the anionic networks, while the large "holes" in the structure accomodate the acid radicals.

In 1938, Meen described and alanyzed a white cancrinite from Bancroft, Ontario. This specimen had a high CaO and H_2O content, but a low Na_2O content; small amounts of SO_3 and Cl were also found. Refractive indices of this specimen were n = 1.528 and n = 1.503. From this analysis Meen proposed the formula $(Na,K)_{3}5Ca_2Al_6Si_6O_{24}\cdot 1\frac{1}{2}CO_2\cdot 3\ 3/4H_2O$. Phoenix and Nuffield (1949) investigated a yellow cancrinite crystal from Blue Mountain, Methuen Township, Ontario. Cell dimensions, obtained from Weissenberg photographs, gave a = 12.60Kx, c = 5.12Kx. Optics of this cancrinite were $n_\omega = 1.515$, $n_\epsilon = 1.496$. The analyses showed 1.37% SO_3 and 0.42% Cl. The general formula computed from eight analyses and based on 24 oxygen atoms was $(Na,K,Ca,Al)^{10+}_{6-8}Si_6Al_6O_{24}{}^{6-}(So_4,CO_3)^{4-}_{1-2}1\text{-}5H_2O$. The present author investigated two cancrinite samples from the same quarry, one an amber yellow colour, the other pink. Results of these investigations are reported elsewhere in this thesis.

This rather lengthy chronology of the literature on cancrinite is presented here in order to emphasize the complex chemistry of this mineral group. Largely as a result of the multitude of analyses that have been published, the name cancrinite has been applied to alumino-silicates, generally having Al:Si ratios of 1:1; and containing varying amounts of the cations potassium, sodium and calcium, the acid radicals carbonate, sulphate and chloride, and water. A synopsis of the various chemical formula and other properties of cancrinites reported in the literature, is given in Table 2.1.

TABLE 2.1

Chemical Formula and Other Properties of Cancrinite Reported in the Literature

Author	Chemical Formula	Locality	Other Properties
Rose (1839)	main constituents-SiO_2, Al_2O_3, CaO, Na_2O, K_2O and CO_2	Miask, Ural Mountains	
Rauff (1878)	$Na_8Al_8Si_9O_{24}\cdot 2(Ca,Na_2)CO_3\cdot 3H_2O$		
Clarke (1886)	$Al_8(SiO_4)_8(CO_4)_2CaNa_8H_6$	Litchfield, Maine	
Thugutt (1892)	$8Na_2Al_2Si_3O_{10}\cdot 3Na_2Al_2O_4\cdot 5CaCO_3\cdot 9H_2O$	Brevig, Norway	
Zambonini (1908)	$mNa_2Al_2Si_2O_8\cdot nNa_4(AlNaCO_3)Si_2O_8\cdot pNa_2Al_2Si_3O_{10}$		
Mauritz (1912)	$H_4(Na_2K_2CaMn)_3Al_4Si_4O_{21}C$	Ditro, Hungary	
Cesaro (1917)	$[Al(AlOH)_2]_5(Na_2Ca)_{6\frac{1}{2}}(Si_2O_7)_8 + 4Na_2CO_3$	From analyses listed by Dana (1892)	Birefringence of Vesuvius Cancrinite = 0.0222-0.0230
Jakob (1920)	$Al(SiO_4)_3Al_2Na_3(CaNa_2)CO_3$	Theoretical formula	
Gossner (1922)	$3NaAlSiO_4\cdot CaCO_3$ or $3Na_2Al_2Si_2O_8\cdot Ca(HCO_2)_2$	Theoretical formula	

Table 2.1 (contd.)

Author	Chemical Formula	Locality	Other Properties
Eitel (1922)	$3NaAlSiO_4 \cdot CaCO_3$ with $3NaAlSiO_4 \cdot Na_2CO_3$	Synthetic	
Biswas (1922)	$11(Na,K)_2O \cdot 7CaO \cdot 11Al_2O_3 \cdot 25SiO_2 \cdot 7CO_2 \cdot 10H_2O$	Kishengarh, Rajputana, India	
Walker and Parsons (1925)	$CaO \cdot 3R_2O \cdot 2Al_2O_3 \cdot 4SiO_2 \cdot CO_2$ where R = Na and K	Dungannon Twp., Ontario	
Larsen and Foshag (1926)	$3NaAlSiO_4 \cdot CaCO_3$ (approx.)	Iron Hill, Colorado	$n_\omega \hat{=} 1.524$ $n_\epsilon = 1.501$
Gossner and Mussgnug (1930)	$3NaAlSiO_4 \cdot CaCO_3$ (2 molecules per unit cell)	Miask, Ural Mountains	$a \doteq 12.60$Å $c = 5.18$Å
Zambonini and Ferrari (1930)	$3(Na_2,Ca)Al_2Si_2O_8 \cdot 1\frac{1}{2}(Na_2,Ca)CO_3nH_2O$ where n = 0.75 to 5.4 (based on X-ray determination of unit cell)	Monte Somma	$a = 12.73$Å $c = 5.10$Å
Borgström (1930)	Isomorphous mixtures of $3Na_2Al_2Si_2O_8 \cdot 2CaCO_3$ + $3Na_2Al_2Si_2O_8 \cdot Na_2CO_3$	Theoretical formula	
Kozu (1931) and Kozu, Seto and Tsurumi (1932)	$2Na_2Al_2Si_2O_8 \cdot CaCO_3 \cdot H_2O$	Dodo, Korea	$n_\omega = 1.5238$ $n_\epsilon = 1.5015'$ $a = 12.72$Å $c = 5.18$Å S.G. = 2.44

Table 2.1 (contd.)

Author	Chemical Formula	Locality	Other Properties
Kozu and Takene (1933)	$2Na_2Al_2Si_2O_8 \cdot CaCO_3 \cdot H_2O$	Dodo, Korea	space group = C_6^6
Berman (1937)	$(Na,K)_{6-8}Al_6Si_6O_{24}(CO_3)_{1-2} \cdot 2\text{-}3H_2O$	From analyses in the literature .	
Meen (1938)	$(Na,K)_{3.5}Ca_2Al_6Si_6O_{24} \cdot 1\frac{1}{2}CO_2 \cdot 3\,3/4H_2O$	Bancroft, Ontario	$n_\omega = 1.528$ $n_\epsilon = 1.503$
Phoenix and Nuffield (1949)	$(Na,K,Ca,Al)^{10+}_{6-8}Si_6Al_6O_{24}{}^{6-}(SO_4,CO_3)^{4-}_{1-2} \cdot 1\text{-}5H_2O$	Methuen Twp., Ontario	$n_\omega = 1.515$ $n_\epsilon = 1.496'$ $a = 12.60Kx$ $c = 5.12Kx$

2. Microsommite, Davyne and Natrodavyne

The name microsommite was first applied by Vom Rath (1873) and Scacchi (1875) to a mineral from which they obtained a calculated formula of $4/5Na_2O.3/5CaO.Al_2O_3.2SiO_2 + NaCl + 1/13CaSO_4$. This formula can be reduced to $3Na_2Al_2Si_2O_8.2(NaCl,Na_2SO_4,Na_2CO_3)$, in which part of the sodium can be replaced by calcium.

Davyne was first named by Rauff (1878). From two analyses performed by him the following formula was proposed:-

$$3\begin{bmatrix} 2(CaAl_2Si_2O_8) \\ Na_2Al_2Si_2O_8 \\ K_2Al_2Si_2O_8 \end{bmatrix} \quad 2\begin{bmatrix} CaSO_4 \\ 4NaCl \end{bmatrix}$$

Presumably this mineral contained three molecules of a calcium, potassium or sodium alumino-silicate together with two molecules of either $CaSO_4$ or NaCl.

In 1910 Zambonini coined the term natrodavyne for a mineral from Vesuvius similar to davyne, but differing from the davyne-microsommite group in containing no potassium and a high CO_2 content.

Spencer (1923) described a davyne-like mineral from St. John's Island in the Red Sea. Two small crystals of this colourless mineral showed a good prismatic cleavage, refractive indices of $n_\omega = 1.530$ and $n_\epsilon = 1.535$, and a chemical analysis corresponding to the formula $(Na,K)_4(Mg,Ca)_4(Al,X)_6Si_5O_{22}.2H_2O$ where $X = (OH)_2,SO_4,CO_3,Cl_2$. This formula differed slightly from previously proposed formulae, and the mineral probably consisted of a mixture of the davyne and microsommites of Vom Rath, Scacchi and Rauff.

In 1925 Gossner quoted the davyne formula as $3[SiO_3, Na_2SiO_2Al_2O_3]$ $CaSO_4.CaCl_2$ and concluded that davyne was a double compound between hauyne and a hypothetical calcium sodalite. Niggli (1926) considered that both microsommite and davyne were a combination of minerals similar to those of the hauyne group; the principal constituent of davyne being $3NaAlSiO_4.CaCl_2$ with NaCl and Na_2SO_4 replacing $CaCl_2$. Gossner and Mussgnug (1930), using a davyne crystal from Monte Somma, Vesuvius, determined the cell dimensions of the hexagonal crystal as a = 12.80Å, c = 5.35Å. The unit rhomb-based cell of this crystal had a maximum molecular weight of 1120 corresponding to two molecules of $3SiO_4AlNa.CaSO_4$ per unit cell. X-ray photographs of davyne and cancrinite suggested a close relationship between these minerals. Gossner and Mussgnug were also able to trace a relationship between davyne and hauyne. By setting the cube diagonal of hauyne parallel to the c axis of davyne, they showed that the cell sides were similar.

The literature on davyne, natrodavyne 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. It appears that no compositional distinction has been made between these three minerals, except for the mineral natrodavyne which contains a high CO_2 content. Although some authors trace a relationship between davyne and members of the sodalite family, particularly hauyne, no clear evidence is sighted as to whether this relationship occurs as solid solution or merely as compositional similarity. A synopsis of the chemical formula and other properties of microsommite, davyne and natrodavyne reported in the literature is given in Table 2.2.

3. Sulphatic Cancrinite and Wischnewite

The first occurrence of sulphatic cancrinite was reported by Larsen and Steiger (1916). Investigating uncompahgrites in the Beaver Creek area of Colorado, these authors discovered a peculiar cancrinite specimen in which almost one half of the CO_2 had apparently been replaced by SO_3. This mineral appeared to be derived from melilite and was associated with apatite and perovskite. Analysis of a pure specimen gave 4.65% SO_3 and 3.18% CO_2. This mineral had a poorly developed cleavage parallel to the prism faces, and showed lower refractive indices and birefringence than normal cancrinites. From considerations of the optical and chemical properties, Larsen and Steiger concluded that cancrinite and sulphatic cancrinite were closely related and that a complete isomorphous series might exist between normal cancrinite and a mineral in which all the carbonate was replaced by sulphate.

In 1929 Zavaritzky described a bluish mineral occurring as small nests and veinlets of nepheline in pegmatite veins in the nepheline syenites of the Ilmen Mountains. Analysis of this mineral indicated that it contained considerably more sulphate than the Colorado specimen ($SO_3 = 6.25\%$, $CO_2 = 0.89\%$), and also had lower refractive indices and birefringence. The lower birefringence with the increased sulphate content seemed to support Larsen and Steiger's (1916) prediction that an isomorphous series might exist between the pure carbonate and pure sulphate end-members in which the birefringence would decrease as the sulphate content increased.

Beljankin (1931) reported a sulphate-cancrinite from the Vishnevy

TABLE 2.2

Chemical Formula and Other Properties of Davyne, Natrodavyne and Microsommite Reported in the Literature

Author	Chemical Formula	Locality	Other Properties
Vom Rath (1872) and Scacchi (1875)	$3Na_2Al_2Si_2O_8 \cdot 2(NaCl, Na_2SO_4, Na_2CO_3)$-microsommite	Monte Somma Vesuvius	
Rauff (1878)	$3\begin{bmatrix} 2(CaAl_2Si_2O_8) \\ Na_2Al_2Si_2O_8 \\ K_2Al_2Si_2O_8 \end{bmatrix} 2 \begin{bmatrix} CaSO_4 \\ 4NaCl \end{bmatrix}$ – davyne	Monte Somma Vesuvius	
Zambonini (1910)	Similar to davyne but containing no potassium and a high CO_2 content – natrodavyne	Vesuvius	
Spencer (1923)	$(Na,K)_4(Mg,Ca)_4(Al,X)_6 Si_5O_{22} \cdot 2H_2O$ where $X = (OH)_2, SO_4, CO_3, Cl_2$ – davyne?	St. John's Island Red Sea	$n_\omega = 1.530$ $n_\epsilon = 1.535$
Gossner (1925)	$3\,[SiO_3, Na_2SiO_2Al_2O_3]\ CaSO_4 \cdot CaCl_2$ – davyne	Theoretical formula	
Niggli (1926)	$3NaAlSiO_4 \cdot CaCl_2$ with $NaCl$ and Na_2SO_4 replacing $CaCl_2$ – davyne	Theoretical formula	
Gossner and Mussgnug (1930)	$3SiO_4 \cdot AlNa \cdot CaSO_4$ – from X-ray determinations of cell dimensions – davyne	Monte Somma Vesuvius	$a = 12.80$Å $c = 5.35$Å

Mountains in the Southern Urals. This specimen had similar physical appearance and optical properties to Zaveritzky's mineral but also showed a good hexagonal prismatic cleavage and occasional fine cross-hatched twinning. Analysis of a specimen containing 8.6% scolecite and 2.4% gibbsite, gave 5.02% SO_3 and 0.26% CO_2. A formula of $3Na_2Al_2Si_2O_8 \cdot Na_2SO_4 \cdot 3H_2O$ was proposed for this mineral. Beljankin also proposed that this mineral be renamed wischnewite rather than sulphatic cancrinite. From the formula given by him, the name hydrous-nosean would have been more appropriate, as the formula corresponds to that of nosean with three molecules of water.

In 1941 Stewart reported an occurrence of sulphatic cancrinite in the pegmatites at Allt a' Mhuillin, Loch Borolan, Scotland. This greyish blue mineral was associated with orthoclase, melanite and dark mica along with accessory calcite, sphene, zircon and orthite. Optically, the refractive indices are similar to the Ilmen Mountains specimen, but the birefringence was slightly lower. Analysis showed the ratio of SO_3:CO_2 to be 5.93 to 1.90. This ratio gives a higher SO_3 content than the Colorado specimen, but a lower SO_3 content than the sulphatic cancrinite from the Ilmen Mountains. A useful comparison between the Scottish sulphatic cancrinite and the wischnewite of Beljankin cannot be made because of the impurities in the wischnewite specimen. Using the general formula for the cancrinite group, proposed by Berman (1937), and the analyses of Stewart, Larsen and Steiger, and Zavaritzky, the general formula for sulphatic cancrinite would be $(Na,K,Ca,Sr)_{6-8}(Si,Al)_{12}O_{24}(SO_4,CO_3) \cdot 1\text{-}5H_2O$. Stewart also suggested that the variable water content might influence the optical properties of these sulphatic cancrinites.

Beljankin (1944), in a further paper on the relationship between wischnewite and sulphatic cancrinite, proposed that all the specimens referred to as sulphatic cancrinite should be called wischnewite. This proposal was based on the fact that no complete isomorphous miscibility between the carbonate and sulphate end-members had been observed. In support of this observation was the fine microcline type twinning noted on the specimen from the Vishnevy Mountains and also the anomalous biaxiality reported for the Scottish specimen.

In an attempt to resolve the question of the nomenclature of the sulphate rich cancrinites using X-ray methods, the author of this thesis synthesized cancrinites with compositions closely resembling those reported by both Stewart (1941) and Beljankin (1944). Both types of synthetic cancrinites produced patterns similar to the pattern given by a specimen of sulphatic cancrinite from Allt a' Mhuillin, kindly supplied by Professor Stewart. Further details of these synthetic sulphatic cancrinites appear later in this thesis. Table 2.3 gives a synopsis of the chemical formula and other properties of sulphatic cancrinites and wischnewites reported in the literature.

4. Field Relationships of the Cancrinite Minerals

Cancrinites normally occur associated with intrusive feldspathoidal rocks. Field relationships indicate that cancrinites have two common genetic habits. They may occur as primary minerals in syenites, or as alteration or reaction products of other minerals, principally nepheline and calcite.

Pirsson and Washington (1907) in their study of the geology of

TABLE 2.3

Chemical Formula and Other Properties of Sulphatic Cancrinite and Wischnewite Reported in the Literature

Author	Chemical Formula	Locality	Other Properties
Larsen and Steiger (1916)	no formula given, but from analyses one-half of the CO_2 had been replaced by SO_3 (sulphatic cancrinite)	Beaver Creek, Colorado	S.G. = 2.443 n_ω = 1.509 n_ϵ = 1.500
Zavaritzky (1929)	no formula given SO_3 = 6.25%, CO_2 = 0.89% (sulphatic cancrinite)	Ilmen Mountains, Russia	n = 1.492-1.493 birefringence = 0.0007 S.G. = 2.35
Beljankin (1931)	$3Na_2Al_2Si_2O_8 \cdot Na_2SO_4 \cdot 3H_2O$ (wischnewite)	Vishnevy Mountains, Southern Urals	n = 1.489 birefringence = 0.0007
Stewart (1941)	$(Na,K,Ca,Sr)_{6-8}(Si,Al)_{12}O_{24}(SO_4,CO_3) \cdot 1\text{-}5H_2O$ – general formula for sulphatic cancrinite	Loch Borolan Scotland	n_ω = 1.502 n_ϵ = 1.497 S.G. = 2.423

Red Hill, New Hampshire, reported microscopic amounts of cancrinite in a hornblendic-grano-miaskose (hornblende syenite?) which forms the greater part of the Red Hill massif. Here the cancrinite occurred as an alteration product of nepheline. They also reported microscopic cancrinite in a nepheline syenite from the same area, where it was associated with the last products of crystallization, namely nepheline and sodalite.

Walker and Parsons (1926) found fairly large masses (3 - 4 inches) of cancrinite in a nepheline syenite from French River, Ontario. Surrounding this cancrinite was an alteration product which they suspected was hydronephelite or ranite.

In 1926 Larsen and Foshag reported an occurrence of cancrinite from Iron Hill, Colorado. In this locality the mineral occurs in at least five genetic habits, (1) as an alteration product of nepheline; (2) as a reaction product between nepheline and calcite; (3) as a mineral in contact metamorphic limestone; (4) as a primary mineral in cancrinite-syenite; (5) as a hydrothermal replacement of melilite. Larsen and Foshag describe in detail the last mode of occurrence. Cancrinite-bearing rock occurs as a veinlet cutting across the partly altered uncompahgrite (a coarse grained rock consisting mainly of melilite with pyroxene, biotite, perovskite and apatite). The cancrinite grains enclose poikolitically grains of monticellite and titaniferous garnet; green hornblende and remnants of perovskite are also present. Toward the borders of the veinlet, phlogopite, calcite, garnet, chlorite and zeolites occur. Larsen and Foshag considered that the cancrinite appeared to be closely associated both in space and in time of formation with the monticellite, vesuvianite and garnet.

Murray-Hughes and Fitch (1929) desc̈ribed a cancrinite-syenite from Nambala, North-western Rhodesia. This rock consisted of microcline, anorthoclase, lepidomelane, hastingsite and riebeckite. Micrometric analysis showed that 6.3% pale yellow or colourless cancrinite and calcite occurred interstitially in the rock, and the authors believed these were late stage magmatic minerals. A sodalite-syenite from the same area showed large crystals of nepheline with irregularly developed patches of cancrinite. In another variety of this rock sodalite appeared to have replaced nepheline and cancrinite along cleavage planes. The association of cancrinite and feldspar in the cancrinite syenite is highly unusual, and might suggest that the cancrinite reported by Murray-Hughes and Fitch did not have the usual silica deficient composition, but was similar to the scapolite type of cancrinite suggested Borgström (1930). Unfortunately no analysis of the cancrinite is given.

Shand (1930), in a theoretical paper supporting Daly's (1910) hypothesis on the origin of feldspathoidal rocks by reaction between magma and limestone, cited field occurrences which he believed proved that cancrinites were formed during the assimilation of limestone by alkaline magmas. Quinn (1937) found a small amount of cancrinite present in the nepheline-sodalite syenites of the Red Hill, New Hampshire, rocks of the White Mountain magma series. Petrographic evidence indicated that this cancrinite was present as an alteration of other feldspathoids, principally nepheline and sodalite. Chayes (1942) found minor amounts of cancrinite in the nepheline rocks of the Bancroft, Ontario, region. Under the microscope the cancrinite appeared lying between nepheline and calcite grains, or occasionally as euhedral crystals independent of nepheline. In many cases the cancrinite was traversed by minute inclusions of sodalite. In coarse pegmatites in the same area Chayes found that cancrinite occasionally replaced sodalite.

Unfortunately, descriptions of field occurrences of cancrinites do not give much indication of the temperature and pressure conditions under which the mineral was formed. The common association of cancrinite with nepheline and calcite is to be expected, the association with sodalite is more complicated. As cancrinite usually occurs only in small amounts, chemical analysis and optical properties are not given in papers dealing with the field relationships. As a result, it is usually impossible to deduce the variety of cancrinite under discussion.

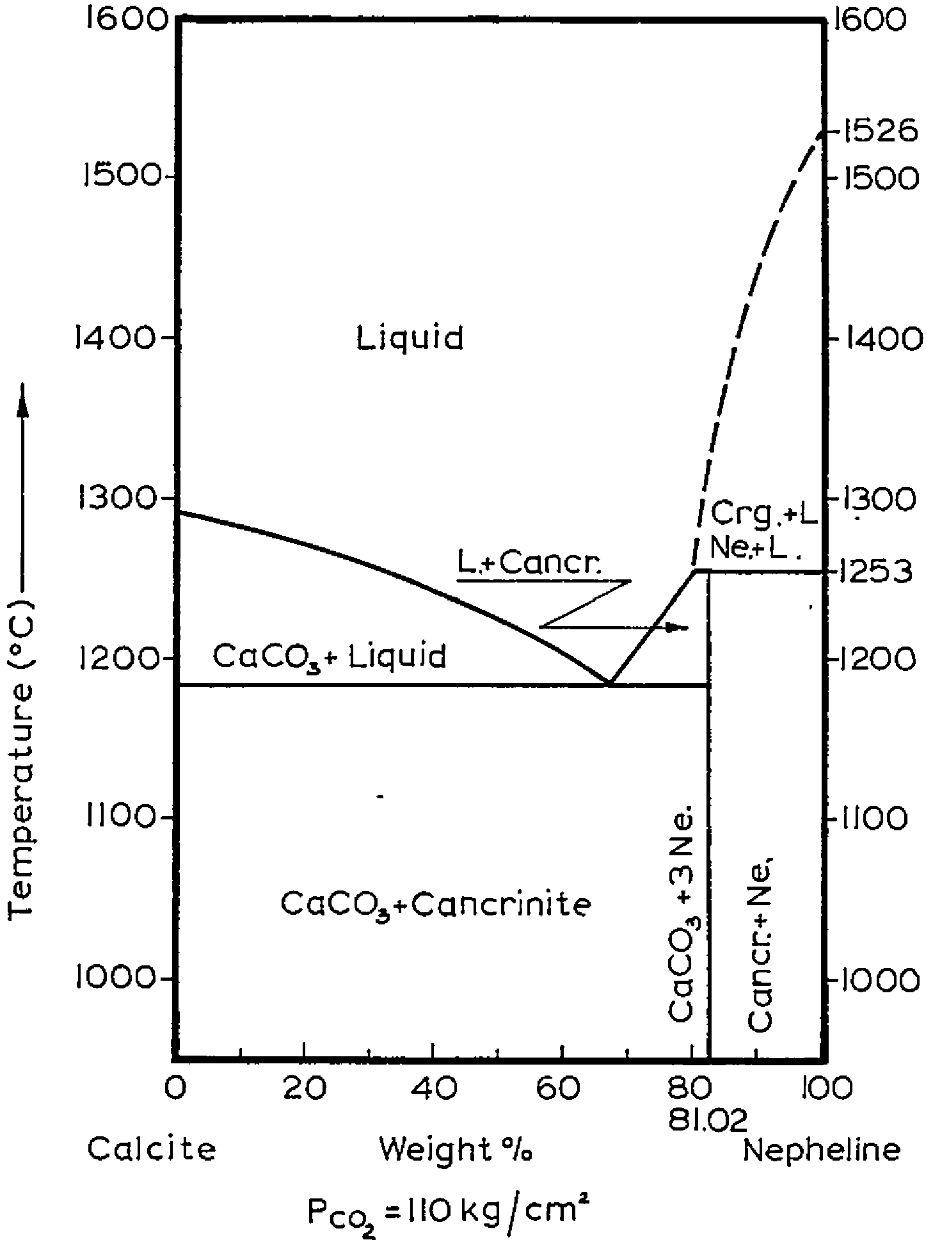
5. Experimental Studies of Cancrinites

The first synthesis of cancrinite was probably performed by Friedel (quoted in Borgström, 1930) in the early nineteen hundreds. Unfortunately no details of this synthetic work are available to the writer.

Eitel (1922) investigated the binary system nepheline-calcium carbonate under a carbon dioxide pressure of approximately 110 Kg/cm^2. Cancrinite of composition $3NaAlSiO_4.CaCO_3$ was found to melt incongruently at 1253°C. as shown in Figure 2.1. This incongruent melting temperature indicates that on cooling a melt of composition 80 to 100 weight per cent nepheline and 0 to 20 weight per cent calcite, the first crystalline phase to appear will be carnegeite followed at some lower temperature by nepheline which, below 1253°C., will form cancrinite and nepheline.

FIGURE 2.1

The system nepheline-calcite showing
field of synthesis of cancrinite (after Eitel)

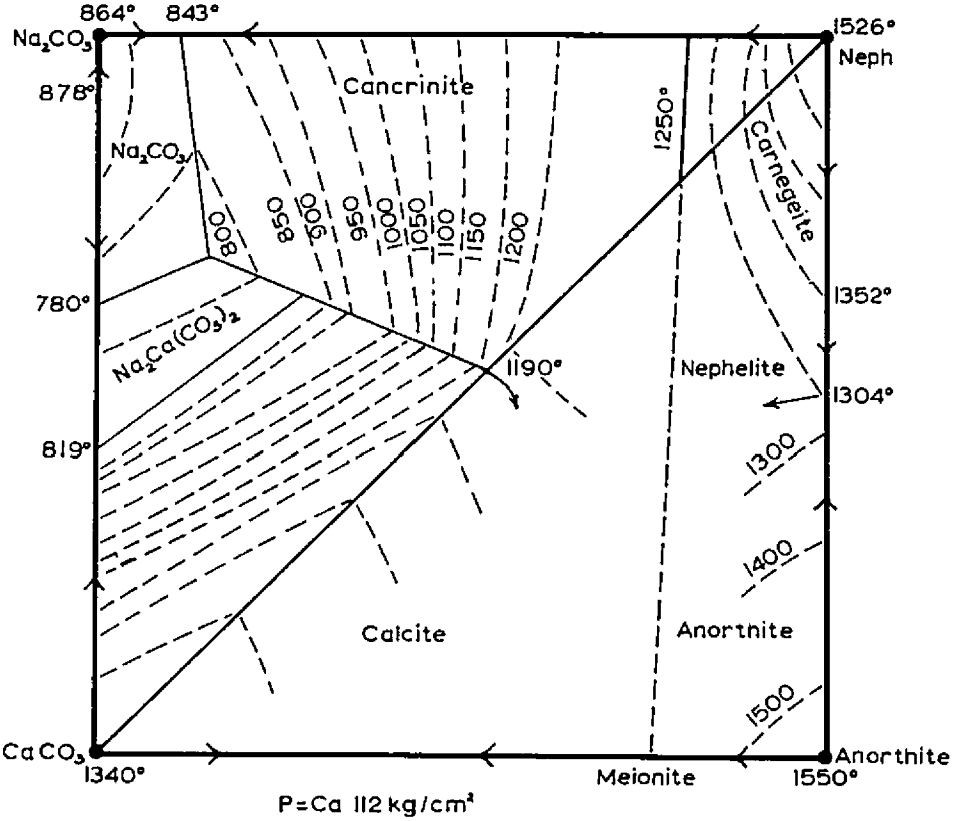

1600
1500
1400
1300
1200
1100
1000
1600
1526
1500
1400
1300
1253
1200
1100
1000
Temperature (°C)
Liquid
L+Cancr.
Crg.+L
Ne+L.
$CaCO_3$+ Liquid
$CaCO_3$+Cancrinite
$CaCO_3$ +3 Ne.
Cancr.+Ne.
0
20
40
60
80
100
81.02
Calcite
Weight %
Nepheline
P_{CO_2} = 110 kg/cm²

Thus, in this composition range the $CaCO_3$ portion of the cancrinite will be dissociated above the incongruent melting temperature; provided the structural formula of cancrinite is $3NaAlSiO_4.CaCO_3$. Eitel's experiments did not however indicate whether the carbonate existed as an ion in the crystal structure, or how it was oriented in the framework of $[SiO_4]$ and $[AlO_4]$ tetrahedral units. Further experimental work on the system $(Na_2,Ca)-(CO_3Al_2Si_2O_8)$, shown in Figure 2.2, failed to prove the existence of a pure sodium carbonate cancrinite, but did indicate a series of crystalline solid solutions existing between the hypothetical sodium carbonate cancrinite and the normal calcium-carbonate cancrinite.

Kozu, Ueda and Tsurumi (1933), using differential thermal analysis techniques, investigated the thermal properties of Korean cancrinite under atmospheric pressure. Measurements of the linear expansion of this mineral, both parallel and perpendicular to the c axis, showed irregularities around 900°C. These irregularities were believed to be due to the rapid escape of the CO_2 at this temperature, causing internal deformation of the crystal and transforming it into the nepheline-type structure. The change in weight of the powdered cancrinite during heating from 20°C. to 1000°C. on a thermo-balance indicated four distinct breaks on the curve at 300°C., 460°C., 800°C. and 910°C. Because chemical analysis of this specimen had shown the essential volatile constituents to be $+H_2O$, $-H_2O$ and CO_2, the authors concluded that the break at 300°C. indicated the complete evaporation of $-H_2O$, the break at 460°C. probably represented both the evaporation of $+H_2O$ and CO_2, with complete

FIGURE 2.2

The system $(Na_2Ca)-(CO_3,Al_2Si_2O_8)$
showing field of synthesis
of sodium carbonate cancrinite (after Eitel)


864°
843°
Na_2CO_3
1526°
Neph
878°
Cancrinite
Na_2CO_3
1250°
Carnegeite
800
850
900
950
1000
1050
1100
1150
1200
780°
1352°
$Na_2Ca(CO_3)_2$
1190°
Nephelite
1304°
819°
1300
1400
Calcite
Anorthite
1500
$CaCO_3$
Anorthite
1340°
Meionite
1550°
P=Ca 112 kg/cm²

evaporation of $+H_2O$ at 800°C. and complete evaporation of CO_2 at 910°C.

Wyart and Michel-Levy (1949) synthesized a mineral of composition $NaAlSiO_4 \cdot \frac{1}{2}H_2O$ that gave the same X-ray pattern as cancrinite, and which they called hydrocancrinite. In the same paper, Wyart and Michel-Levy described an artificial hydrothermal product that contained no calcium, but gave a cancrinite pattern, which they named paracancrinite. In a later paper, Wyart (1949) reported synthesizing a cancrinite from mixtures of K_2O, Na_2O, Al_2O_3, SiO_2 and Na_2CO_3. This cancrinite together with minor analcite formed at temperatures of 360° to 420°C., and had parameters of $a = 12.65 \pm 0.02Å$, $c = 5.15 \pm 0.02Å$. If excess Na_2CO_3 was used, both cancrinite and sodalite were synthesized as well developed crystals, the former having $n_\omega = 1.492$; $n_\epsilon = 1.489$, and a chemical composition corresponding to the formula

$$Na_{0.87}Al_{0.89}Si_{1.12} \cdot O_4(H_2O_{0.81}, Na_2CO_{3_{0.162}})$$

If this cancrinite was then treated at 500°C. with a solution rich in Na_2CO_3 Na-nepheline was formed.

Unfortunately in Wyart and Michel-Levy's work neither the pressure nor the temperatures could be accurately determined. The autoclaves which they used could withstand a maximum pressure of 700 Kg/cm^2 at 500°C. The names hydrocancrinite and paracancrinite seem undesirable, because the former resembles nepheline hydrate in composition and the latter is probably similar to the davyne or natrodavyne of Winchell and Winchell (1951).

Barrer and White (1952) succeeded in synthesizing a cancrinite of composition $3(Na_2O,Al_2O_3,2SiO_2),Na_2CO_3$ by using a gel, of composition $Na_2O,Al_2O_3,2SiO_2$, treated with excess of aqueous sodium carbonate. At atmospheric pressure in the temperature interval 300° to 420°C. the cancrinite synthesized had $n_\omega = 1.500$, $n_\epsilon = 1.497$ and unit cell dimensions of $a = 12.63Å$, $c = 5.18Å$. In addition, these investigators synthesized a "basic" cancrinite containing no carbonate ion at temperatures of about 390°C. and, in the presence of excess sodium hydroxide, this cancrinite gave an X-ray powder pattern almost identical with natural cancrinite, but the unit cell dimensions varied from $a = 12.47Å$ to $a = 12.71Å$, and c from 5.07Å to 5.20Å.

In a further paper Barrer, Hinds and White (1953) described cancrinite synthesis using a gel of the analcite composition which, in the presence of excess sodium hydroxide, produced a 100 per cent yield of cancrinite at 450°C. in a period of four days. Using an excess of Na_2SeO_4 and 5 cc of NaOH, cancrinite was produced at 360°C. in a period of two days. This mineral was called selenatic cancrinite, and has not been found in nature.

Sand, Roy and Osborn (1957), studying the system $Na_2O-Al_2O_3-SiO_2-H_2O$ using hydrothermal bombs and gels obtained from solutions of metal-organic compounds, synthesized cancrinite in the temperature range 250° to 460°C. and at a pressure of 15,000 psi. This cancrinite was of the sodium carbonate type. In addition a hydroxy cancrinite containing no carbonate ion was encountered.

III. EXPERIMENTAL AND ANALYTICAL METHODS

1. Description of Apparatus

The apparatus used in this study consists of an hydraulic pump to supply pressure. This pump was connected to six pressure vessels or "bombs" containing the charges to be synthesized, and heated by controlled furnaces to supply the temperature required.

(i) The Hydraulic Pump

The hydraulic pump used was supplied by the American Instrument Company, Inc., Silver Spring, Maryland, under the model number 46-2175. Pressures up to 30,000 psi can be developed rapidly, using the long handle and lever system supplied with this model. The dimensions of this pump are as follows:- piston diameter, ¼ inch; stroke, 1.15 inches; displacement per stroke, 0.06 cubic inches; and oil reservoir volume, 254 cubic inches. The pressure was recorded on a Bourdon gauge and could be maintained to within ± 500 psi. High pressure tubing was used to conduct the water pressure to each pressure vessel.

(ii) The Pressure Vessels

The pressure vessels, of bombs, used in these experiments were the cold seal test tube type designed by Tuttle (1949). These bombs, manufactured from "Stellite 25", - an alloy of cobalt, chromium and tungsten - are capable of withstanding high temperatures and pressures. The dimensions of each bomb are as follows:- outside diameter, 1¼ inches; inside diameter, 3/8 inch; and length, 12 inches. These can be operated for prolonged periods of time (i.e. over two days) at temperatures of approximately 850°C.

under a pressure of 20,000 psi. At lower pressures higher temperatures are permissible. The temperature is maintained in each bomb by a cylindrical furnace, as described below.

(iii) The Temperature Apparatus

Each bomb was heated by a "Hevi-Duty" furnace, and controlled by a Bristol Indicating Millivoltmeter Pyrometer Controller (model 478L) and a chromel-alumel thermocouple.

The cylindrical furnace, manufactured by the Ideal Furnace Company, has an inside diameter approximately the same as the outside diameter of the bomb. Temperatures as high as 1100°C. can be produced by this furnace. The heating element consists of heavy duty nicrome wire with an asbestos insulation. Each furnace was closed by a loop of wire attached to the framework supporting the bombs.

The controllers used in the first part of this study were not correctly calibrated, and a working curve of actual temperature versus recorded temperature had to be used for each controller and its thermocouple. These working curves are accurate to ± 10°C. During the latter half of this study the controllers had been correctly calibrated using a potentiometer, and were believed accurate to ± 5°C.

Each thermocouple consisted of a positive chromel wire (containing approximately 90 per cent nickel and 10 per cent chromium), and a negative alumel wire (containing approximately 95 per cent nickel, 5 per cent aluminium, manganese and silicon). The wires used were No. 8 AWG. The high nickel content and the large diameter of this thermocouple wire made it resistant to oxidation and therefore capable of recording temperatures from 0° to 1250°C. Using these thermocouples the controllers were able to record temperatures from room temperature to 1100°C.

Although the pressure had to be the same for the six bombs, the temperature for each bomb could be individually controlled.

2. Experimental Methods

(i) Sample Preparation

Dry mixtures of the various cancrinite compositions were prepared by first mixing the components of $NaAlSiO_4$, and then adding the required weight of carbonate, sulphate, hydroxide or chloride in the correct molecular proportion. The manufacturer's name, grade and lot number of the various chemicals used in these mixtures are given in Table 3.1.

TABLE 3.1

Chemicals Used in the Preparation of Synthetic Cancrinite Mixtures

Formula	Manufacturer	Grade	Lot No.
$Na_2SiO_3.9H_2O$	Fisher Scientific Co.	Technical	763366
$AlCl_3.6H_2O$	"	C.P.	772760
$SiO_2.xH_2O$	Mallinckrodt Chemical Works	C.P.	75908
$CaCO_3$	Baker and Adamson	A.C.S.	K 120
Na_2CO_3	British Drug Houses	"Analar"	430574
$NaHCO_3$	"	"Analar"	17906
$CaSO_4.2H_2O$	"	"Analar"	14883
K_2CO_3	Unknown	Unknown	Unknown
$KHCO_3$	British Drug Houses	"Analar"	24574
$Ca(OH)_2$	Unknown	Unknown	Unknown
$CaCl_2$	British Drug Houses	"Analar"	735828
$NaHSO_4$	"	"Analar"	675762

The composition $NaAlSiO_4$ was prepared by mixing αSiO_2, γAl_2O_3 and Na_2SiO_3 together by weight in the molecular proportion: Na_2SiO_3, 43%: γAl_2O_3, 36%: αSiO_2, 21%. αSiO_2 and γAl_2O_3 were used because they are reactive components, and were prepared separately by heating spectrographically pure silicic acid and aluminium chloride at 1525°C. for three hours and 750°C. for one hour respectively in order to achieve the required transformations. The Na_2SiO_3 was prepared from $Na_2SiO_3 \cdot 9H_2O$ by evaporating the water in a drying oven and weighing the compound as Na_2SiO_3.

After the three chemicals had been weighed out in the correct proportions to form $NaAlSiO_4$, they were placed in an hour-glass mixer, or in a wig-l-bug, and mixed until the powder became homogeneous. Throughout this study periodic checks were made by heating this mixture under water pressure and ascertaining that the product synthesized was actually nepheline. The fact that nepheline was easily synthesized indicated that the mixing was adequate.

The molecular proportions by weight of nepheline to the various carbonates, sulphates and hydroxides are given in Table 3.2. The dry mixtures of cancrinite composition were then placed in a dessicator until required.

(ii) Sealing of Sample

The different types of cancrinite were synthesized by placing the starting material and water in gold cylinders which were then sealed and weighed. The method of sealing the cylinders is one which was described by Yoder (1958). The procedure, with minor changes made by the author, was as follows. One end of a gold cylinder, 25.0 mm. long, outside diameter 3.0 mm., inside diameter 2.5 mm., was crimped and peened with a small hammer and anvil, and then welded shut in a carbon arc. Approximately 10 to 15 mg. of distilled water was then added to the cylinder by means of a capillary tube. About 40 to 50 mg. of the powdered starting material was added, and the top edge and inside lip of the cylinder wiped with a "Kleenex" tissue. Four to 6 mm. of the open end of the cylinder were then crimped and peened. The crimped end of the cylinder was placed in a small vise whose jaws were approximately 1 mm. thick, and the vise tightened.

TABLE 3.2

Molecular Proportions of Nepheline to Other Compounds in Synthetic Cancrinite Mixtures

Name of Cancrinite	Formula	Weight Per Cent Nepheline
Cancrinite proper	$3NaAlSiO_4 \cdot CaCO_3$	80.98
Sulphatic cancrinite (Winchell)	$3NaAlSiO_4 \cdot CaSO_4$	71.23
Wischnewite (Winchell)	$3NaAlSiO_4 \cdot NaHSO_4$	78.02
Davyne proper	$3NaAlSiO_4 \cdot K_2CO_3$	75.51
Bicarbonate davyne	$3NaAlSiO_4 \cdot KHCO_3$	80.98
Natrodavyne proper	$3NaAlSiO_4 \cdot Na_2CO_3$	80.08
Bicarbonate natrodavyne	$3NaAlSiO_4 \cdot NaHCO_3$	83.53
Microsommite (Winchell)	$3NaAlSiO_4 \cdot CaCl_2$	79.34
Hydroxy cancrinite	$3NaAlSiO_4 \cdot Ca(OH)_2$	85.19

The vise was then placed in a direct current electrical system. This system consisted of a 110 volt D.C. supply, a variable resistor set at 20 ohms, a switch and a spectrographic carbon electrode contained in an insulated holder. Upon completion of the weld, the cylinder was examined under a binocular microscope (35x) for defects. If none were present the cylinder was removed from the vise, weighed, and placed in one of the bombs.

(iii) Starting of Run

At the beginning of each run sealed cylinders containing the mixture of the sample to be synthesized were placed in each bomb. Each run consisted of six bombs, and each bomb contained one to four cylinders. The bombs were inserted into the pressure circuit, tightened, and the pressure raised to the desired value. If no leaks developed in the pressure circuit, the thermocouples were inserted, and the furnaces placed in position. As the temperature increased, the pressure also increased, and it was necessary to lower the pressure to the required value by a pressure release valve.

(iv) Quenching of Runs

At the end of each run the furnaces and pyrometer controllers were unplugged and the furnaces swung open. A bucket of cold water was raised immediately under each bomb. As the temperature decreased it was necessary to maintain the pressure at the required value in order that the gold cylinders would not burst. After each of the bombs had been cooled to room temperature, the pressure was released, the bombs loosened, and the gold cylinders removed and weighed. If the weight remained the same, or within ± 0.0002 gms. of the starting weight, the experiment was considered to have taken place in a closed system. If the weight had changed the experiment was considered to have taken place in an open system, and therefore to have absorbed water or leached material. Those runs involving open systems could not be used in determination of fields of synthesis, of cell dimensions, nor in the determination of solid solution between end-members.

3. Analytical Methods

(i) Description of X-ray Unit

All of the products synthesized in the bombs were X-rayed on a Philips X-ray unit fitted with a Norelco High Angle Diffractometer. The settings on the X-ray machine were as follows:- voltage, 30 kv.; amperage, 15 ma.; angular aperture, 1°; receiving slit, 0.006 inches. For determinations of the phases present, the diffractometer settings used were scanning rate 1°2θ per minute; chart speed, 1/8 inch per minute; rate meter scale factor, 4; multiplier, 1; and time constant, 4. For determinations of d spacings and solid solution phenomena the diffractometer settings used were scanning rate, 1/4°2θ per minute; chart speed, 1/8 inch per minute; rate meter scale factor, 4; multiplier, 1; and time constant, 4. At high 2θ angles the rate meter scale factor was set at 2.

All phase determinations and solid solution measurements were made using CuKα radiation with a nickel filter. Determinations of d spacings were made using CuKα radiation with a nickel filter, and in a few cases with FeKα radiation and a manganese filter.

(ii) X-ray Determination of Phase(s)

In order to X-ray the synthesized product(s), the powder was removed from the gold cylinders and ground in an agate mortar. Toluene was added to the mortar to facilitate grinding. Each run was ground to pass 200 mesh, thus minimizing any error introduced by varying grain size. The ground powder was then run upon the diffractometer to determine the phase(s) present. The machine was allowed to run from 10 to $60^{\circ}2\theta$ as this interval contained sufficient peaks to permit identification of the product(s) encountered in this study.

(iii) X-ray Determination of d Spacings and Cell Dimensions

In order to determine the d spacings of the synthetic cancrinites the ground powder was mixed with some quartz of the same grain size. The quartz specimen used was collected from Oliver, B.C. The purity of this specimen was checked by mixing it with C.P. NaCl (Fisher Scientific Co., Lot number 781836) and comparing the d spacings of the quartz with those given in the A.S.T.M. index (1954). Table 3.3 gives the comparison between the calculated d spacings and the observed d spacings for the Oliver, B.C. quartz. The powdered mineral with quartz standard was run upon the diffractometer from 10° to approximately $120^{\circ}2\theta$.

TABLE 3.3

Comparison between Calculated and Observed

d Spacings for Oliver, B.C., Quartz

Plane	d (calc.)	d (obs.)
$10\bar{1}0$	4.26	4.26
$10\bar{1}1$	3.343	3.343
$10\bar{1}2$	2.282	2.283
$20\bar{2}0$	2.128	2.128
$11\bar{2}2$	1.817	1.815
$21\bar{3}1$	1.541	1.541

The diffractometer pattern was removed and the quartz peaks identified and indexed. Each peak on the pattern was bisected at approximately two-thirds of its height, using an architects ruler. Perpendicular lines were then drawn from the mid-point of the peak to the base of the pattern. The distance between each cancrinite peak and a neighbouring quartz peak was then measured, using the architects ruler. The distances obtained were converted to degrees. Hence from a knowledge of the values of 2θ for the quartz peaks, the 2θ value for each cancrinite peak was obtained. Finally, the d spacings were found from tables.

An approximate value of the cell dimensions of each synthetic cancrinite was also determined from the powder pattern. The value of $\sin^2\theta$ for each cancrinite peak was calculated. These observed $\sin^2\theta$ values were compared with the calculated $\sin^2\theta$ values for every possible plane, thus indexing each peak on the powder pattern. The cell dimensions of all planes were then found from the equation:-

$$\mathrm{Sin}^2\theta_{hkl_{obs.}} = \frac{\lambda^2}{3a^2}\,(h^2 + hk + k^2) + \frac{\lambda^2}{4c^2}\,l^2$$

where λ = wavelength of radiation used

a = a dimension

c = c dimension

For planes of the type $hk\bar{i}o$ and 0001 the a and c dimensions could be obtained directly from this equation. For planes of the type $hk\bar{i}l$ the values of $\sin^2\theta$ obs. were taken for two planes, having similar 2θ values, and the a and c dimensions found by solving these equations simultaneously.

The a and c dimensions obtained for each plane were then plotted as a function of $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$. This function rapidly approaches zero as θ approaches 90°. For example at 10°θ, the value of the function is 5.572; at 25°θ the value is 1.913; and at 50°θ the value is 0.506. Theoretically the value of the a and c dimension extrapolated to the zero value of this function, or 90°θ, should give a good estimate of the true a and c dimensions. This method was proposed by Nelson and Riley (1945).

(iv) X-ray Determination of Solid Solution Phenomena

In order to investigate whether solid solution existed between the various end-members of the cancrinite group, intermediate members were prepared and synthesized. The intermediate and end-members of the solid solution series being investigated were mixed with quartz and run upon the diffractometer which was set to oscillate over the interval 26-28°2θ. At least six patterns were run over this range which contained the peaks $10\bar{1}1$ quartz and $21\bar{3}1$ cancrinite. The distances between peaks were then measured on the Norelco Film Illuminator and Measuring Device. The distances between peaks were plotted as a function of composition to determine the extent of solid solution. A discussion of the usefulness of this method is included in a later section entitled "Discussion of Results".

4. Problems Encountered and Sources of Error

A number of problems were encountered during this study. First, the pressure was very sensitive to changes in room temperature, slight draughts causing considerable fluctuations in pressure. The pressure was believed accurate to ± 500 psi for most experiments. Second, the pyrometers were not correctly calibrated for the first half of this study, and a set of correction curves had to be constructed, so that one could determine the temperature of the bombs. These curves, it is believed, were accurate to ± 10°C. During the second half of the study the pyrometers were correctly calibrated and the temperature controlled to within ± 5°C. The position of the thermocouple in relation to the bomb was also found to be important, and plasticine was used to keep the thermocouples rigidly in place.

The third and most important difficulty was caused by leaching and absorption of water in the gold cylinders. Because many of the carbonates and sulphates used in the starting mixtures were soluble in water, runs which had leached or absorbed water had to be discarded. It was also found that synthesis which had taken place in an open system could not be reproduced. In a few runs, under temperature and pressure conditions that produced cancrinite in a closed system, nepheline was produced in an open system. This would indicate that the carbonate had been leached by water.

Fourth, the rate of quenching the runs was important as the formation of metastable phases had to be prevented. Throughout this study no metastable phases were encountered except at lower temperatures where analcite appeared, possibly as a metastable phase. Fifth, the compositional errors in preparing the starting mixtures were believed to be negligible.

There were three sources of error in the analytical methods used in this study. First, errors caused by the X-ray diffractometer; second, errors in the cell dimensions and d spacings caused by the measuring technique; and third, errors in the solid solution measurements. The latter two errors were the most important.

Errors in the X-ray diffractometer may have been caused by diffractometer response, variation in the goniometer speed and/or chart speed. The X-ray diffractometer used was new, and although it had a known error it was believed to give constant readings. Thus the errors caused by diffractometer response, and the goniometer and chart speed were believed to be negligible.

The errors in the determinations of d spacings of the synthetic cancrinites were caused by the rather diffuse peaks produced by the synthetic material, possibly as a result of disorder, and by the method of measuring these peaks. The former made accurate bisection of some of the peaks difficult. Using the architects ruler and a sharp 4H pencil, the distance between peaks could be measured to ± 0.01°2θ. Thus at low values of 2θ the d spacings are accurate to ± 0.01Å, and at higher values of 2θ to ± 0.001Å.

Because the determinations of cell dimensions were made from the same diffractometer patterns used in the determinations of the d spacings, similar types of errors apply. The average error in $\sin^2\theta$ was ± 0.0002. This results in a large error in a and c dimensions at small 2θ angles, but at larger 2θ angles this error is much smaller. For example at 8°2θ the error in the a dimension is ± 0.25Å, whereas at 50°2θ there is an almost negligible error in the a dimension, of ± 0.0001Å. Examination of the graphs of a and c versus $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ show that the error in a is approximately ± 0.02Å, and the error in c is about ± 0.02Å.

Solid solution measurements were made by oscillating each sample three times between 26 and 28°2θ. The calculated standard deviation was less than 0.016°2θ for the distance $2\theta_{10\bar{1}1}$ quartz $- 2\theta_{21\bar{3}1}$ cancrinite.

IV. EXPERIMENTAL RESULTS

The cancrinites investigated were easily synthesized at the pressure and temperature conditions used in this study. Of the twelve possible end-members suggested by Winchell and Winchell (1951), comprising two end-members for each of the six named varieties of this mineral, three do not produce a cancrinite-type mineral when synthesized from their constituents. The end-members that could not be synthesized to a cancrinite, produced, in each case, a mineral of the sodalite family. The following compositions failed to produce cancrinites:-

$3NaAlSiO_4 \cdot CaCl_2$ – microsommite (Winchell)
$3NaAlSiO_4 \cdot HNaSO_4$ – wischnewite (Winchell)
$3NaAlSiO_4 \cdot CaSO_4$ – sulphatic cancrinite (Winchell)

As a result of synthesizing cancrinites of differing compositions, but given the same name as Winchell and Winchell, it is suggested that the following revised nomenclature be used for the cancrinites:-

cancrinite proper – $3NaAlSiO_4 \cdot CaCO_3$
hydroxy cancrinite – $3NaAlSiO_4 \cdot Ca(OH)_2$
davyne proper – $3NaAlSiO_4 \cdot K_2CO_3$
bicarbonate davyne – $3NaAlSiO_4 \cdot KHCO_3$
natrodavyne proper – $3NaAlSiO_4 \cdot Na_2CO_3$
bicarbonate natrodavyne – $3NaAlSiO_4 \cdot NaHCO_3$
microsommite – $4[3NaAlSiO_4 \cdot Ca(OH)_2] + [3NaAlSiO_4 \cdot CaCl_2]$
sulphatic cancrinite – $7[3NaAlSiO_4 \cdot CaCO_3] + [3NaAlSiO_4 \cdot NaHSO_4]$

The latter two names do not strictly apply to end-members as they are combinations of cancrinite-type molecules and molecules of the sodalite type. It was found for microsommite and sulphatic cancrinite that these combinations produced a diffraction pattern that was closest to the pattern given by natural cancrinite specimens.

Using the revised nomenclature, the cancrinites can be conveniently divided into five carbonate and bicarbonate varieties, one hydroxide variety and two mixed varieties; one containing hydroxide and chloride radicals, and the other carbonate and bisulphate radicals. It is probable that a number of other end-members may exist. For example, it is known that the composition of nepheline and sodium hydroxide produce a cancrinite. This is discussed in Chapter V.

1. Carbonate and Bicarbonate End-members

(i) Cancrinite Proper ($3NaAlSiO_4 \cdot CaCO_3$)

Field of Synthesis

Cancrinite proper was found to be stable in the closed system up to 775°C. at a water pressure of 20,000 psi, this being the approximate temperature limit of the apparatus at this pressure. Nepheline was encountered in the open systems at temperatures greater than 550°C., at a water pressure of 10,000 psi, and at temperatures greater than 600°C., at a water pressure of 30,000 psi. This breakdown curve is of little significance, as it can be caused either by the leaching of the $CaCO_3$, or by the dissociation of $CaCO_3$ at these elevated temperatures and pressures.

At temperatures of 200°C. and less and at water pressures ranging from 10,000 to 25,000 psi analcite together with cancrinite occurs in the closed systems. The field of this analcite was not ascertained.

Attempts were made to synthesize and dissociate cancrinite using KOH solution instead of water, CO_2 (in the form of dry ice) instead of water, and dry synthesis. The latter case failed to synthesize cancrinite or to give a recognizable product. The other cases produced a cancrinite but did not assist in its breakdown. It is interesting that cancrinites can be synthesized by replacing the water pressure by CO_2 pressure. The resulting cancrinite has d spacings and cell parameters similar to cancrinites synthesized under water pressure. The results of all cancrinite syntheses are given in Table 4.1.

d Spacings and Cell Dimensions

The d spacings, lattice planes and cell dimensions of regular synthetic cancrinite are given in Table 4.2. A graph of a and c dimensions and also of cell volumes ($0.866\ a^2c$) versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ is given in Figure 4.1. The d spacings obtained differ slightly from those given in the A.S.T.M. (1954) card index, probably due to compositional differences. The cell dimensions of synthetic cancrinite are $a = 12.59 \pm .02\text{Å}$ (approximately) $c = 5.17 \pm .02\text{Å}$ (approximately), with a resulting cell volume of $710 \pm 5\text{Å}^3$. Also included in Table 4.2 are the d spacings, lattice planes and cell dimensions of cancrinite synthesized with CO_2 pressure only.

(ii) Davyne Proper ($3NaAlSiO_4 \cdot K_2CO_3$)

Field of Synthesis

The experimental data and dissociation curve for davyne proper are given in Table 4.3 and Figure 4.2 respectively. Davyne proper dissociates into nepheline, and possibly K_2CO_3, between 425° and 450°C. at a water pressure of 10,000 psi, and between 450° and 500°C. at a water pressure of 30,000 psi. In the pressure range 15,000 to 30,000

TABLE 4.1

Experimental Data on Cancrinite Proper

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
1 (X)	0.6080	0.6080	15,000	550	156	Cancrinite
2 (X)	0.6143	0.6143	15,000	525	156	Cancrinite
3 (X)	0.6153	0.6153	15,000	500	156	Cancrinite
4 (X)	0.6263	0.6262	15,000	600	156	Cancrinite
5 (X)	0.6125	0.6123	20,000	520	135	Cancrinite
6	0.5923	0.5900	20,000	550	135	Cancrinite
7	0.5961	0.5931	20,000	650	135	Nepheline
8 (X)	0.5862	0.5861	15,000	625	156	Cancrinite
9	0.6051	0.6041	15,000	650	156	Cancrinite + Nepheline
10	0.5860	0.5826	15,000	675	156	Cancrinite + Nepheline
11	0.6058	0.6047	15,000	425	156	Cancrinite
12 (X)	0.5760	0.5760	10,000	550	235	Cancrinite
13	0.5901	0.5975	10,000	600	235	Cancrinite + Minor Nepheline
14 (X)	0.5804	0.5804	10,000	650	235	Cancrinite
15	0.6021	0.6001	10,000	525	235	Cancrinite + Nepheline
16 (X)	0.5978	0.5977	23,000	600	120	Cancrinite
18	0.6038	0.6029	23,000	700	120	Cancrinite + Nepheline ?
19	0.6043	0.6018	30,000	650	96	Nepheline + ?
20	0.5942	0.5933	30,000	725	96	Cancrinite + Minor Nepheline
21 (X)	0.6037	0.6039	20,000	625	144	Cancrinite
22 (X)	0.5753	0.5753	20,000	600	120	Cancrinite
23 (X)	0.5928	0.5927	37,000	725	140	Cancrinite
24 (X)	0.5867	0.5867	37,000	650	140	Cancrinite
25 (X)	0.5836	0.5836	15,000	350	192	Cancrinite
26	0.5852	0.5847	20,000	675	228	Cancrinite + Minor Nepheline
27	0.5860	0.5856	20,000	700	228	Cancrinite
28 (X)	0.5808	0.5806	20,000	650	228	Cancrinite + v. Minor Nepheline
29 (X)	0.5713	0.5712	20,000	650	228	Cancrinite
30* (X)	0.5682	0.5680	20,000	675	228	Cancrinite + v. Minor Nepheline ?

Table 4.1 (contd.)

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temper-ature (°C.)	Time (hrs.)	Phases
31* (X)	0.5708	0.5707	20,000	650	228	Cancrinite + v. Minor Nepheline?
32	0.5912	0.5901	15,000	650	516	Cancrinite
33 (X)	0.5896	0.5895	15,000	650	516	Cancrinite
34 (X)	0.5724	0.5725	15,000	700	516	Cancrinite
35	0.5936	0.5900	15,000	700	516	Cancrinite
36 (X)	0.5748	0.5748	15,000	650	516	Cancrinite
37	0.5736	0.5800	20,000	650	520	Nepheline
38 (X)	0.5854	0.5853	20,000	775	520	Cancrinite
39	0.5803	0.5837	20,000	550	520	Nepheline
40(Dry)(X)	0.5924	0.5925	20,000	550	520	?
41(KOH)	0.5657	0.5764	23,000	525	168	Cancrinite + Nepheline
42(KOH)	0.5614	0.5634	23,000	650	168	Cancrinite
43(CO_2 only)(X)	0.5957	0.5957	23,000	650	168	Cancrinite
44(CO_2 +H_2O)	0.5685	0.5682	23,000	525	168	Cancrinite
45(CO_2 +H_2O)(X)	0.5731	0.5731	23,000	675	168	Cancrinite
46 (X)	0.5546	0.5546	23,000	250	168	Analcite + Cancrinite
47(CO_2 +H_2O)	0.5887	0.5950	23,000	700	168	Nepheline + ct (?)
48 (X)	0.5862	0.5862	15,000	250	156	Cancrinite
49	0.5782	0.5806	15,000	300	144	Cancrinite
50(KOH)	0.6012	0.6117	15,000	700	144	Cancrinite
51(CO_2 only)	0.5670	0.6110	15,000	250	144	Analcite + Nepheline ?
52(Dry)	0.5510	0.5816	15,000	250	144	Analcite + Nepheline ?
53(CO_2 only)(X)	0.5611	0.5613	15,000	550	144	Cancrinite
54 (X)	0.6020	0.6020	10,000	300	232	Cancrinite
55 (X)	0.5871	0.5870	10,000	200	67	Cancrinite + Analcite ?
56 (X)	0.6102	0.6104	25,000	200	48	Cancrinite
57 (X)	0.6099	0.6101	25,000	200	48	Cancrinite + Analcite
58 (X)	0.5872	0.5873	20,000	150	50	Cancrinite + Analcite

Table 4.1 (contd.)

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
59 (X)	0.5761	0.5762	15,000	200	408	Cancrinite + Analcite + Minor Calcite
60 (X)	0.5886	0.5886	15,000	200	408	Cancrinite + Analcite + Calcite
63 (S)(X)	0.5912	0.5912	15,000	200	142	Cancrinite + Analcite + Calcite

* - material used in these runs consisted of cancrinite previously synthesized in the closed system.

(S) - "seeded" with natural cancrinite.

(X) - closed system

TABLE 4.2

d Spacings, Cell Dimensions and Cell Volumes of Synthetic Cancrinite Proper, Synthesized with H_2O and CO_2 Pressure

Radiation = CuKα, Filter = Ni, Standard = Quartz

S.C.54
Regular cancrinite pr.
Synthesized with H_2O pressure

d	I (visual)	$hk\bar{i}l$	a(Å)	c(Å)	cell vol.(Å^3)
6.35	35	$11\bar{2}0$	12.67	-	-
4.65	65	$10\bar{1}1$	12.57(1)	5.15	705
3.649	40	$30\bar{3}0$	12.63	-	-
3.217	100	$21\bar{3}1$	12.59*(1)	5.14	705
3.035	15	$31\bar{4}0$	12.63	-	-
2.923	7	$30\bar{3}1$?	?	?	-
2.735	20	$40\bar{4}0$	12.63	-	-
2.611	15	$31\bar{4}1$	12.63(1)	5.12	707
2.564	15	$00\bar{0}2$	-	5.13	-
2.503	5(diff.)	$32\bar{5}0$	12.60	-	-
2.411	12	$40\bar{4}1$	12.59(2)	5.17	710
2.162	5(diff.)	$41\bar{5}1$	12.59(2)	5.17	710
2.101	12	$33\bar{6}0$	12.60	-	-
1.870	5	$40\bar{4}2$	12.59*(2)	5.14	706
1.791	5(diff.)	$43\bar{7}0$	12.58	-	-
1.745	5	$52\bar{7}0$	12.58	-	-
1.582	5(diff.)	$61\bar{7}1$	12.59(2)	5.14	706
1.562	5	$51\bar{6}2$	12.59(3)	5.17	710
1.492	5(v.diff.)	$53\bar{8}1$	12.59(3)	5.17	710
1.082	1	$54\bar{9}3$	12.59(3)	5.17	710

S.C.43
Cancrinite pr.
Synthesized with CO_2 pressure

d	I (visual)	$hk\bar{i}l$	a(Å)	c(Å)	cell vol.(Å^3)
4.63	65	$10\bar{1}1$	12.65(1)	5.11	708

Table 4.2 (contd.)

d	I (visual)	$hk\bar{i}l$	a(Å)	c(Å)	cell vol.(Å^3)
3.646	50	$30\bar{3}0$	12.62	–	–
3.485	30	?	?	?	
3.217	100	$21\bar{3}1$	12.65(1)	5.11	708
2.909	25	$30\bar{3}1$?	?	?	
2.734	15	$40\bar{4}0$	12.62(2)	–	–
2.607	7	$31\bar{4}1$	12.59*	5.15	707
2.554	30(diff.)	0002	–	5.10	–
2.503	5	$32\bar{5}0$	12.61	–	–
2.095	5	$33\bar{6}0$	12.57	–	–
1.741	15	$52\bar{7}0$	12.55	–	–
1.602	7	?	?	?	–
1.333	5	$53\bar{8}2$	12.62(2)	5.13	708

* – determined by comparison of $\sin^2\theta$ obs. and $\sin^2\theta$ calc. values.

( ) – numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation.

FIGURE 4.1

Cell dimensions and cell volumes

versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ for synthetic cancrinite proper

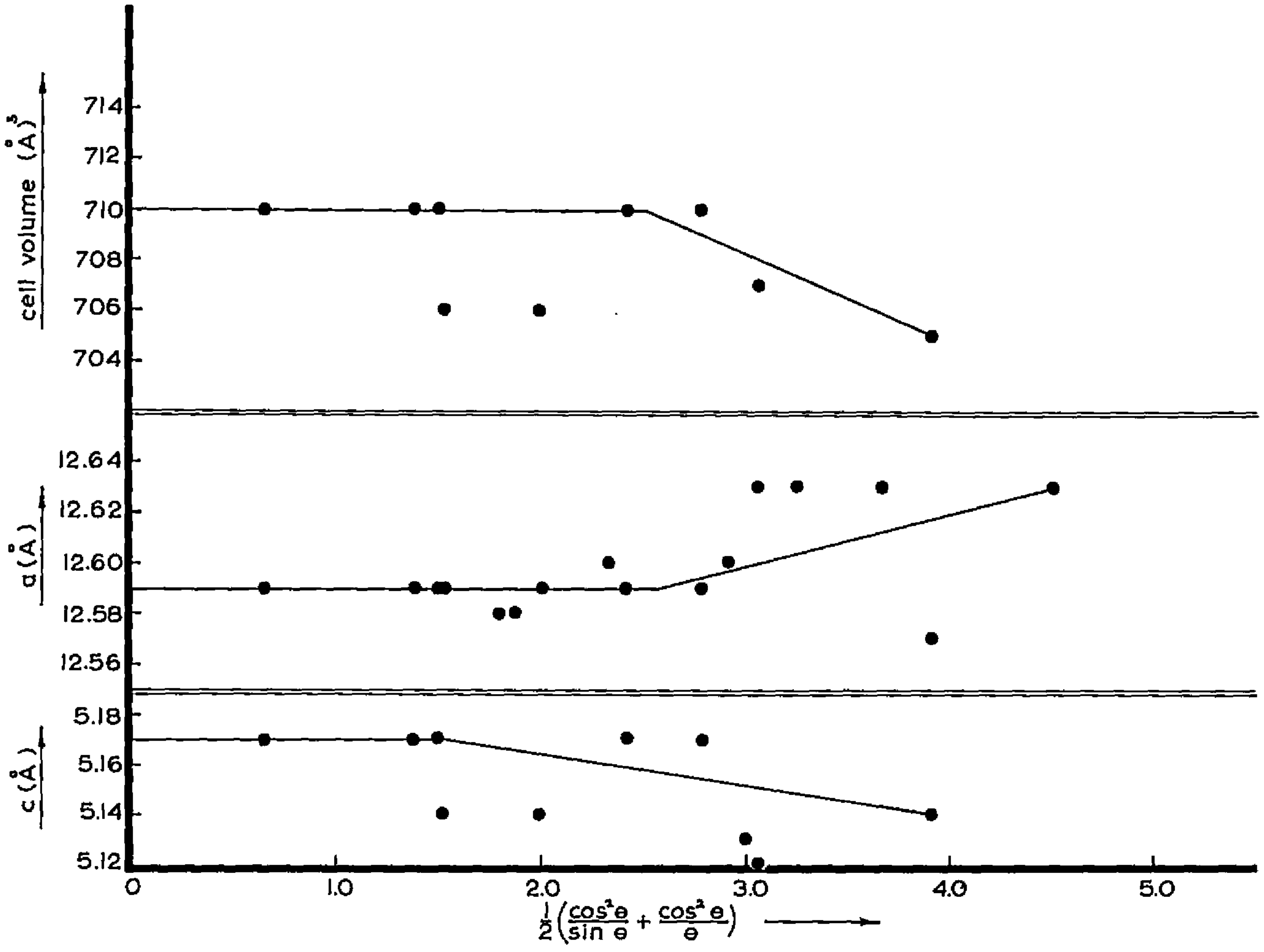

cell volume (Å^3)
714
712
710
708
706
704
a (Å)
12.64
12.62
12.60
12.58
12.56
c (Å)
5.18
5.16
5.14
5.12
0
1.0
2.0
3.0
4.0
5.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

TABLE 4.3

Experimental Data for Davyne Proper

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
D14X*	0.6082	0.6080	10,000	500	232	Davyne
D15X	0.6038	0.6452	10,000	450	232	Nepheline
D21X*	0.5995	0.5995	25,000	450	186	Davyne
D22X	0.6013	0.5973	25,000	500	186	Nepheline
D23X	0.5940	0.5951	25,000	200	48	Davyne
D24X*	0.5821	0.5822	15,000	400	100	Davyne
D27X*	0.6183	0.6181	15,000	450	100	Davyne
D28X*	0.6027	0.6026	15,000	600	100	Nepheline
D31X	0.6030	0.5958	20,000	550	50	Nepheline
D32X	0.5859	0.5844	20,000	150	50	Davyne + Nepheline ?
D33X*	0.5907	0.5907	20,000	450	50	Davyne
D34X	0.5757	0.5784	20,000	500	50	Davyne + Nepheline
D36X*	0.6082	0.6082	15,000	600 400	68 76	Nepheline + Minor Davyne ?
D37X	0.5990	0.5884	15,000	500	140	Nepheline
D38X	0.6092	0.6116	25,000	500	95	Davyne + Nepheline
D41X	0.6007	0.5979	20,000	500	95	Nepheline + Very Minor Davyne
D43X	0.6164	0.6145	25,000	500	95	Davyne + Nepheline
D46X	0.5955	0.5933	10,000	450	190	Nepheline + Davyne
D47X*	0.5956	0.5957	10,000	500	190	Nepheline
D48X	0.6196	0.6185	10,000	400	190	Nepheline + Minor Davyne
D49X*	0.6168	0.6168	20,000	500	122	Davyne + Nepheline
D50X	0.6067	0.6075	15,000	500	162	Davyne + Nepheline
D51X*	0.5860	0.5862	20,000	250	162	Davyne
D56X	0.6032	0.5910	10,000	450	188	Nepheline + Minor Davyne
D57X*	0.5957	0.5955	10,000	450	188	Nepheline
D58X*	0.5892	0.5892	10,000	400	188	Davyne
D62X*	0.5968	0.5970	29-30,000	500	95	Nepheline
D63X	0.5866	0.5884	29-30,000	450	95	Nepheline
D64X*	0.5828	0.5828	29-30,000	400	95	Davyne
D65X*	0.5563	0.5563	20,000	550	148	Nepheline
D66X	0.5654	0.5685	15,000	500	144	Nepheline
D68X*	0.5780	0.5778	15,000	550	144	Nepheline

Table 4.3 (contd.)

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
D69X*	0.5570	0.5568	10,000	425	195	Davyne + Very Minor Nepheline
D71X*	0.5460	0.5460	15,000	500	145	Nepheline
D73X*	0.5289	0.5288	20,000	650	72	
				575	13	
				500	11	Nepheline
				400	70	
D75X	0.5611	0.5465	15,000	650	72	Nepheline
				400	88	
D77XE(1)	0.5784	0.5683	10,000	650	160	Nepheline
D78X	0.5997	0.5980	25,000	500	61	Nepheline
D82XE(1)	0.5905	0.5749	10,000	650	224	Nepheline
D83X*	0.6028	0.6028	25,000	500	126	Nepheline + Davyne ?
D84X*	0.5943	0.5944	25,000	500	126	Nepheline
D85X*	0.5672	0.5672	25,000	550	126	Nepheline
D87XE(2)*	0.5650	0.5652	25,000	650	126	Nepheline
D94X	0.6043	0.6013	30,000	450	75	Nepheline

(1) - starting mixture contained 42 weight % K_2CO_3 in excess of stoichiometric requirements, charge contained .0058 gms H_2O
.0153 gms powder

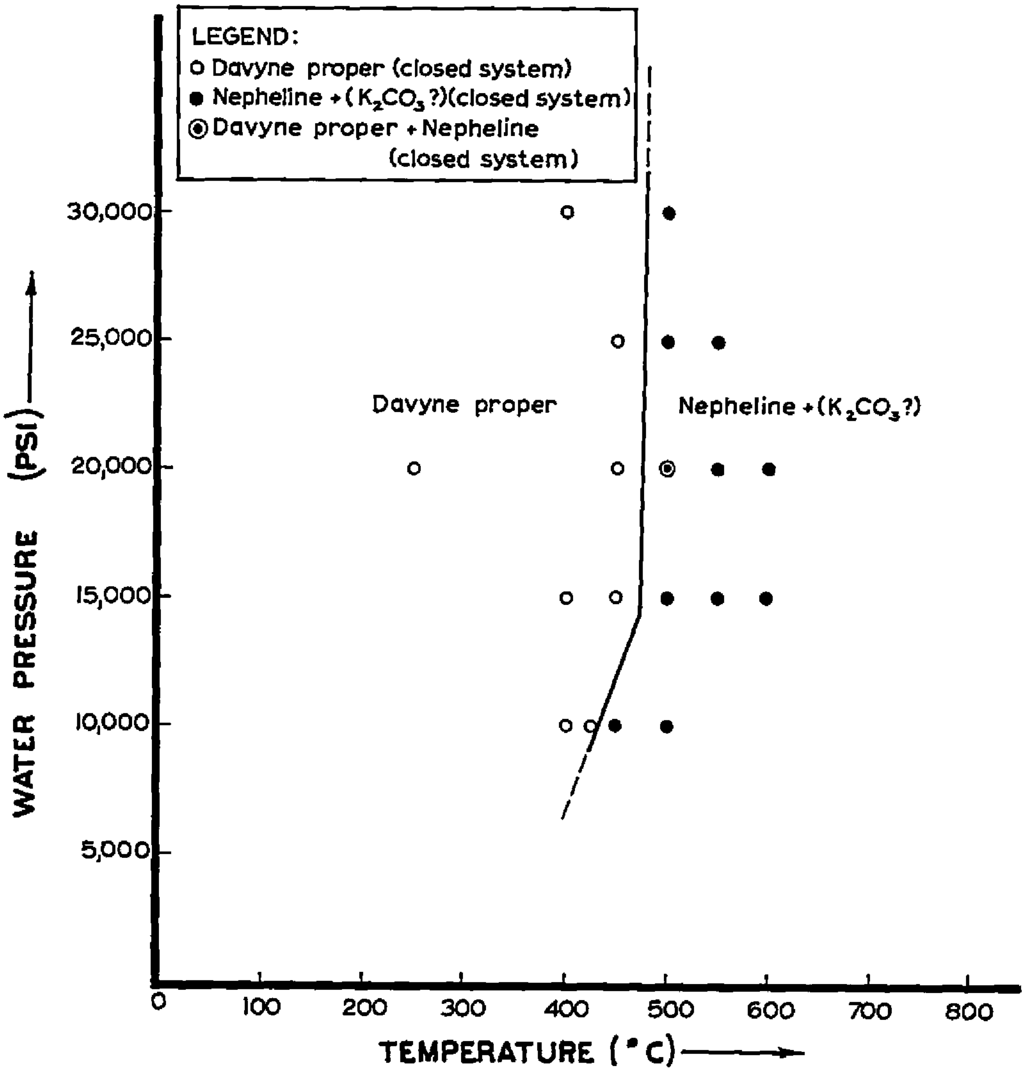
(2) - starting mixture contained 42 weight % K_2CO_3 in excess of stoichiometric requirements, charge contained .0042 gms H_2O
.0166 gms powder

* - closed system

<u>FIGURE 4.2</u>

Field of synthesis of davyne proper

(closed system, curve drawn visually)


LEGEND:
○ Davyne proper (closed system)
● Nepheline + (K_2CO_3?)(closed system)
⊙ Davyne proper + Nepheline (closed system)
Davyne proper
Nepheline + (K_2CO_3?)
WATER PRESSURE (PSI)
30,000
25,000
20,000
15,000
10,000
5,000
0
100
200
300
400
500
600
700
800
TEMPERATURE (°C)

psi, this breakdown curve is essentially vertical, implying that the reaction involved in the dissociation of davyne proper in this pressure range is almost wholly temperature dependent. No K_2CO_3 was detected in the dissociated products, possibly due to the K_2CO_3 going into solution and remaining in solution even in the quenched products; or due to the inability to detect K_2CO_3 in the X-ray patterns. Both of these possibilities will be discussed more fully in a later chapter.

No analcite was detected in the closed systems at temperatures as low as 150°C.

d Spacings and Cell Dimensions

The d spacings, lattice planes and cell dimensions of davyne proper are given in Table 4.4. A graph of a and c dimensions and also of cell volumes versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ is given in Figure 4.3. The cell dimensions of synthetic davyne proper obtained from this graph are $a = 12.73 \pm .02\text{Å}$ (approximately), $c = 5.17 \pm .02\text{Å}$ (approximately), with a resulting cell volume of $727 \pm 5\text{Å}^3$.

(iii) Bicarbonate Davyne ($3NaAlSiO_4.KHCO_3$)

Field of Synthesis

The field of synthesis of bicarbonate davyne is almost identical with that of davyne proper. Again, the dissociation product given by the X-ray pattern is nepheline only. In this case, the absence of $KHCO_3$ in these patterns could be caused by this product being present as a glass at the dissociation temperatures. At atmospheric pressure, $KHCO_3$ melts at temperatures ranging from 100° to 200°C. Minor analcite was detected in one run at a temperature of 150°C. and at a water pressure of 20,000 psi, in the closed system. The experimental data and breakdown

TABLE 4.4

d Spacings, Cell Dimensions and Cell Volumes of Synthetic Davyne Proper

Sample No. – D21X
Radiation – CuKα
Filter – Ni
Standard – Quartz

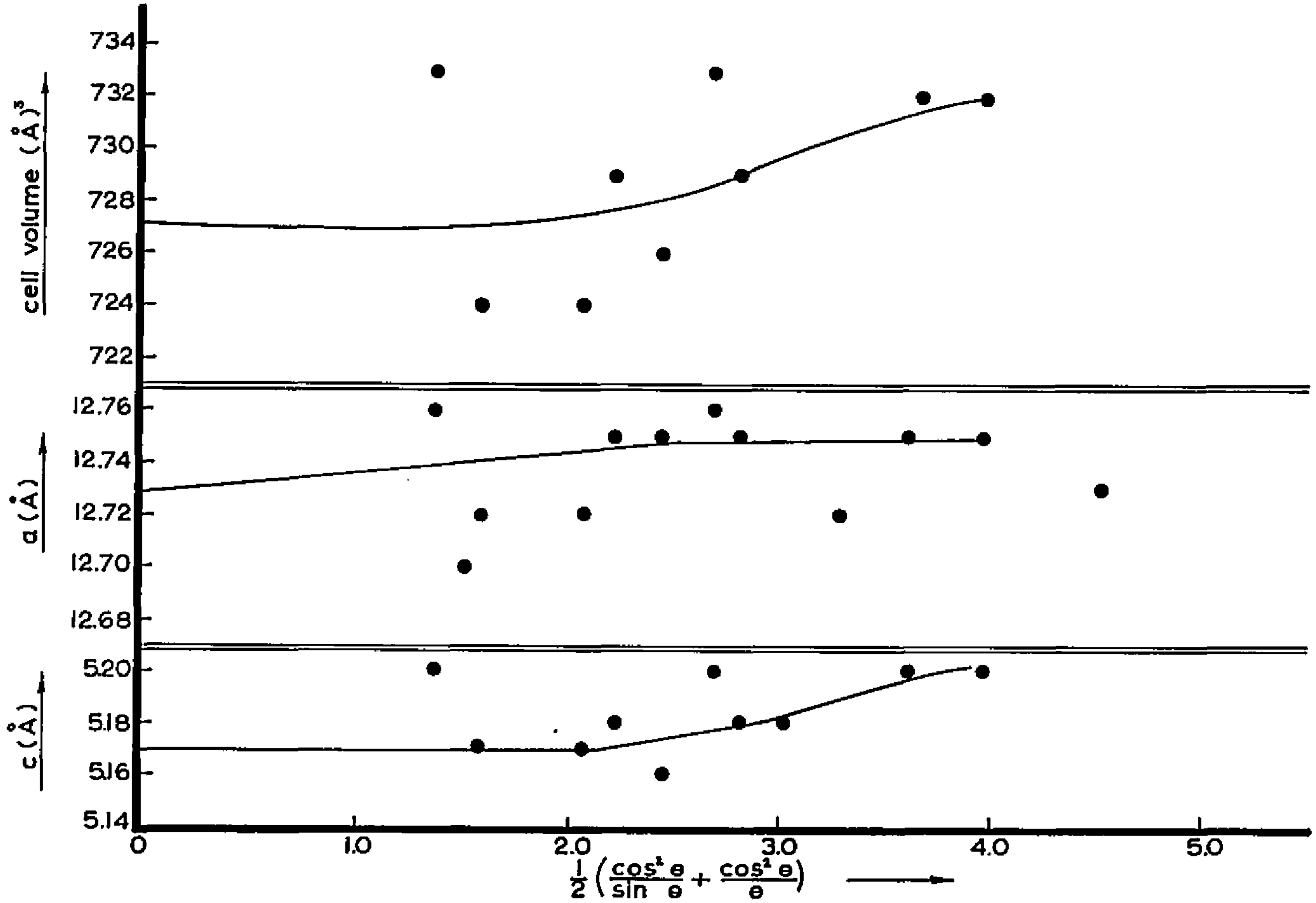
d	I (visual)	hkil	a(Å)	c(Å)	Cell Volume (Å^3)
4.70	50	$10\bar{1}1$	12.75	5.18	729
3.979	50	$11\bar{2}1$	12.59	5.14	706
3.672	35	$30\bar{3}0$	12.73	–	–
3.251	70	$21\bar{3}1$	12.75(1)	5.20	732
3.115	100	$31\bar{4}0$	12.95 ?	–	–
2.997	10	$30\bar{3}1$	12.75(1)	5.20	732
2.754	20	$40\bar{4}0$	12.72	–	–
2.579	40	0002	–	5.18	–
2.436	15	$40\bar{4}1$	12.75(2)	5.18	729
2.353	15	$20\bar{2}2$	12.76(3)	5.20	733
2.178	10 (diff.)	$41\bar{5}1$	12.75(5)	5.16	726
2.033	5	$50\bar{5}1$	12.75(2)(5)	5.18	729
1.931	5 (diff.)	$42\bar{6}1$	12.72(4)	5.17	724
1.621	7	$42\bar{6}2$	12.72(4)	5.17	724
1.572	7 (diff.)	$53\bar{8}0$	12.70	–	–
1.489	10	$43\bar{7}2$	12.76(3)	5.20	733

( ) – numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation.

FIGURE 4.3

Cell dimensions and cell volumes

versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ for synthetic davyne proper


cell volume (Å)³
734
732
730
728
726
724
722
a (Å)
12.76
12.74
12.72
12.70
12.68
c (Å)
5.20
5.18
5.16
5.14
0
1.0
2.0
3.0
4.0
5.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

curve for bicarbonate davyne are given in Table 4.5 and Figure 4.4 respectively.

d Spacings and Cell Dimensions

The d spacings, lattice planes and cell dimensions of bicarbonate davyne are shown in Table 4.6. A graph of a and c dimensions together with cell volumes versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ is given in Figure 4.5. The cell dimensions of synthetic bicarbonate davyne, obtained from this graph, are similar to davyne proper, the a dimension being 12.73 ± .02Å (approximately) and c dimension being 5.20 ± .02Å (approximately), with resulting cell volume of 726 ± 5Å^3.

(iv) Natrodavyne Proper ($3NaAlSiO_4.Na_2CO_3$)

Field of Synthesis

Natrodavyne proper transforms at a temperature between 600° and 650°C. in the water pressure range from 10,000 to 30,000 psi into a high temperature form with d spacings and cell dimensions similar to nosean ($6NaAlSiO_4.Na_2SO_4$). The transformation curve, given in Figure 4.6 is almost independent of pressure. No low temperature runs were carried out in this system, although one run at 250°C. and water pressure of 20,000 psi failed to show any analcite. The experimental data for natrodavyne proper are given in Table 4.7.

d Spacings and Cell Dimensions

The d spacings, lattice planes and cell dimensions of natrodavyne proper are presented in Table 4.8; the plot of a and c dimensions and cell volume versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ is shown in Figure 4.7. This curve yields an a dimension 12.67 ±.02Å (approximately) and a c dimension of 5.18 ± .02Å (approximately), and a resulting cell volume of 719 ± 5Å^3.

TABLE 4.5

Experimental Data for Bicarbonate Davyne

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
D1	0.5930	0.5900	20,000	725	163	Nepheline
D2	0.5991	0.5940	20,000	500	163	Nepheline
D3*	0.5835	0.5834	20,000	650	163	Nepheline
D4*	0.5796	0.5796	20,000	550	163	Nepheline
D5	0.5866	0.5863	20,000	450	163	Davyne
D6	0.5806	0.5811	15,000	250	144	Davyne ?
D7*	0.5874	0.5875	15,000	300	144	Davyne
D8*	0.5828	0.5829	15,000	500	144	Nepheline
D9*	0.5705	0.5706	15,000	550	144	Nepheline
D10	0.5780	0.5730	15,000	700	144	Nepheline
D11*	0.5927	0.5925	10,000	500	232	Davyne + Minor Nepheline
D12*	0.5786	0.5788	10,000	450	232	Nepheline
D13	0.6000	0.5968	10,000	400	232	Nepheline
D16*	0.5755	0.5755	10,000	300	232	Davyne
D17*	0.5823	0.5823	25,000	500	186	Nepheline
D18	0.6025	0.6767	25,000	200	48	Davyne + Nepheline
D19	0.5952	0.6484	25,000	450	186	Analcite + Minor Nepheline
D20	0.6089	0.6516	25,000	550 400	48 138	Nepheline
D25*	0.5993	0.5993	15,000	400	100	Davyne
D26	0.6056	0.6010	15,000	450	100	Nepheline
D29	0.6055	0.6052	20,000	500	138	Nepheline
D30*	0.6242	0.6242	20,000	150	50	Davyne + Analcite + Minor Nepheline
D35*	0.5771	0.5771	15,000	450	140	Davyne
D39	0.5976	0.5912	25,000	450	95	Nepheline ?
D40*	0.5914	0.5914	25,000	500	95	Nepheline + V. Minor Davyne ?
D42*	0.6050	0.6050	25,000	450	95	Nepheline
D44	0.5969	0.6339	10,000	400	190	Analcite + ?
D45*	0.6009	0.6007	10,000	500	190	Nepheline
D52*	0.5981	0.5983	20,000	550	162	Nepheline
D53	0.6152	0.6459	20,000	300	162	Analcite
D54*	0.5929	0.5929	10,000	400	188	Davyne
D55*	0.5998	0.5998	10,000	400	188	Davyne

Table 4.5 (contd.)

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
D59*	0.5927	0.5928	30,000	500	95	Nepheline
D60	0.5922	0.5773	30,000	450	95	Nepheline
D61	0.5776	0.6118	30,000	400	95	Analcite + Nepheline
D70*	0.5760	0.5758	10,000	425	195	Davyne + Nepheline
D74*	0.5517	0.5518	20,000	650	72	
				575	13	Nepheline
				500	11	
				400	70	
D76	0.5538	0.5521	15,000	650	72	Nepheline
				400	88	
D80	0.5834	0.5784	25,000	400	61	Davyne
D86*	0.5893	0.5893	25,000	450	126	Nepheline
D90*	0.5811	0.5811	30,000	450	75	Nepheline
D91*	0.5800	0.5800	30,000	400	75	Davyne
D93*	0.5815	0.5815	30,000	450	75	Nepheline

* – closed system

FIGURE 4.4

Field of synthesis of bicarbonate davyne

(closed system, curve drawn visually)

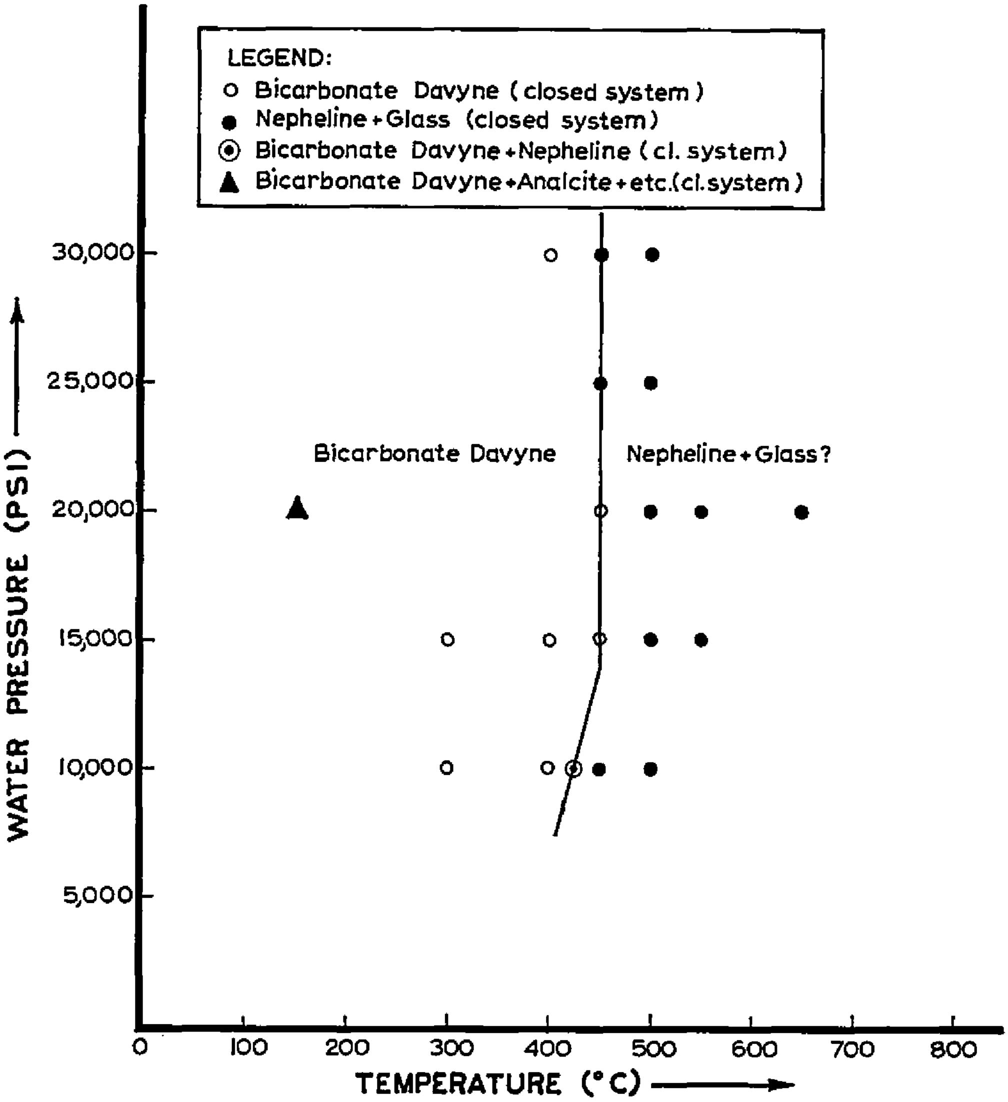

LEGEND:
○ Bicarbonate Davyne (closed system)
● Nepheline + Glass (closed system)
⊙ Bicarbonate Davyne + Nepheline (cl. system)
▲ Bicarbonate Davyne + Analcite + etc. (cl. system)
Bicarbonate Davyne
Nepheline + Glass?
30,000
25,000
20,000
15,000
10,000
5,000
WATER PRESSURE (PSI)
0
100
200
300
400
500
600
700
800
TEMPERATURE (°C)

TABLE 4.6

d Spacings, Cell Dimensions and Cell Volumes of Bicarbonate Davyne

Sample No. – D25
Radiation – CuKα
Filter – Ni
Standard – Quartz

d	I (visual)	hk$\bar{i}$l	a(Å)	c(Å)	Cell Volume (Å^3)
6.36	35	11$\bar{2}$0	12.68	–	–
4.70	60	10$\bar{1}$1	*12.75(1)	5.18	729
3.670	50	30$\bar{3}$0	12.70	–	–
3.246	100	21$\bar{3}$1	12.72(1)	5.18	726
3.114	30	–	?	?	?
2.757	30	40$\bar{4}$0	12.73	–	–
2.635	15	31$\bar{4}$1	12.72(2)	5.19	727
2.587	20 (v.diff.)	0002	–	5.17	–
2.438	15	40$\bar{4}$1	12.72(2)	5.19	727
2.178	5 (diff.)	41$\bar{5}$1	12.70(3)	5.20	726
1.764	5 (diff.)	41$\bar{5}$2	12.70(3)(4)	5.20	726
1.594	5 (diff.)	44$\bar{8}$0	12.75	–	–
1.252	5	43$\bar{7}$3	12.62(4)	5.24	723

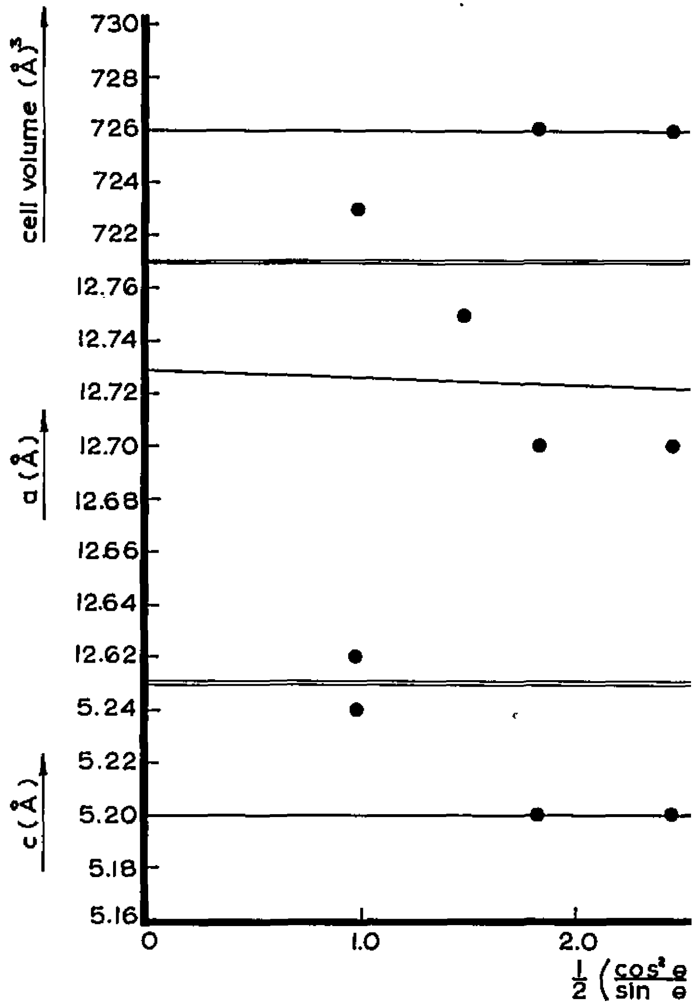
( ) – numbers in brackets refer to groups of a and c values solved simultaneously. In cases where the same equation has been used to determine two sets of values, the most reasonable set of a and c values has been taken. Other values determined from a single equation.

* – values determined by direct comparison of theoretical $\sin^2\theta$ value with observed $\sin^2\theta$ values.

FIGURE 4.5

Cell dimensions and cell volumes

versus $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ for synthetic bicarbonate davyne


cell volume (Å)^3
730
728
726
724
722
12.76
12.74
12.72
a (Å)
12.70
12.68
12.66
12.64
12.62
5.24
c (Å)
5.22
5.20
5.18
5.16
0
1.0
2.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}\right.$

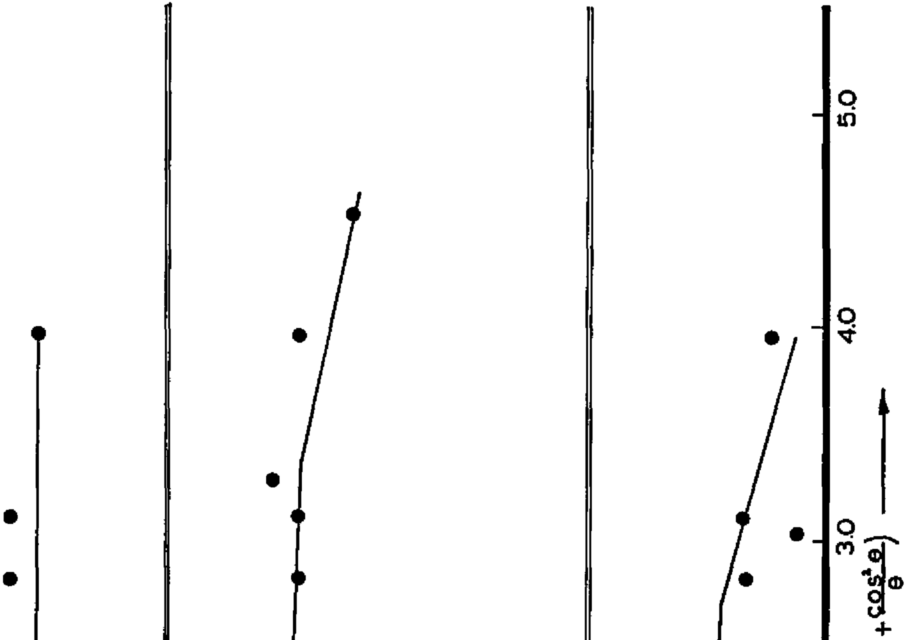

5.0
4.0
3.0
$+\frac{\cos^2\theta}{\theta})$

FIGURE 4.6

Field of synthesis of natrodavyne proper

(closed system, curve drawn visually)

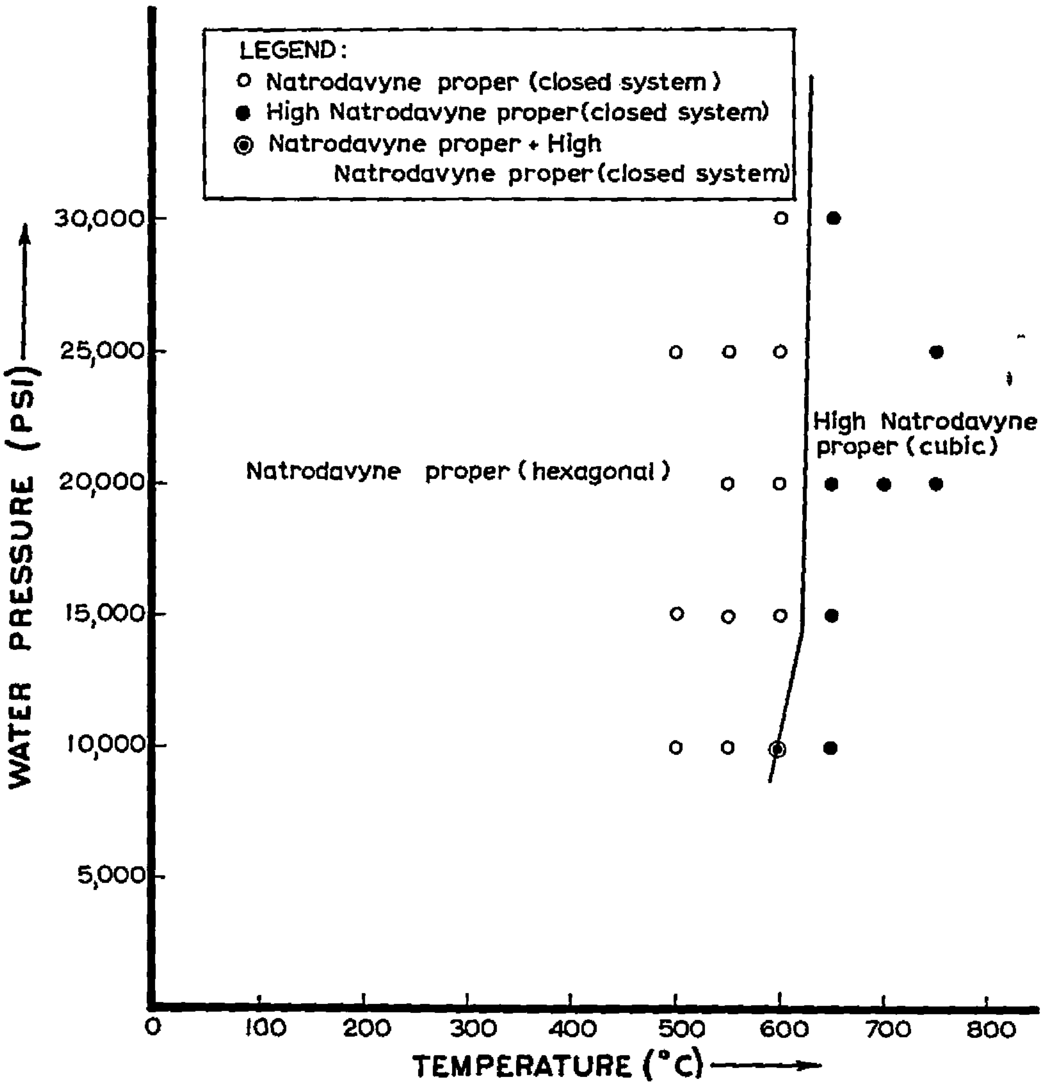

LEGEND:
○ Natrodavyne proper (closed system)
● High Natrodavyne proper(closed system)
◉ Natrodavyne proper + High Natrodavyne proper(closed system)
Natrodavyne proper (hexagonal)
High Natrodavyne proper (cubic)
WATER PRESSURE (PSI)
30,000
25,000
20,000
15,000
10,000
5,000
0
100
200
300
400
500
600
700
800
TEMPERATURE (°C)

TABLE 4.7

Experimental Data for Natrodavyne Proper

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
F20X*	0.5888	0.5890	20,000	750	95	High Natrodavyne
F21X*	0.5828	0.5828	20,000	700	95	High Natrodavyne
F23X	0.5985	0.6011	20,000	500	95	Natrodavyne proper
F24X	0.5923	0.5933	20,000	400	95	Natrodavyne proper
F25X	0.6273	0.6252	25,000	450	95	Natrodavyne proper
F26X	0.6186	0.6055	25,000	700	95	Nepheline
F27X	0.5984	0.5973	25,000	500	95	Natrodavyne proper
F28X*	0.5782	0.5782	25,000	750	95	High Natrodavyne
F35X	0.5898	0.5948	10,000	800	190	High Natrodavyne
F36X	0.5950	0.5958	10,000	550	190	Natrodavyne proper
F37X*	0.5756	0.5758	10,000	500	190	Natrodavyhe proper
F40X*	0.6209	0.6209	20,000	550	122	Natrodavyne proper
F41X	0.6157	0.6148	15,000	550	140	Natrodavyne proper
F43X*	0.5590	0.5590	15,000	500	140	Natrodavyne proper
F46X	0.6114	0.6131	20,000	250	162	Natrodavyne proper
F51X*	0.5970	0.5970	10,000	550	188	Natrodavyne proper
F52X*	0.5747	0.5749	10,000	600	188	Natrodavyne Proper + High Natrodavyne
F55X	0.5436	0.5773	30,000	500	95	Analcite + Natrodavyne proper (minor)
F56X	0.5803	0.5792	30,000	550	95	Natrodavyne proper
F57X*	0.5914	0.5915	30,000	600	95	Natrodavyne proper
F58X	0.5725	0.5864	20,000	600	148	Nepheline
F59X	0.5640	0.6124	15,000	550	144	Nepheline
F60X	0.5727	0.5712	15,000	600	144	Natrodavyne proper
F64X	0.5625	0.5537	10,000	650	195	Natrodavyne proper + Nepheline
F66X*	0.5676	0.5676	10,000	650	195	High Natrodavyne + v. Minor Natrodavyne proper
F67X	0.5465	0.5369	15,000	650	145	Nepheline + Minor Natrodavyne proper
F68X*	0.5509	0.5509	15,000	550	145	Natrodavyne proper
F69X*	0.5668	0.5666	15,000	650	145	High Natrodavyne
F70X	0.5703	0.5708	20,000	650	72	
				575	13	Natrodavyne proper + Nepheline
				500	11	
				400	70	

Table 4.7 (contd.)

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
F72X	0.5616	0.5591	15,000	650	160	High Natrodavyne + Natrodavyne proper
F73X*	0.5610	0.5612	25,000	500	61	Natrodavyne proper
F75X	0.5777	0.5556	15,000	650 400	72 88	Nepheline
F80X*	0.6052	0.6052	25,000	550	61	Natrodavyne proper
F81X*	0.5866	0.5868	25,000	600	61	Natrodavyne proper
F89X	0.5888	0.5838	25,000	650	126	Nepheline
F92X	0.5594	0.5493	15,000	650	141	Nepheline + High Natrodavyne
F94X*	0.5562	0.5562	15,000	600	141	Natrodavyne proper
F98X	0.5745	0.5765	30,000	650	75	Natrodavyne proper
F99X*	0.5673	0.5674	30,000	650	75	High Natrodavyne
F103X*	0.6010	0.6012	20,000	650	168	High Natrodavyne
F104X*	0.5872	0.5870	20,000	600	168	Natrodavyne proper
F110X	0.5886	0.5985	15,000	700 400	82 84	High Natrodavyne
F111X*	0.5824	0.5824	15,000	700 400	82 84	Natrodavyne proper

* - closed system

TABLE 4.8

d Spacings, Cell Dimensions and Cell Volumes of Synthetic Natrodavyne Proper

Sample No. – F40X
Radiation – CuKα
Filter – Ni
Standard – Quartz

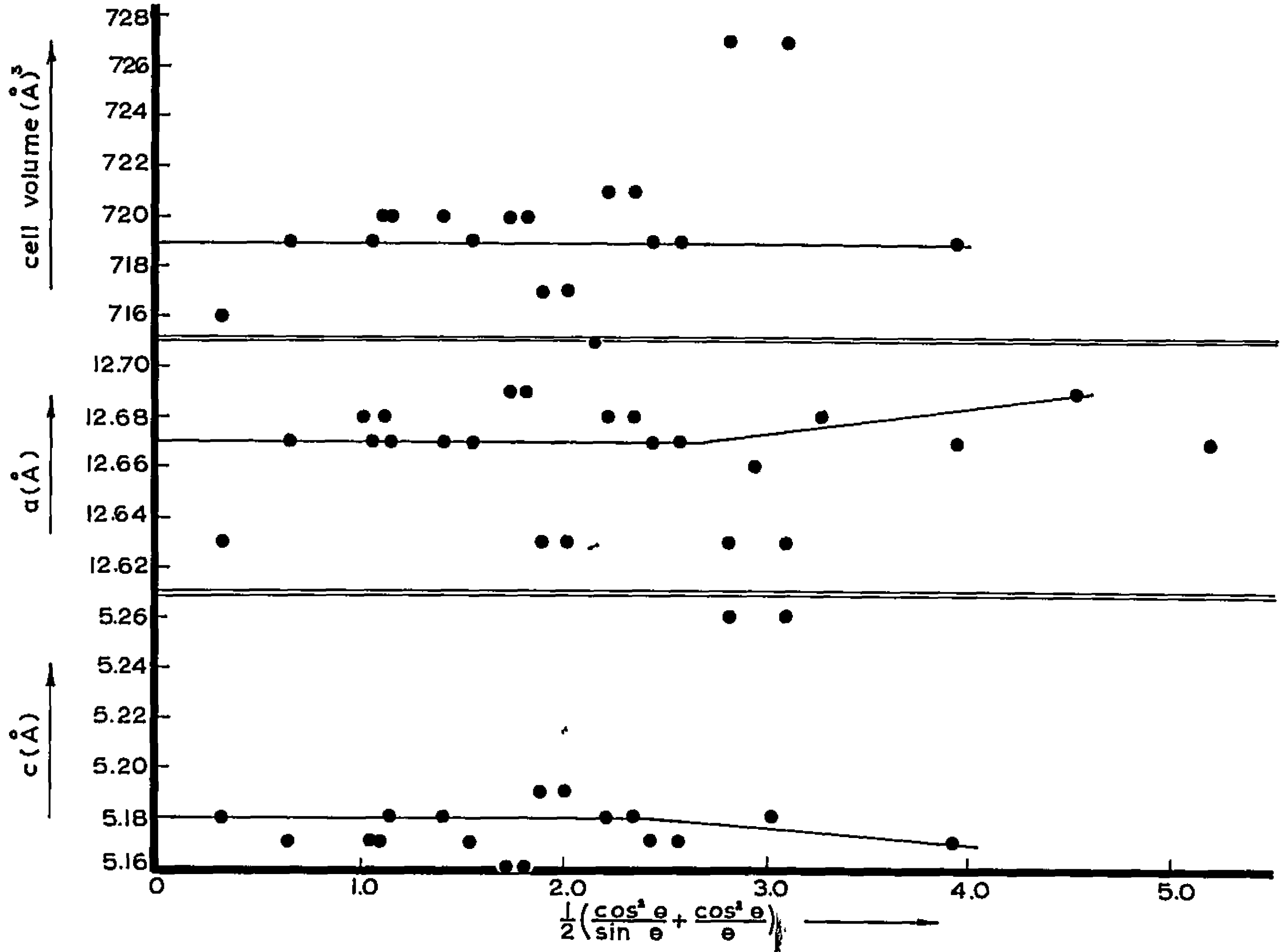
d	I (visual)	$hk\bar{i}l$	a(Å)	c(Å)	Cell Volume (Å^3)
6.36	50	$11\underline{2}0$	12.67	–	–
4.69	65	$10\underline{1}1$	12.67	5.17	719
4.15	15	$21\underline{3}0$	12.67	–	–
3.663	70	$30\underline{3}0$	12.69	–	–
3.234	100	$21\underline{3}1$	12.67	5.17	719
2.747	50	$40\underline{4}0$	12.68	–	–
2.628	10	$31\underline{4}1$	12.63 (1)	5.26	727
2.589	15	$00\underline{0}2$	–	5.18	–
2.515	5	$32\underline{5}0$	12.66	–	–
2.426	20	$40\underline{4}1$	12.63 (1)	5.26	727
2.264	7 (diff.)	$32\underline{5}1$	12.67 (2)	5.17	719
2.172	5	$41\underline{5}1$	12.67 (2)	5.17	719
2.113	15	$30\underline{3}2$	12.68 (3)	5.18	721
2.021	5 (diff.)	$50\underline{5}1$	12.68 (3)	5.18	721
1.977	5 (diff.)	$51\underline{6}0$	12.71	–	–
1.883	7	$40\underline{4}2$	12.63 (4)	5.19	717
1.804	7	$32\underline{5}2$	12.63 (4)	5.19	717
1.758	10 (diff.)	$41\underline{5}2$	12.69 (5)	5.16	720
1.705	5 (diff.)	$43\underline{7}1$	12.69 (5) (6)	5.16	720
1.590	10 (diff.)	$21\underline{3}3$	12.67 (7)	5.17	719
1.500	7 (diff.)	$53\underline{8}1$	12.67 (8)	5.18	720
1.351	5 (diff.)	$44\underline{8}2$	12.67 (8)	5.18	720
1.327	7 (diff.)	$42\underline{6}3$	12.68 (6)	5.17	720
1.297	5 (diff.)	$51\underline{6}3$	12.67 (7)	5.17	719
1.268	5 (diff.)	$5,5,\underline{10},0$	12.68	–	–
1.081	5	$51\underline{6}4$	12.67 (7) (9)	5.17	719
0.9161	5 (diff.)	5165	12.63 (9)	5.18	716

( ) – numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation or from comparison of $\sin^2\theta$ calc. and $\sin^2\theta$ obs. values.

FIGURE 4.7

Cell dimensions and cell volumes

versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ for synthetic natrodavyne proper


cell volume (Å)³
728
726
724
722
720
718
716
a (Å)
12.70
12.68
12.66
12.64
12.62
c (Å)
5.26
5.24
5.22
5.20
5.18
5.16
0
1.0
2.0
3.0
4.0
5.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

The d spacings, lattice planes and cell dimensions of the high temperature natrodavyne form, similar to nosean, are given in Table 4.9. This mineral is cubic and gives an a dimension of about 9.02Å which compares with the a dimension of nosean, given as 9.04Å on the A.S.T.M. index card. This high temperature form has been named high natrodavyne.

(v) Bicarbonate Natrodavyne ($3NaAlSiO_4.NaHCO_3$)

Field of Synthesis

The experimental data and breakdown curve of bicarbonate natrodavyne are given in Table 4.10 and Figure 4.8 respectively. Bicarbonate natrodavyne also transforms into a nosean-type mineral between 600° and 650°C. in the water pressure range 15,000 to 25,000 psi. No analcite was detected for this composition in the closed system.

d Spacings and Cell Dimensions

The d spacings, cell dimensions and lattice planes for bicarbonate natrodavyne are given in Table 4.11. A graph of a and c dimensions together with cell volumes versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ is shown in Figure 4.9. This graph gives a = 12.67 ± .02Å (approximately); c = 5.16 ± .02Å (approximately), and a resulting cell volume of 717 ± 5Å^3. Both these dimensions are slightly smaller than those of natrodavyne proper. The d spacings, lattice planes and cell dimensions of the high temperature form of bicarbonate natrodavyne are given in Table 4.9. This high temperature form has been named high bicarbonate natrodavyne.

2. Sulphate, Hydroxide and Chloride End-members

(i) Failure to Synthesize the Microsommite, Wischnewite and Sulphatic Cancrinite End-members, Proposed by Winchell and Winchell (1951)

Attempts to synthesize the microsommite end-member, using the

TABLE 4.9

d Spacings, Lattice Planes and Cell Dimensions of the High-Temperature Natrodavyne "Polymorphs"

Sample No. – F21X F31
Radiation – CuKα CuKα
Filter – Ni Ni
Standard – Quartz Quartz

d	I (visual)	d for nosean (A.S.T.M.)	hkl	d	I (visual)	hkl
6.38	70	6.40	110	6.40	30	110
4.64	10	4.52	200	–	–	–
3.676	100	3.69	211	3.676	100	211
3.206	10	–	220	–	–	–
2.848	25	2.86	310	2.852	25	310
2.600	35	2.61	222	2.603	40	222
2.496	5	–	320	–	–	–
2.404	10	–	321	2.406	5	321
2.249	5	2.26	400	–	–	–
2.120	20	2.13	411	2.125	20	411
1.764	12	1.78	510	1.765	7	510
1.589	7	1.60	440	1.589	5	440
1.498	5	–	600	1.499	5	600
1.461	5	–	611 or 532	1.460	5	611 or 532
1.388	5	–	541	–	–	–
1.356	5	–	622	1.357	5	622
1.327	5	–	631	1.325	5 (diff.)	631
1.299	5	–	444	1.299	5 (diff.)	444

Table 4.9 (contd.)

Determination of cell dimension:

$$\sin^2\theta_{obs} = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

$$= K(h^2 + k^2 + l^2)$$

= lowest common multiple of $\sin^2\theta$ X integer

$$K = \frac{\lambda^2}{4a^2}$$

$$a^2 = \frac{\lambda^2}{4K^2}$$ (where K = 0.0073 from observation)

$$= \frac{2.3771}{4x.0073} = \frac{2.3771}{0.0292} = 81.41$$

Hence a = 9.02Å

Determination of cell dimension:

$$\sin^2\theta_{obs} = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

$$= K(h^2 + k^2 + l^2)$$

= lowest common multiple of $\sin^2\theta$ X integer

$$K = \frac{\lambda^2}{4a^2}$$

$$a^2 = \frac{\lambda^2}{4K^2}$$ (where K = 0.0073 from observation)

$$= \frac{2.3771}{4x.0073} = \frac{2.3771}{0.0292}$$

$$= 81.41$$

Hence a = 9.02Å

TABLE 4.10

Experimental Data for Bicarbonate Natrodavyne

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
F1	0.6096	0.6027	20,000	650	50	Nepheline + Bicarb.-Natrodavyne
F2	0.5952	0.6215	20,000	700	50	Nepheline
F3*	0.6067	0.6069	20,000	550	50	Bicarb.-Natrodavyne
F4	0.6041	0.6606	20,000	500	50	Nepheline
F5	0.6095	0.6183	20,000	450	50	Nepheline ?
F6	0.5863	0.5880	20,000	150	50	Analcite + Bicarb.-Natrodavyne
F7*	0.6240	0.6240	15,000	700	140	High Bicarb.-Natrodavyne
F8	0.6200	0.6512	15,000	150	140	Analcite + Bicarb.-Natrodavyne ?
F9	0.5824	0.5941	15,000	500	140	Nepheline
F10	0.5904	0.5920	15,000	450	140	Bicarb.-Natrodavyne + Analcite ?
F11*	0.5788	0.5786	15,000	650	140	High Bicarb.-Natrodavyne
F12	0.5895	0.6051	25,000	450	95	Analcite + Minor Bicarb.-Natrodavyne
F13*	0.5902	0.5902	25,000	650	95	High Bicarb.-Natrodavyne
F14*	0.5990	0.5990	25,000	600	95	Bicarb.-Natrodavyne
F15	0.6107	0.6016	25,000	550	95	Nepheline
F16	0.6032	0.6020	20,000	700	95	?
F17	0.6127	0.6074	20,000	750	95	High Bicarb.-Natrodavyne + Nepheline
F18	0.5982	0.6080	20,000	600	95	Nepheline
F19	0.6257	0.6247	20,000	500	95	Nepheline + Minor Bicarb.-Natrodavyne
F29	0.6140	0.6153	25,000	500	95	Bicarb.-Natrodavyne
F30*	0.5850	0.5850	25,000	750	95	High Bicarb.-Natrodavyne
F31*	0.6008	0.6007	25,000	750	95	High Bicarb.-Natrodavyne
F32	0.6013	0.5902	10,000	800	190	Nepheline
F33	0.6094	0.6106	10,000	550	190	Nepheline + Bicarb.-Natrodavyne
F34*	0.5929	0.5931	10,000	500	190	Bicarb.-Natrodavyne

Table 4.10 (contd.)

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
F38*	0.6155	0.6155	20,000	650	122	High Bicarb.-Natrodavyne
F39*	0.6046	0.6046	20,000	600	122	Bicarb.-Natrodavyne + v. Minor Nepheline
F44	0.5888	0.5865	15,000	550	140	Nepheline
F45*	0.6104	0.6103	15,000	600	140	Bicarb.-Natrodavyne
F47	0.6132	0.6123	20,000	300	162	Bicarb.-Natrodavyne
F48	0.5818	0.5783	20,000	400	162	Bicarb.-Natrodavyne + Minor Analcite
F49	0.5922	0.5930	20,000	250	162	Analcite + Minor Bicarb.-Natrodavyne
F50*	0.5666	0.5666	10,000	550	188	Bicarb.-Natrodavyne
F53	0.6130	0.6041	30,000	650	95	Nepheline
F54*	0.5932	0.5933	30,000	600	95	High Bicarb.-Natrodavyne
F62	0.5541	0.5431	10,000	650	195	Nepheline + Bicarb.-Natrodavyne
F65	0.5705	0.5631	10,000	650	195	Nepheline + Bicarb.-Natrodavyne
F74	0.5836	0.5825	10,000	650	160	Bicarb.-Natrodavyne + Nepheline
F76	0.6075	0.6057	10,000	600	160	Nepheline + Bicarb.-Natrodavyne
F84	0.5665	0.5743	10,000	650	224	Nepheline + High Bicarb.-Natrodavyne + Bicarb.-Natrodavyne
F86	0.5921	0.6034	10,000	600	224	Nepheline
F95	0.5896	0.5885	30,000	550	75	Nepheline
F96	0.5636	0.5652	30,000	550	75	Nepheline
F100	0.5956	0.5818	20,000	700	108	
				450	60	Nepheline
F107*	0.5874	0.5874	10,000	650	188	High Bicarb.-Natrodavyne
F108*	0.6050	0.6049	10,000	600	188	Bicarb.-Natrodavyne

* – closed system

FIGURE 4.8

Field of synthesis of bicarbonate natrodavyne

(closed system, curve drawn visually)

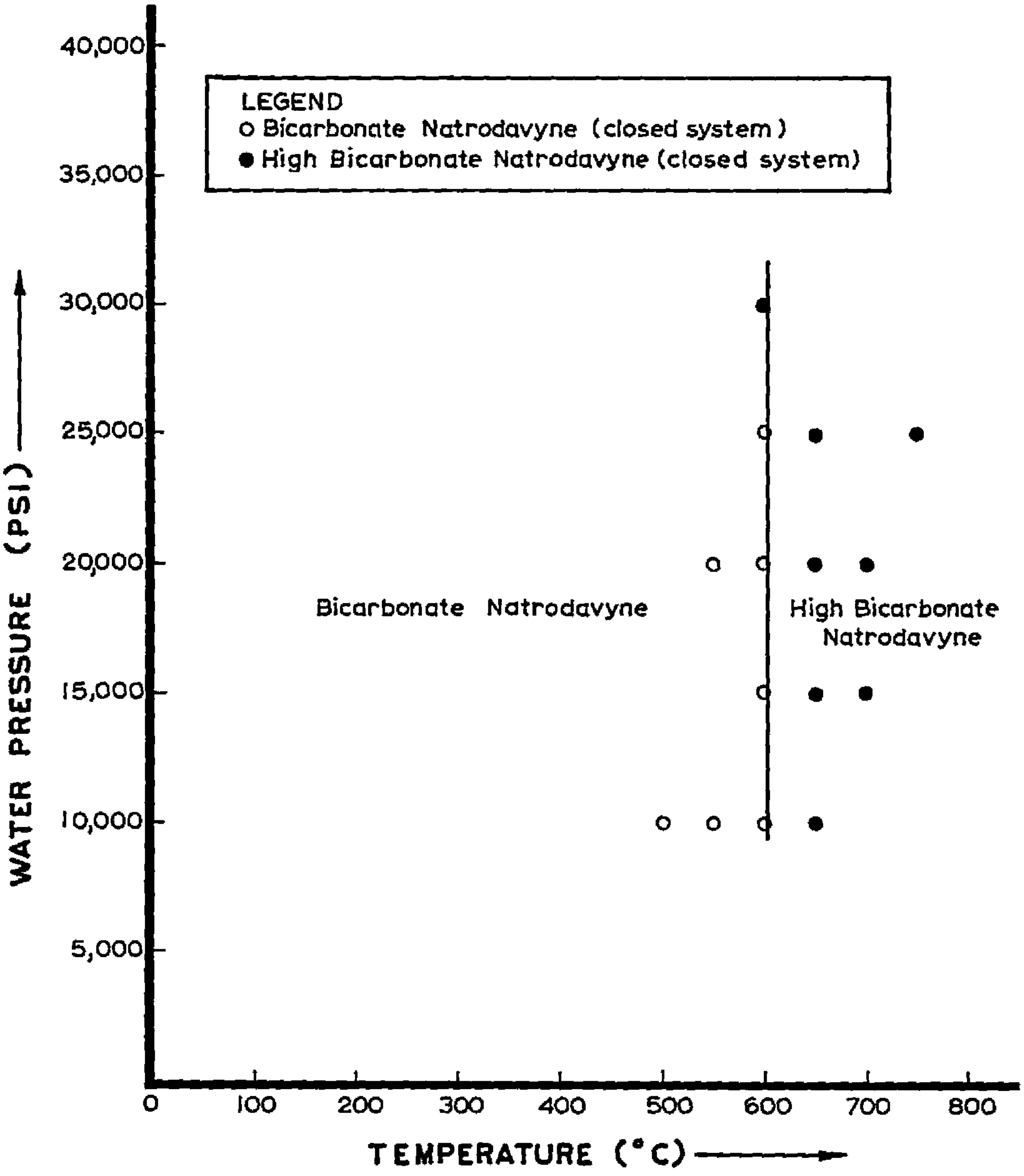

LEGEND
○ Bicarbonate Natrodavyne (closed system)
● High Bicarbonate Natrodavyne (closed system)
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
WATER PRESSURE (PSI)
Bicarbonate Natrodavyne
High Bicarbonate Natrodavyne
0
100
200
300
400
500
600
700
800
TEMPERATURE (°C)

TABLE 4.11

d Spacings, Cell Dimensions and Cell Volumes of Bicarbonate Natrodavyne

Sample No. – F3
Radiation – CuKα
Filter – Ni
Standard – Quartz

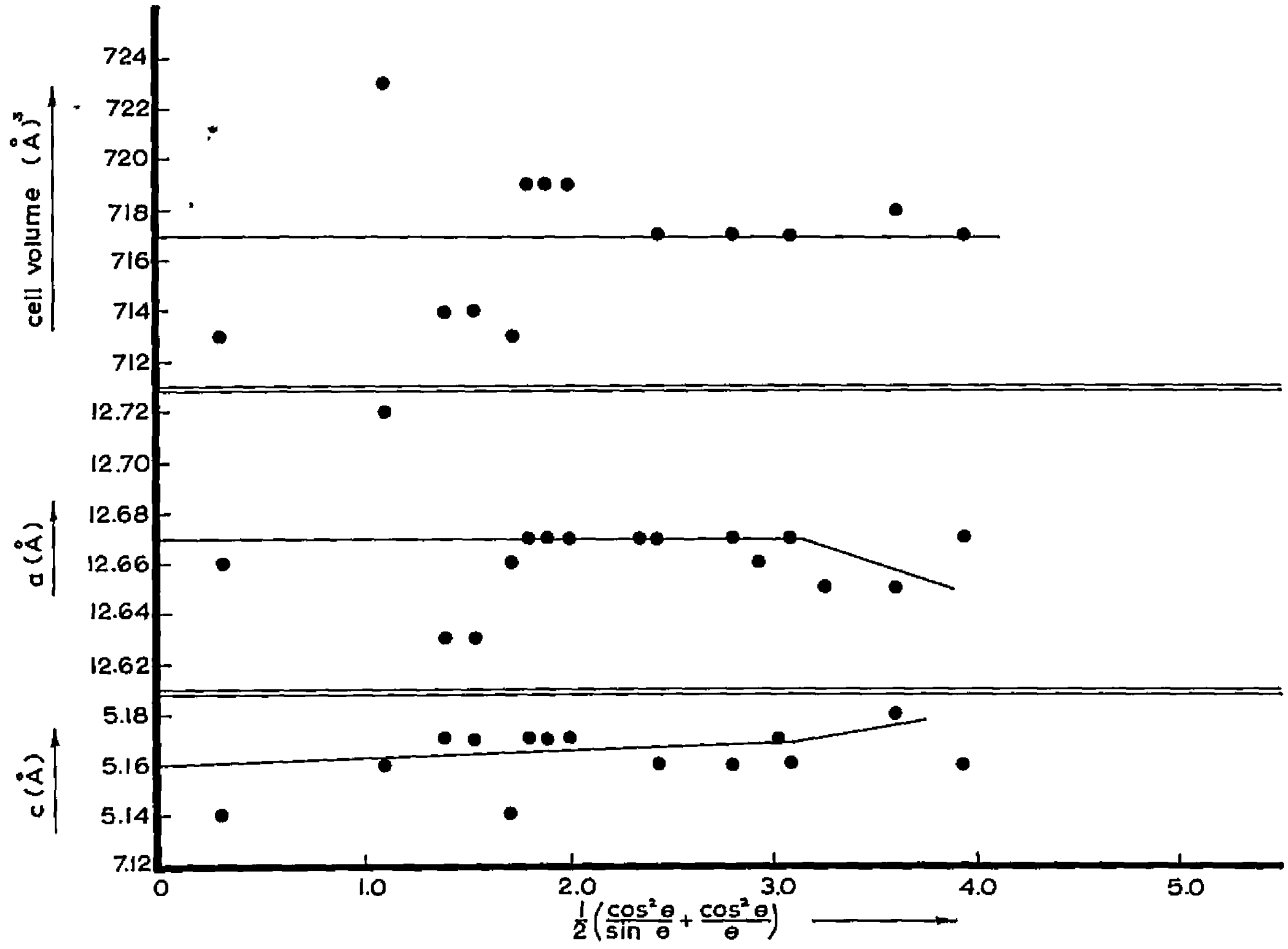
d	I (visual)	$hk\bar{i}l$	a(Å)	c(Å)	Cell Volume (Å^3)
6.33	40	$11\bar{2}0$	12.63	–	–
4.68	75	$10\bar{1}1$	12.67$^{(1)}$	5.16	717
3.837*	15	?	?	?	–
3.397*	75	?	?	–	–
3.234	100	$21\bar{3}1$	12.67$^{(1)(2)}$	5.16	717
2.996	10	$30\bar{3}1$	12.65$^{(2)}$	5.18	718
2.741	50	$40\bar{4}0$	12.65	–	–
2.622	25	$31\bar{4}1$	12.67$^{(3)}$	5.16	717
2.584	30	$00\bar{0}2$	–	5.17	–
2.516	10	$32\bar{5}0$	12.66	–	–
2.422	25	$40\bar{4}1$	12.67$^{(3)(4)}$	5.16	717
2.239*	10 (diff.)	?	?	–	–
2.172	10 (v.diff.)	$41\bar{5}1$	12.67$^{(4)}$	5.16	717
2.112	7 (v.diff.)	$33\bar{6}0$	12.67	–	–
1.880	10 (diff.)	$40\bar{4}2$	12.67$^{(5)}$	5.17	719
1.803	15 (diff.)	$32\bar{5}2$	12.67$^{(5)(6)}$	5.17	719
1.757	15 (diff.)	$41\bar{5}2$	12.67$^{(6)}$	5.17	719
1.702	10 (v.diff.)	$43\bar{7}1$	12.66$^{(7)}$	5.14	713
1.590	15 (v.diff.)	$21\bar{3}3$	12.63$^{(8)}$	5.17	714
1.498	10 (v.diff.)	$31\bar{4}3$	12.63$^{(8)}$	5.17	714
1.325	5 (diff.)	$42\bar{6}3$	12.72$^{(9)}$	5.16	723
0.9112	5	$51\bar{6}5$	12.66$^{(7)(9)}$	5.14	713

* – possibly represents an unidentifiable second phase.

( ) – numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation.

FIGURE 4.9

Cell dimensions and cell volumes versus $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ for synthetic bicarbonate natrodavyne


cell volume (Å)^3
724
722
720
718
716
714
712
12.72
12.70
12.68
a (Å)
12.66
12.64
12.62
5.18
c (Å)
5.16
5.14
7.12
0
1.0
2.0
3.0
4.0
5.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

formula $3NaAlSiO_4.CaCl_2$ resulted in a mixture of sodalite ($3NaAlSiO_4.NaCl$), anorthite ($CaAl_2Si_2O_8$), nepheline and possibly NaCl and $CaCl_2$. Sodalite, anorthite and possibly nepheline were detected in the X-ray pattern of the products. A possible reaction can be written:-

2 microsommite mixture + $nH_2O \longrightarrow$ sodalite + anorthite + nepheline + NaCl + $CaCl_2$.

i.e. $6NaAlSiO_4.2CaCl_2 + nH_2O \longrightarrow 3NaAlSiO_4.NaCl. + CaAl_2Si_2O_8 + NaAlSiO_4 + NaCl + CaCl_2$.

The theoretically possible NaCl and $CaCl_2$ may be masked by other products in the X-ray pattern.

The composition $3NaAlSiO_4.NaHSO_4$, termed wischnewite by Winchell and Winchell (1951), synthesized to a nosean-type mineral. This product was found to be stable at temperatures as high as 800°C. in the water pressure range 10,000 to 25,000 psi. At temperatures lower than 500° to 525°C. in this pressure range, analcite appeared along with the nosean-type mineral in the closed system. Regular synthetic nosean ($6NaAlSiO_4.Na_2SO_4$) produces no analcite phase when synthesized in the temperature range 200° to 800°C. (Van Peteghem - personal communication).

The composition $3NaAlSiO_4.CaSO_4$, called sulphatic cancrinite by Winchell and Winchell (1951), synthesized to a hauyne-nosean structure and was found to be stable up to about 800°C. at water pressures of 10,000 to 30,000 psi.

These results indicate either that pure sulphate and chloride cancrinites do not exist in nature or that they exist under radically different conditions from their carbonate counterparts. An attempt to determine the amount of sulphate radical that could be accommodated in the regular formula of cancrinite proper was made by synthesizing a series of products between cancrinite proper ($3NaAlSiO_4.CaCO_3$) and bisulphate nosean ($3NaAlSiO_4.NaHSO_4$). It was found that compositions richer in sulphate than seven cancrinite molecules to one bisulphate nosean molecule produced a product having a diffraction pattern more characteristic of the nosean-type mineral. Compositions of approximately this seven to one ratio produced a product with X-ray patterns similar to the cancrinite mineral. This composition was arbitrarily named sulphatic cancrinite and has the formula:-

$$7[3NaAlSiO_4.CaCO_3] + [3NaAlSiO_4.NaHSO_4]$$

Similarly by synthesizing a series of products between the compositions of hydroxy cancrinite ($3NaAlSiO_4.Ca(OH)_2$) and $3NaAlSiO_4.CaCl_2$ (the microsommite of Winchell) it was found that the ratio four hydroxy cancrinite to one microsommite resulted in a product similar to cancrinite. This composition was arbitrarily termed microsommite and has the formula:-

$$4[3NaAlSiO_4.Ca(OH)_2] + [3NaAlSiO_4.CaCl_2]$$

(ii) Sulphatic Cancrinite ($7[3NaAlSiO_4.CaCO_3] + [3NaAlSiO_4.NaHSO_4]$)

Field of Synthesis

Sulphatic cancrinite of this composition can be synthesized in the closed system from 400° to 800°C. in the water pressure range 10,000 to 25,000 psi. Analcite appeared at temperatures below 300°C. in the water pressure range of 10,000 to 20,000 psi. The experimental data for sulphatic cancrinite are given in Table 4.12.

d Spacings and Cell Dimensions

The d spacings, lattice planes and cell dimensions of sulphatic

TABLE 4.12

Experimental Data for Sulphatic Cancrinite

$$7\,[3NaAlSiO_4 \cdot CaCO_3] + [3NaAlSiO_4 \cdot NaHSO_4]$$

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
A30	0.6089	0.6075	25,000	750	95	Sulphatic Cancrinite
A31	0.6198	0.6202	25,000	700	95	Sulphatic Cancrinite
A32*	0.6372	0.6372	25,000	500	95	Sulphatic Cancrinite
A33	0.5911	0.5947	25,000	450	95	Sulphatic Cancrinite
A34	0.5723	0.5740	10,000	450	190	Sulphatic Cancrinite
A35	0.5968	0.5940	10,000	550	190	Sulphatic Cancrinite
A36*	0.5914	0.5914	10,000	500	190	Sulphatic Cancrinite
A37*	0.5850	0.5850	10,000	400	190	Sulphatic Cancrinite
A38*	0.6010	0.6008	20,000	600	122	Sulphatic Cancrinite
A39	0.6132	0.6114	20,000	650	122	Sulphatic Cancrinite
A40	0.5942	0.5907	15,000	775	140	Sulphatic Cancrinite + Nepheline
A41*	0.5905	0.5905	15,000	450	140	Sulphatic Cancrinite
A42	0.5865	0.5856	20,000	300	162	Sulphatic Cancrinite + Analcite + Nepheline
A43*	0.5916	0.5916	20,000	400	162	Sulphatic Cancrinite
A44*	0.5895	0.5894	20,000	250	162	Sulphatic Cancrinite + Analcite
A45	0.5596	0.5647	10,000	300	158	Sulphatic Cancrinite + Analcite
A46	0.5690	0.5682	10,000	800	188	Nepheline + Sulphatic Cancrinite
A47	0.5725	0.5740	30,000	650	95	Sulphatic Cancrinite
A48*	0.5694	0.5694	20,000	750	148	Sulphatic Cancrinite
A50	0.5471	0.5382	10,000	800	195	Sulphatic Cancrinite + Nepheline
A52*	0.5749	0.5748	15,000	300	160	Sulphatic Cancrinite + Analcite
A53	0.5986	0.6321	10,000	800	160	Nepheline
A55*	0.5897	0.5896	10,000	800	224	Sulphatic Cancrinite
M16*	0.6065	0.6065	25,000	600	95	Sulphatic Cancrinite

* - closed system

cancrinite are given in Table 4.13. A graph of the a and c dimensions together with cell volumes versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ is given in Figure 4.10. This graph yields an a dimension of approximately 12.59 ± .02Å and a c dimension of approximately 5.18 ± .02Å with resulting cell volume of 712 ± 5Å^3. These results are very similar to those obtained for cancrinite proper.

(iii) Hydroxy Cancrinite ($3NaAlSiO_4 \cdot Ca(OH)_2$)

Field of Synthesis

The experimental data of synthetic cancrinite are given in Table 4.14. Cancrinite of this composition is found in the closed system between 400° and 800°C. at water pressures between 10,000 and 30,000 psi. At temperatures around 400°C. in the water pressure range 10,000 to 20,000 psi, analcite appears in addition to hydroxy cancrinite.

d Spacings and Cell Dimensions

The d spacings, lattice planes and cell dimensions of hydroxy cancrinite are given in Table 4.15; the plot of a and c dimensions and cell volumes versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ is shown in Figure 4.11. This graph gives a = 12.60 ± .02Å (approximately), c = 5.14 ± .02Å (approximately), and a resulting cell volume of 708 ± 5Å^3. The dimensions are also similar to those of cancrinite proper.

(iv) Microsommite $4[3NaAlSiO_4 \cdot Ca(OH)_2] + [3NaAlSiO_4 \cdot CaCl_2]$

No field of synthesis was determined for this mineral

d Spacings and Cell Dimensions

The d spacings, lattice planes and cell dimensions of microsommite are given in Table 4.16, and the plot of a and c dimensions and cell volumes versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ are given in Figure 4.12. This graph

TABLE 4.13

d Spacings. Cell Dimensions and Cell Volumes of Synthetic Sulphatic Cancrinite

Sample No. – A32
Radiation – CuKα
Filter – Ni
Standard – Quartz

d	I (visual)	$hk\bar{i}l$	a(Å)	c(Å)	Cell Volume (Å^3)
6.34	35	$11\overline{\underline{2}}0$	12.63	–	–
4.67	50	$10\underline{1}1$	12.57$^{(1)}$	5.16	706
4.14	15	$21\underline{3}0$	12.64	–	–
3.652	50	$30\underline{3}0$	12.64	–	–
3.219	100	$21\underline{3}1$	12.57$^{(1)}$	5.16	706
3.035	5 (diff.)	$31\underline{4}0$	12.63	–	–
2.970	5 (diff.)	$30\underline{3}1$	12.59$^{(2)}$	5.15	707
2.731	30	$40\underline{4}0$	12.61	–	–
2.611	20	$31\underline{4}1$	12.59$^{(2)}$	5.15	707
2.569	20	$00\underline{0}2$	–	5.14	–
2.502	5 (diff.)	$32\underline{5}0$	12.59	–	–
2.415	20	$40\underline{4}1$	12.59$^{(3)}$	5.21	715
2.255	7	$32\underline{5}1$	12.59$^{(3)(4)}$	5.21	715
2.164	7	$41\underline{5}1$	12.59$^{(4)}$	5.21	715
2.103	25	$33\underline{6}0$	12.62	–	–
2.013	5	$50\underline{5}1$	12.65$^{(5)}$	5.11	708
1.869	10 (diff.)	$40\underline{4}2$	12.65$^{(5)}$	5.11	708
1.793	10 (diff.)	$43\underline{7}0$	12.59	–	–
1.746	10 (diff.)	$52\underline{7}0$	12.59	–	–
1.580	7 (v.diff.)	$61\underline{7}1$	12.57$^{(6)}$	5.16	706
1.492	7 (diff.)	$53\underline{8}1$	12.59$^{(7)}$	5.19	712
1.449	7 (diff.)	$52\underline{7}2$	12.59$^{(7)}$	5.19	712
1.320	5 (diff.)	$42\underline{6}3$	12.57$^{(6)}$	5.16	706
1.259	5 (v.diff.)	$5,5,\underline{10},0$	12.58	–	–
1.214	5	$63\underline{9}2$	12.56$^{(8)}$	5.21	712
1.133	5 (diff.)	5,5,10,2	12.56$^{(8)}$	5.21	712

( ) – numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation.

FIGURE 4.10

Cell dimensions and cell volumes versus $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ for synthetic sulphatic cancrinite

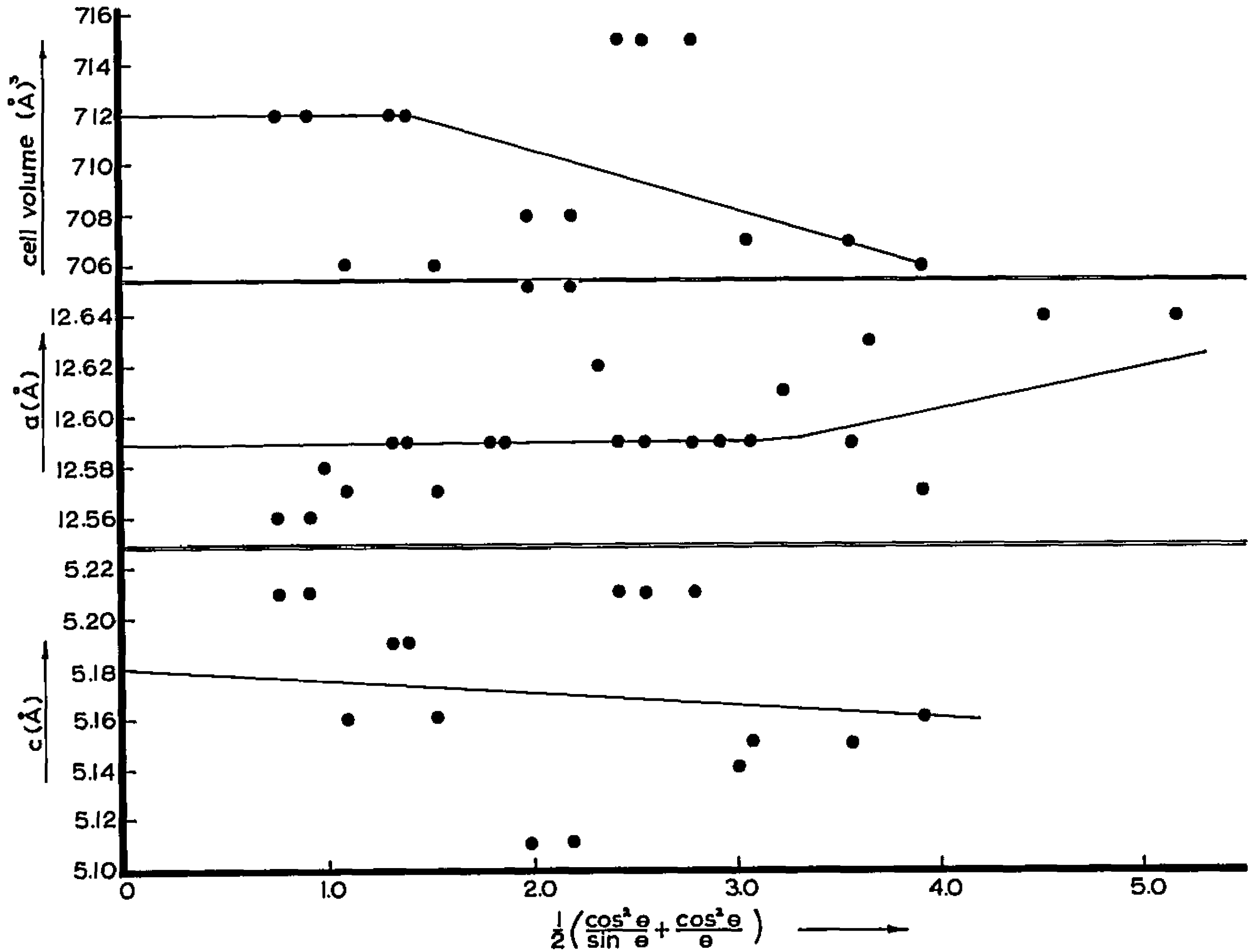

cell volume (Å^3)
716
714
712
710
708
706
a (Å)
12.64
12.62
12.60
12.58
12.56
c (Å)
5.22
5.20
5.18
5.16
5.14
5.12
5.10
0
1.0
2.0
3.0
4.0
5.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

TABLE 4.14

Experimental Data for Hydroxy Cancrinite

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
G1	0.5988	0.6023	25,000	600	95	Hydroxy Cancrinite
G2	0.6146	0.6171	25,000	450	95	Hydroxy Cancrinite
G3	0.6088	0.5992	15,000	500	140	Nepheline
G4	0.6016	0.6244	15,000	550	140	Hydroxy Cancrinite
G5	0.5783	0.5770	15,000	600	140	Hydroxy Cancrinite + Nepheline
G6	0.6028	0.5925	15,000	775	140	Nepheline
G7	0.5834	0.5855	20,000	550	162	Hydroxy Cancrinite
G8*	0.6001	0.6001	20,000	450	162	Hydroxy Cancrinite + v. Minor Analcite
G9	0.5957	0.6075	20,000	400	162	Hydroxy Cancrinite
G10*	0.6000	0.6002	20,000	300	162	Hydroxy Cancrinite + Analcite
G11*	0.5510	0.5510	10,000	300	188	Hydroxy Cancrinite + Analcite
G12	0.5645	0.5630	10,000	600	188	Nepheline
G13*	0.5629	0.5629	10,000	550	188	Hydroxy Cancrinite
G14	0.5751	0.5987	10,000	800	188	Nepheline
G15	0.5611	0.5553	30,000	650	95	Hydroxy Cancrinite
G16	0.5637	0.5654	30,000	550	95	Hydroxy Cancrinite
G17*	0.5690	0.5692	30,000	500	95	Hydroxy Cancrinite
G18*	0.5870	0.5872	30,000	400	95	Hydroxy Cancrinite
G19*	0.5315	0.5315	20,000	600	148	Hydroxy Cancrinite
G20	0.5515	0.5521	20,000	750	148	Hydroxy Cancrinite
G21*	0.5669	0.5667	20,000	550	148	Hydroxy Cancrinite
G22*	0.5593	0.5593	20,000	450	148	Hydroxy Cancrinite + Minor Analcite ?
G23	0.5427	0.5342	15,000	600	144	Hydroxy Cancrinite
G24	0.5802	0.5784	15,000	550	144	Hydroxy Cancrinite
G25	0.5210	0.5160	10,000	800	195	Nepheline + ?
G26*	0.5520	0.5518	15,000	300	160	Hydroxy Cancrinite + Analcite
G27*	0.5622	0.5620	15,000	800	160	Hydroxy Cancrinite
G28	0.5961	0.5857	10,000	800	160	Nepheline
G30	0.5942	0.5870	10,000	800	224	Nepheline

* – closed system

TABLE 4.15

d Spacings, Cell Dimensions and Cell Volumes of Hydroxy Cancrinite

Sample No. – G17
Radiation – CuKα
Filter – Ni
Standard – Quartz

d	I (visual)	$hk\bar{i}l$	a(Å)	c(Å)	Cell Volume (Å^3)
4.63	40	$10\bar{1}1$	12.61$^{(1)}$	5.12	705
3.842	15	?	?	?	–
3.641	25	$30\bar{3}0$	12.60	–	–
3.211	100	$21\bar{3}1$	12.61$^{(1)}$	5.12	705
2.999	15 (diff.)	$31\bar{4}0$	12.48	–	–
2.879	10	?	?	?	–
2.731	40	$40\bar{4}0$	12.61	–	–
2.603	25	$31\bar{4}1$	12.67$^{(2)}$	5.13	713
2.571	40	0002	–	5.14	–
2.411	20	$40\bar{4}1$	12.67$^{(2)}$	5.13	713
2.101	15	$33\bar{6}0$	12.60	–	–
1.867	5 (diff.)	$40\bar{4}2$	12.59$^{(3)}$	5.12	703
1.747	5 (diff.)	$41\bar{5}2$	12.61$^{(4)}$	5.14	708
1.504	5 (v.diff.)	$44\bar{8}1$	12.59$^{(3)(6)}$	5.12	704
1.492	7 (v.diff.)	$53\bar{8}1$	12.61$^{(4)(5)}$	5.14	708
1.319	5 (v.diff.)	$42\bar{6}3$	12.61$^{(5)}$	5.15	709
1.152	5 (v.diff.)	$53\bar{8}3$	12.58$^{(6)}$	5.14	704

( ) – numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation.

FIGURE 4.11

Cell dimensions and cell volumes versus $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$

for synthetic hydroxy-cancrinite

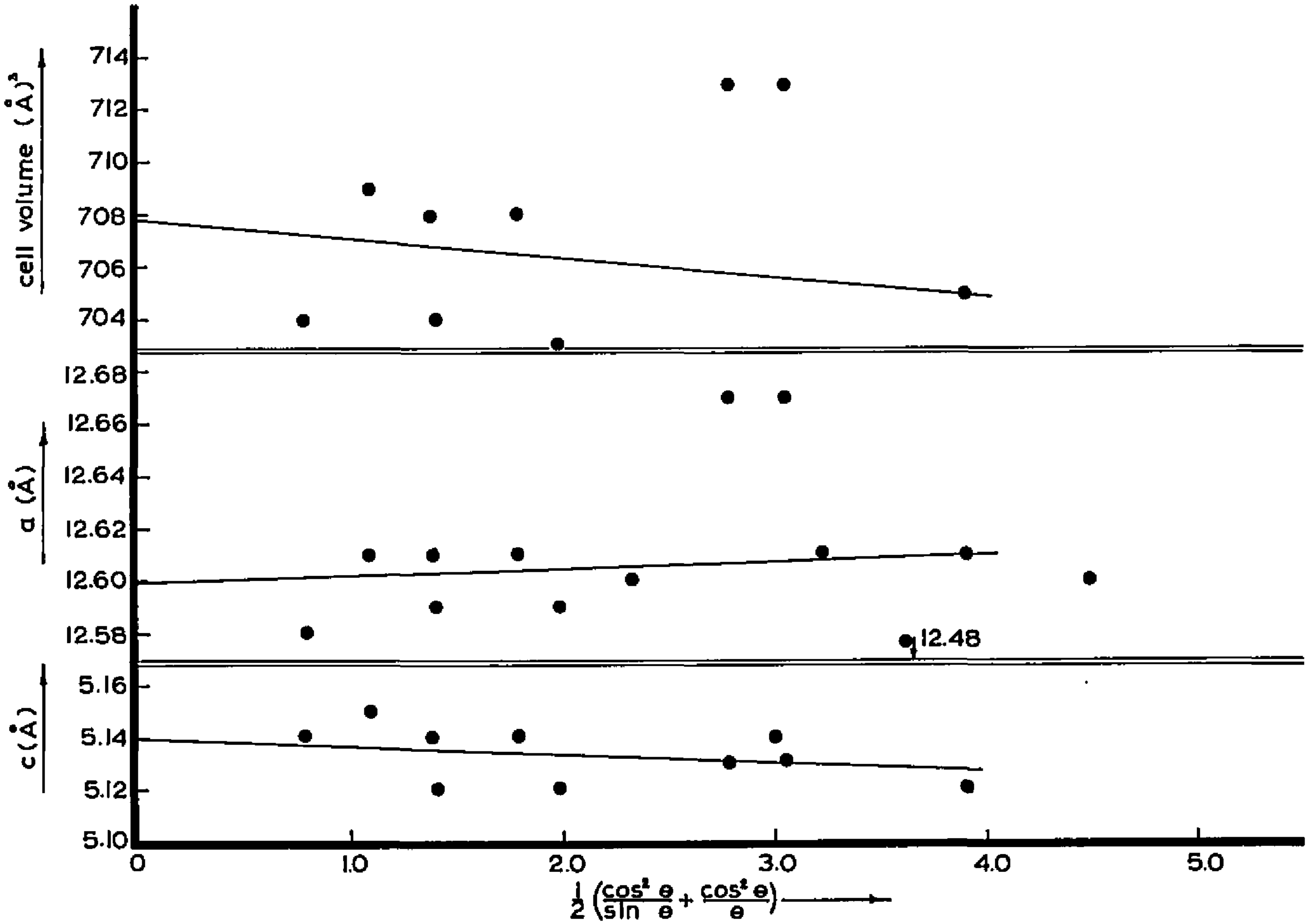

cell volume (Å)³
714
712
710
708
706
704
a (Å)
12.68
12.66
12.64
12.62
12.60
12.58
12.48
c (Å)
5.16
5.14
5.12
5.10
0
1.0
2.0
3.0
4.0
5.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

TABLE 4.16

d Spacings, Cell Dimensions and Cell Volumes of Microsommite

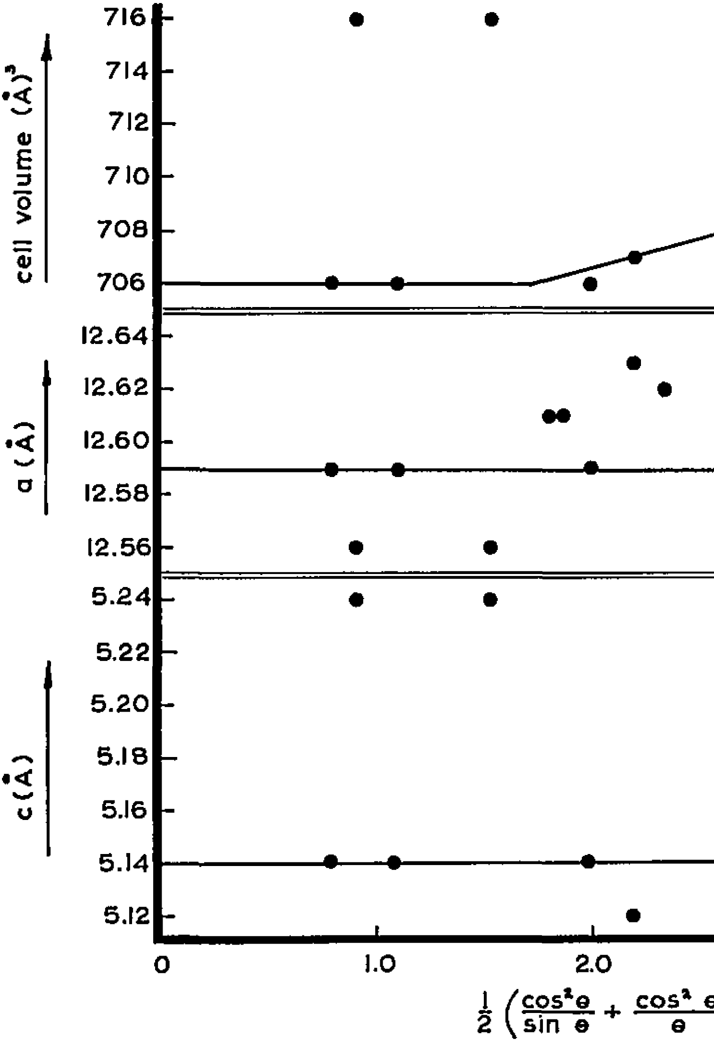
Sample No. – M24
Radiation – CuKα
Filter – Ni
Standard – Quartz

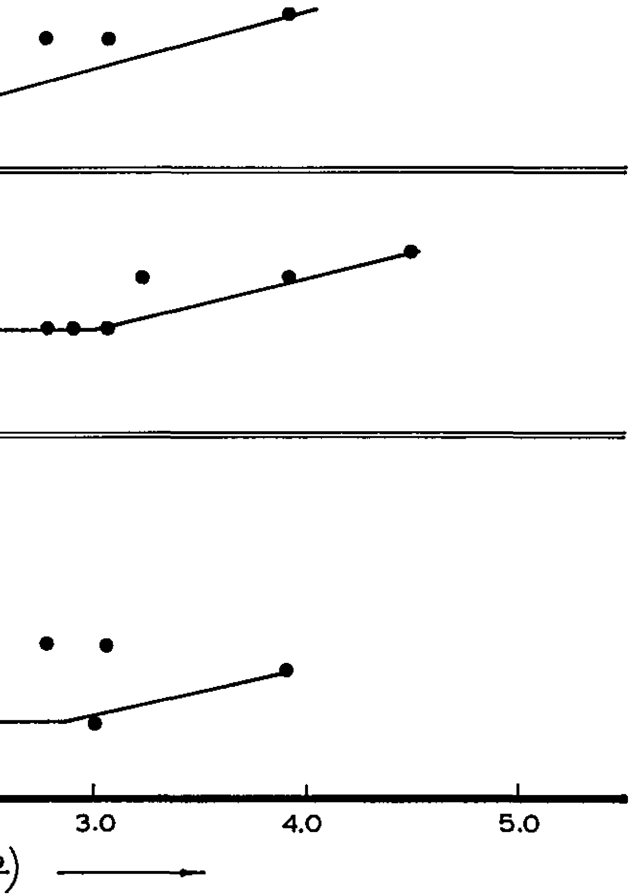
d	I (visual)	$hk\bar{i}l$	a(Å)	c(Å)	Cell Volume (Å^3)
6.34	25	$11\underline{2}0$	12.63	–	–
4.66	50	$10\underline{1}1$	$12.61^{(1)}$	5.16	711
3.644	45	$30\underline{3}0$	12.62	–	–
3.223	100	$21\underline{3}1$	$12.61^{(1)}$	5.16	711
2.731	25	$40\underline{4}0$	12.61	–	–
2.612	25	$31\underline{4}1$	$12.59^{(2)}$	5.17	710
2.572	25	$00\underline{0}2$	–	5.14	–
2.502	7	$32\underline{5}0$	12.59	–	–
2.411	30	$40\underline{4}1$	$12.59^{(2)(3)}$	5.17	710
2.103	25	$33\underline{6}0$	12.62	–	–
2.011	10	$50\underline{5}1$	$12.63^{(3)}$	5.12	707
1.870	7	$40\underline{4}2$	12.59	5.14	706
1.795	7	$43\underline{7}0$	12.61	–	–
1.748	10	$52\underline{7}0$	12.61	–	–
1.582	7	$61\underline{7}1$	$12.56^{(4)}$	5.24	716
1.493	5	$31\underline{4}3$	?	?	–
1.486	5	$53\underline{8}1$	?	?	–
1.319	5 (diff.)	$42\underline{6}3$	$12.59^{(5)}$	5.14	706
1.214	5 (diff.)	$6,4,\underline{10},1$	$12.56^{(4)}$	5.24	716
1.153	5	5383	$12.59^{(5)}$	5.14	706

( ) – numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation or by direct comparison of $\sin^2\theta$ calc. and $\sin^2\theta$ obs. values.

FIGURE 4.12

Cell dimensions and cell volumes versus $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ for synthetic microsommite


cell volume (Å)^3
716
714
712
710
708
706
a (Å)
12.64
12.62
12.60
12.58
12.56
c (Å)
5.24
5.22
5.20
5.18
5.16
5.14
5.12
0
1.0
2.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right.$


3.0
4.0
5.0

gives $a = 12.59 \pm .02$Å (approximately), $c = 5.14 \pm .02$Å (approximately), and a resulting cell volume of 706 ± 5Å^3.

3. Solid Solution Measurements

The possibility of solid solution existing between the carbonate and bicarbonate end-members of the cancrinites was investigated by synthesizing various mixtures of intermediate composition. The intermediate products from closed systems were X-rayed, using quartz as a standard, by oscillating six times between 26°2θ and 28°2θ. This interval contains the $10\bar{1}1$ quartz peak and the $21\bar{3}1$ cancrinite peak. The distance between these peaks was measured six times and the average distance plotted against composition. The standard deviation was also calculated and plotted. If these curves are linear it is probable that complete solid solution exists between the end-members; non-linear curves, or absence of smooth curves, probably indicate the absence of solid solution. This theory is more fully explained in Chapter V.

(i) Cancrinite-Natrodavyne Proper

The results of solid solution measurements between these end-members are given in Table 4.17 and a plot of $2\theta_{(10\bar{1}1 \text{ qtz.} - 21\bar{3}1 \text{ canc.})}$ versus composition is shown in Figure 4.13. This curve indicates that a possible solid solution exists between pure cancrinite and 50 weight per cent cancrinite and between pure natrodavyne proper and 50 weight per cent natrodavyne.

(ii) Cancrinite-Bicarbonate Natrodavyne

The results of solid solution on these end-members are given in Table 4.17 and a plot of $2\theta_{(10\bar{1}1 \text{ qtz.} - 21\bar{3}1 \text{ canc.})}$ versus composition is shown in Figure 4.14. This curve is similar to that for cancrinite-

TABLE 4.17

Results of Solid Solution Measurements

(i) Cancrinite-Natrodavyne Proper; Temperature = 450°C.; Pressure = 20,000 psi

Sample Number	Composition (weight per cent)	Average $2\theta_{10\bar{1}1}$ qtz.-$21\bar{3}1$ canc. (degrees)	Standard Deviation (degrees)
S.C.54	100% Cancrinite	1.064	± 0.024
M26	75% Canc. + 25% Nadav.	1.076	± 0.022
M37	50% Canc. + 50% Nadav.	1.099	± 0.016
M29	25% Canc. + 75% Nadav.	1.007	± 0.013
F52X	100% Natrodavyne	0.928	± 0.011

(ii) Cancrinite-Bicarbonate Natrodavyne; Temperature = 500°C.; Pressure = 20,000 psi

Sample Number	Composition (weight per cent)	Average $2\theta_{10\bar{1}1}$ qtz.-$21\bar{3}1$ canc. (degrees)	Standard Deviation (degrees)
S.C.54	100% Cancrinite	1.064	± 0.024
M58	76% Canc. + 24% Bi-nadav.	1.059	± 0.012
M55	51% Canc. + 49% Bi-nadav.	1.105	± 0.011
M53	26% Canc. + 74% Bi-nadav.	1.019	± 0.013
F34	100% Bicarbonate Natrodavyne	0.929	± 0.015

(iii) Davyne Proper - Natrodavyne Proper; Temperature = 450°C.; Pressure = 15,000 psi

Sample Number	Composition (weight per cent)	Average $2\theta_{10\bar{1}1}$ qtz.-$21\bar{3}1$ canc. (degrees)	Standard Deviation (degrees)
D21X	100% Davyne Proper	0.770	± 0.017
M51	76% Dav. + 24% Nadav.	0.757	± 0.019
M33	51.5% Dav. + 48.5% Nadav.	0.776	± 0.018
M31	26% Dav. + 74% Nadav.	0.820	± 0.002
F52X	100% Natrodavyne Proper	0.928	± 0.011

(iv) Bicarbonate Davyne - Bicarbonate Natrodavyne; Temperature = 400°C.; Pressure = 20,000 psi

Sample Number	Composition (weight per cent)	Average $2\theta_{10\bar{1}1}$ qtz.-$21\bar{3}1$ canc. (degrees)	Standard Deviation (degrees)
D25	100% Bicarbonate Davyne	0.787	± 0.016
M44	76% Bi-dav. + 24% Bi-nadav.	0.768	± 0.014
M45	51% Bi-dav. + 49% Bi-nadav.	0.892	± 0.022
M60	26% Bi-dav. + 74% Bi-nadav.	0.887	± 0.013
F34	100% Bicarbonate Natrodavyne	0.929	± 0.015

Table 4.17 (contd.)

Sample Number	Composition (weight per cent)	Average $2\theta_{10\bar{1}1}$ qtz.-$21\bar{3}1$ canc. (degrees)	Standard Deviation (degrees)
(v) Cancrinite-Bicarbonate Davyne: Temperature = 400°C.; Pressure = 20,000 psi			
S.C.54	100% Cancrinite	1.064	± 0.024
M18	75% Canc. + 25% Bi-dav.	1.091	± 0.013
M8	50% Canc. + 50% Bi-dav.	1.118	± 0.021
M7	25% Canc. + 75% Bi-dav.	1.083	± 0.013
M42	10% Canc. + 90% Bi-dav.	0.981	± 0.024
D25	100% Bicarbonate Davyne	0.787	± 0.016

FIGURE 4.13

Possible solid solution in the system cancrinite-natrodavyne proper

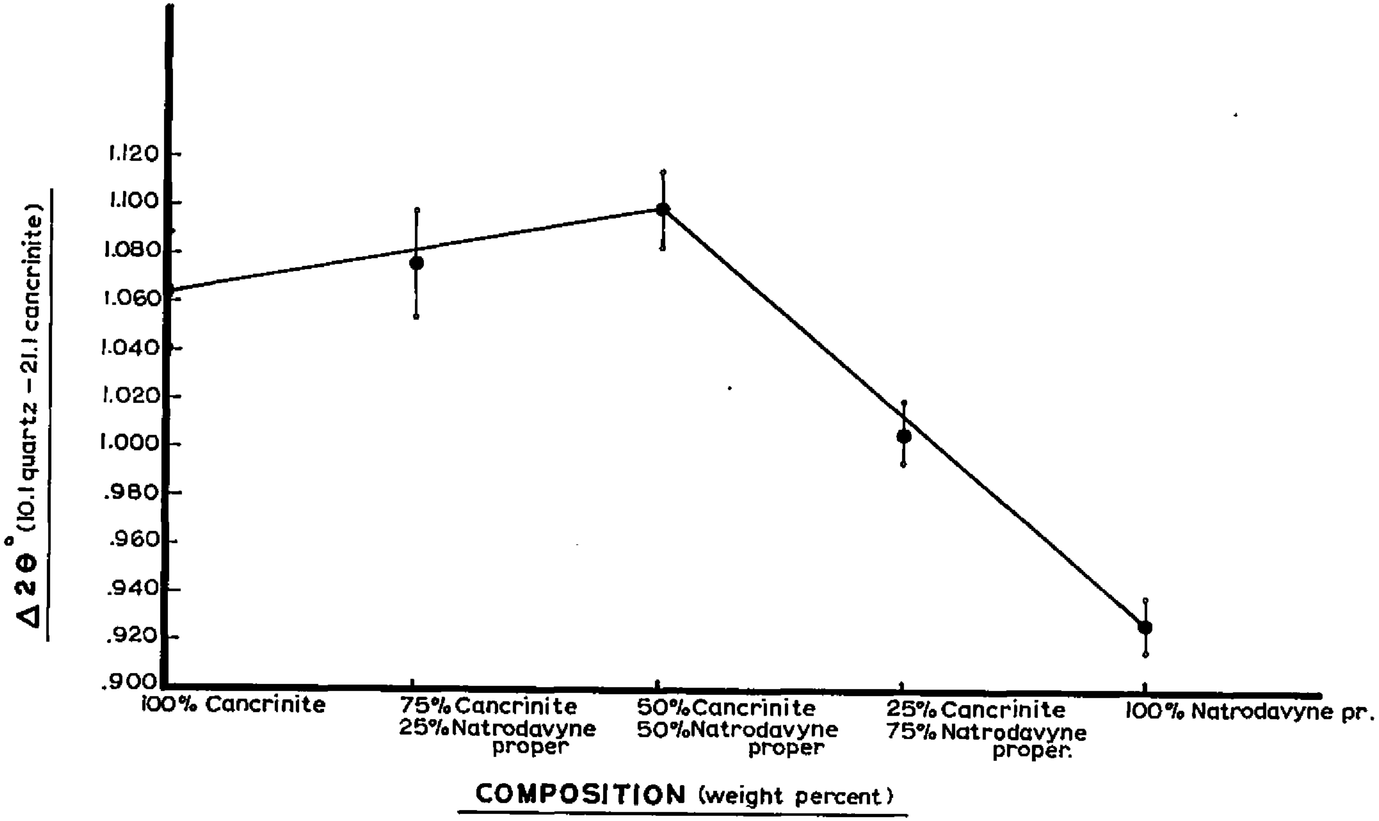
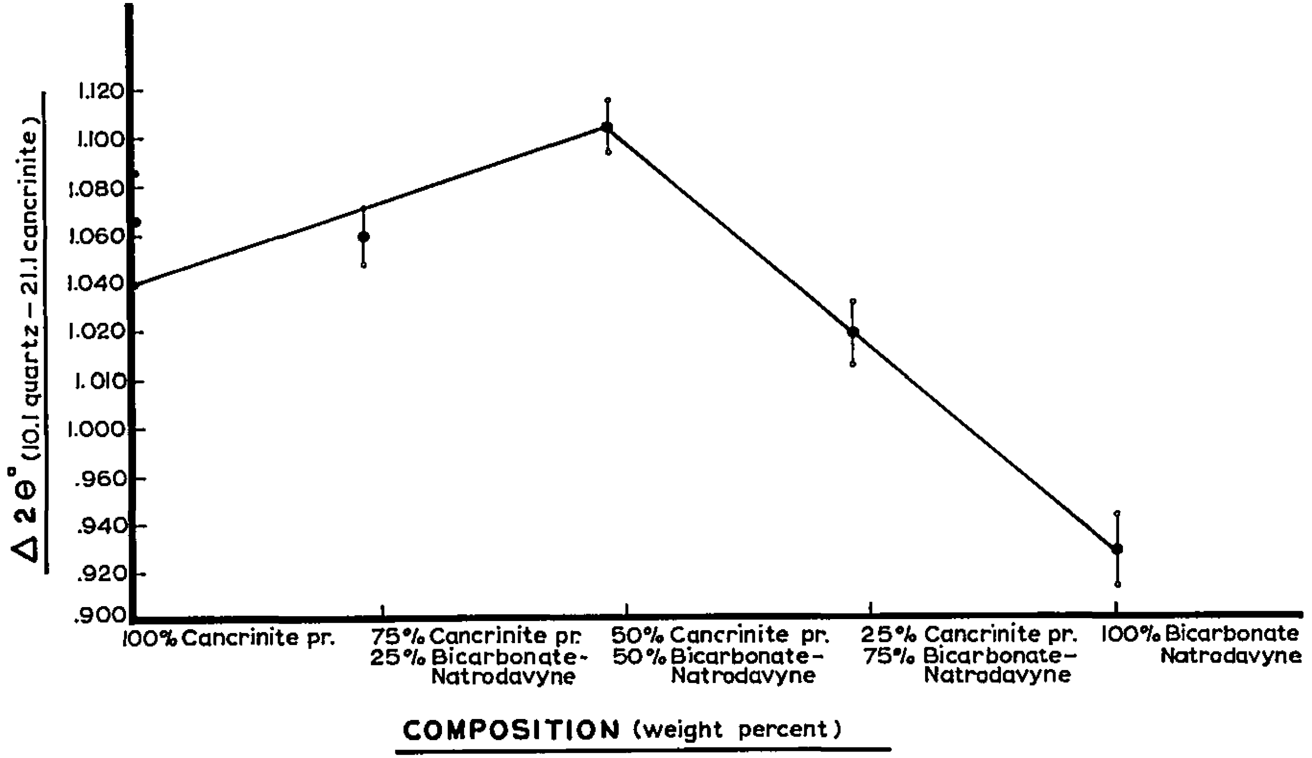

$\Delta 2\Theta^\circ$ (10.1 quartz − 21.1 cancrinite)
1.120
1.100
1.080
1.060
1.040
1.020
1.000
.980
.960
.940
.920
.900
100% Cancrinite
75% Cancrinite 25% Natrodavyne proper
50% Cancrinite 50% Natrodavyne proper
25% Cancrinite 75% Natrodavyne proper.
100% Natrodavyne pr.
COMPOSITION (weight percent)

FIGURE 4.14

Possible solid solution in the system

cancrinite-bicarbonate natrodavyne


Δ 2Θ° (10.1 quartz – 21.1 cancrinite)
1.120
1.100
1.080
1.060
1.040
1.020
1.010
1.000
.960
.940
.920
.900
100% Cancrinite pr.
75% Cancrinite pr.
25% Bicarbonate-Natrodavyne
50% Cancrinite pr.
50% Bicarbonate-Natrodavyne
25% Cancrinite pr.
75% Bicarbonate-Natrodavyne
100% Bicarbonate Natrodavyne
COMPOSITION (weight percent)

natrodavyne proper in that it indicates possible solid solution between pure bicarbonate natrodavyne and 50 weight per cent bicarbonate natrodavyne, and that possible solid solution exists between pure cancrinite and a 50 weight per cent cancrinite.

(iii) Davyne Proper-Natrodavyne Proper

The results of solid solution measurements on davyne proper-natrodavyne proper are given in Table 4.17, and the graph of $2\theta_{(10\bar{1}1 \text{ qtz.} - 21\bar{3}1 \text{ canc.})}$ versus composition is shown in Figure 4.15. This graph indicates possible solid solution in the composition range 25 to 75 weight per cent davyne proper, but that no solid solution appears to exist between the pure end-members and intermediate products.

(iv) Bicarbonate Davyne-Bicarbonate Natrodavyne

The results of solid solution measurements between these end-members are given in Table 4.17, and the graph of $2\theta_{(10\bar{1}1 \text{ qtz.} - 21\bar{3}1 \text{ canc.})}$ versus composition is shown in Figure 4.16. This graph indicates that possible solid solution exists between 50 and 100 weight per cent bicarbonate natrodavyne.

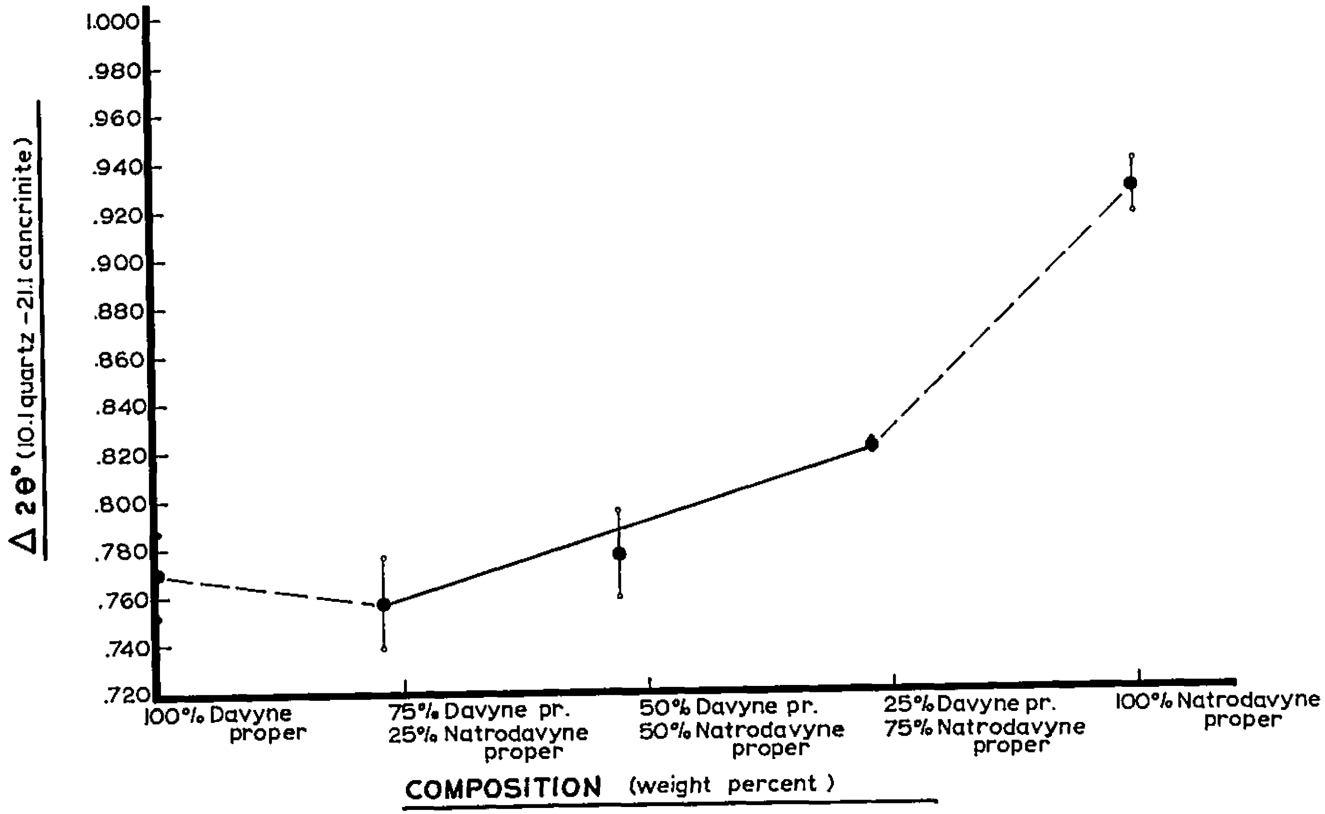
(v) Cancrinite Proper-Bicarbonate Davyne

The results of solid solution measurements on cancrinite proper and bicarbonate davyne are given in Table 4.17, and the graph of $2\theta_{(10\bar{1}1 \text{ qtz.} - 21\bar{3}1 \text{ canc.})}$ versus composition in Figure 4.17. This graph indicates that solid solution may exist between pure cancrinite and 50 weight per cent cancrinite. No solid solution appears to exist in cancrinite rich compositions.

FIGURE 4.15

Possible solid solution in the system

davyne proper-natrodavyne proper



Δ 2θ° (10.1 quartz −21.1 cancrinite)
1.000
.980
.960
.940
.920
.900
.880
.860
.840
.820
.800
.780
.760
.740
.720
100% Davyne proper
75% Davyne pr. 25% Natrodavyne proper
50% Davyne pr. 50% Natrodavyne proper
25% Davyne pr. 75% Natrodavyne proper
100% Natrodavyne proper
COMPOSITION (weight percent)

FIGURE 4.16

Possible solid solution in the system bicarbonate davyne-bicarbonate natrodavyne

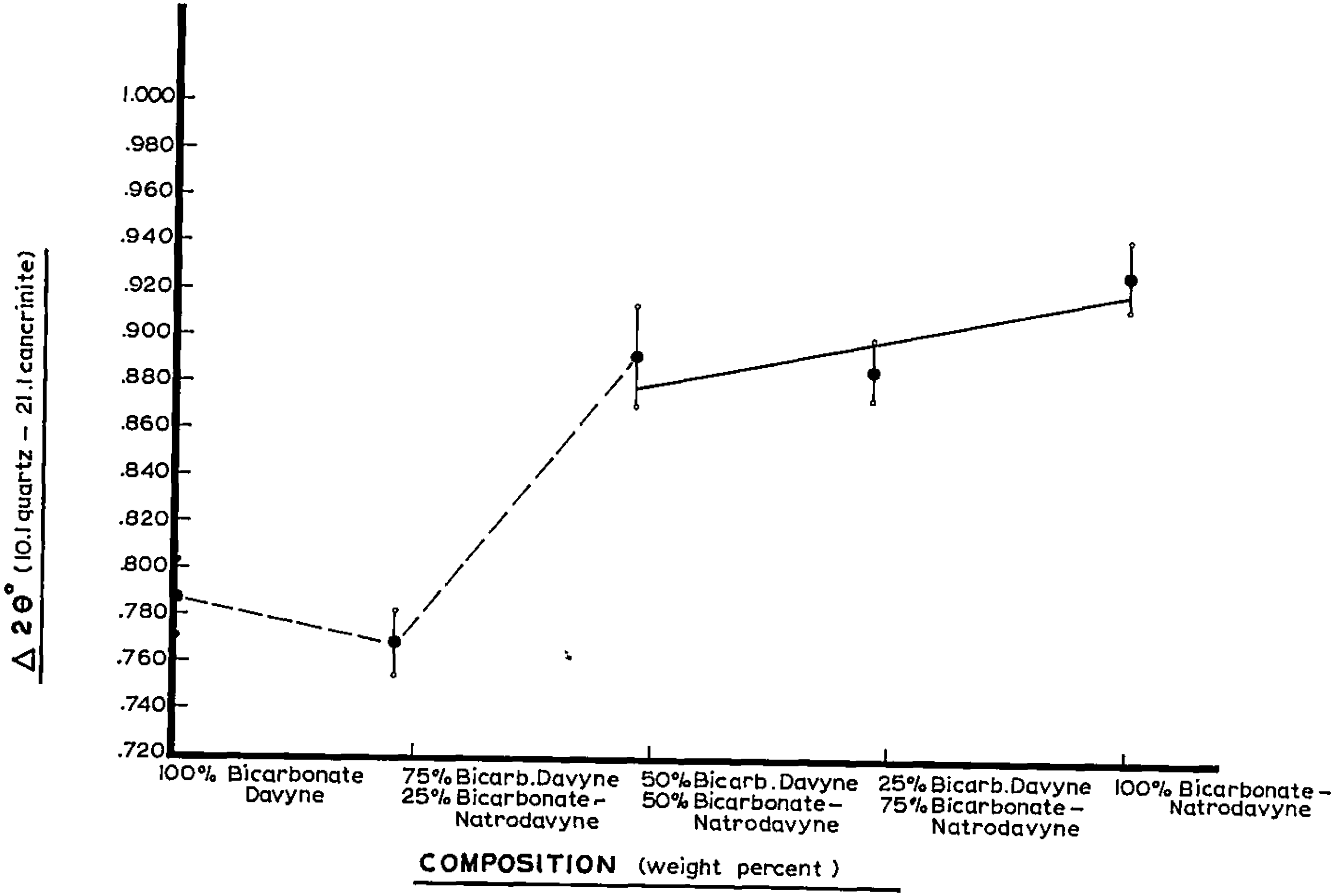
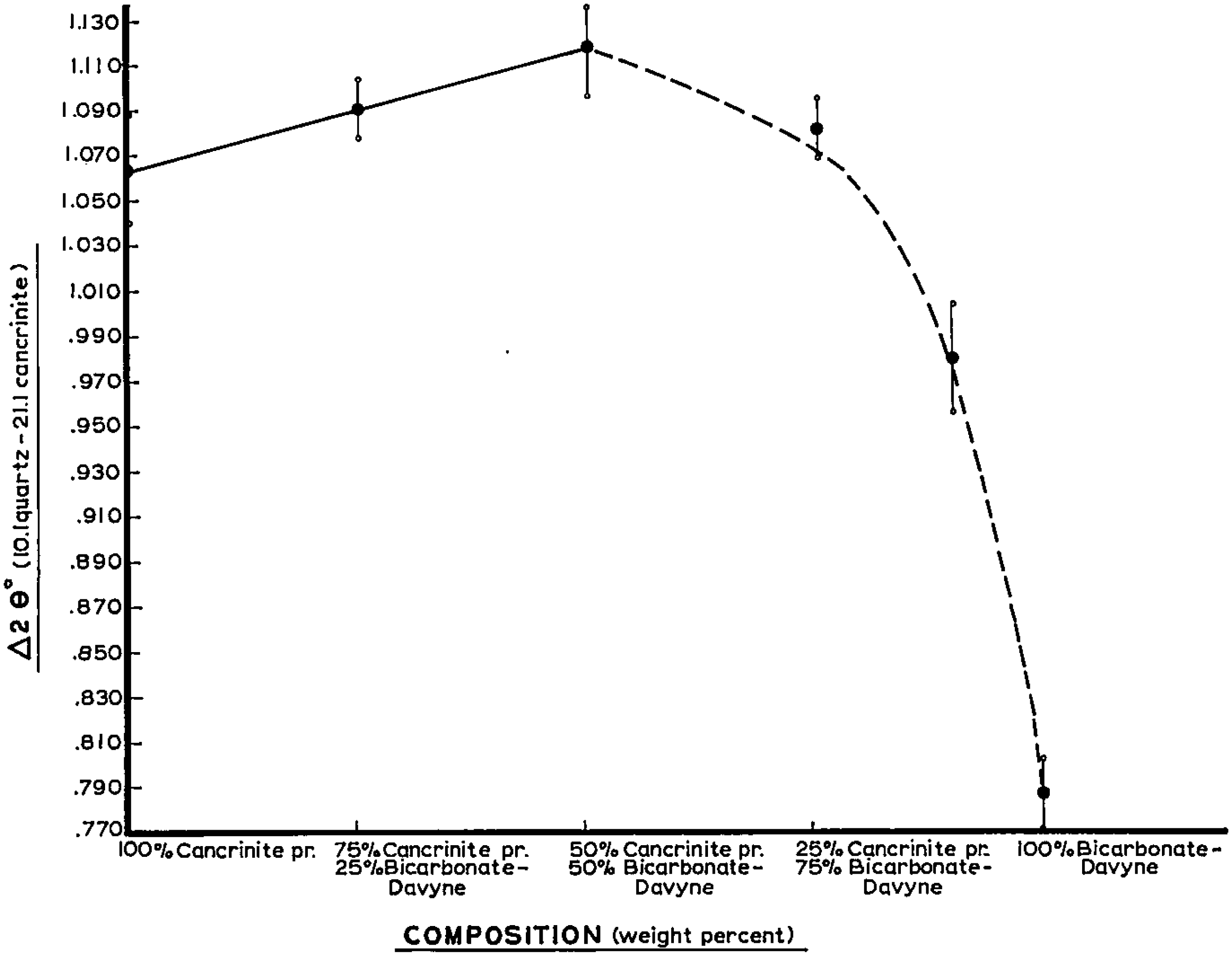

Δ 2Θ° (10.1 quartz – 21.1 cancrinite)
1.000
.980
.960
.940
.920
.900
.880
.860
.840
.820
.800
.780
.760
.740
.720
100% Bicarbonate Davyne
75% Bicarb. Davyne 25% Bicarbonate-Natrodavyne
50% Bicarb. Davyne 50% Bicarbonate-Natrodavyne
25% Bicarb. Davyne 75% Bicarbonate-Natrodavyne
100% Bicarbonate-Natrodavyne
COMPOSITION (weight percent)

FIGURE 4.17

Possible solid solution in the system cancrinite-bicarbonate davyne


1.130
1.110
1.090
1.070
1.050
1.030
1.010
.990
.970
.950
.930
.910
.890
.870
.850
.830
.810
.790
.770
Δ2 θ° (10.1 quartz - 21.1 cancrinite)
100% Cancrinite pr.
75% Cancrinite pr. 25% Bicarbonate-Davyne
50% Cancrinite pr. 50% Bicarbonate-Davyne
25% Cancrinite pr. 75% Bicarbonate-Davyne
100% Bicarbonate-Davyne
COMPOSITION (weight percent)

4. Synthesis of Sulphatic Cancrinite, Using the Formula of Stewart (1941); and Wischnewite, Using the Formula of Beljankin (1944)

An attempt was made to solve the controversy about the difference between sulphatic cancrinite and wischnewite, by synthesizing minerals with approximately the same composition as that given by Stewart (1941) for sulphatic cancrinite from Loch Borolan, Scotland, and that given by Beljankin (1944) for wischnewite from the Wishnevy Gory Mountains.

For sulphatic cancrinite, the constituents used were made up according to the proportions given in Stewart's (1941) analysis, omitting the minor amount of SrO (0.32 weight per cent) quoted by him. Wischnewite was prepared by mixing in the correct proportions the constituents quoted by Beljankin (1944), omitting minor amounts of TiO_2 (0.10 weight per cent), Fe_2O_3 (0.56 weight per cent), FeO (0.11 weight per cent), MnO (0.09 weight per cent), MgO (0.09 weight per cent) and Cl_2 (0.09 weight per cent).

Both these starting compositions synthesized a cancrinite-type mineral in the temperature range 300° to 450°C. at a water pressure of 15,000 to 20,000 psi. A comparison of the d spacings of both synthetic sulphatic cancrinite and synthetic wischnewite, listed in Table 4.18, shows that there is considerable difference in these synthetic minerals, and therefore no justification in Beljankin's (1944) suggestion that sulphatic cancrinites should be called wischnewites.

TABLE 4.18

d Spacings of Sulphatic Cancrinite and Wischnewite Synthesized Using the Formulae Given by Beljankin (1944)

Sulphatic Cancrinite
Radiation – CuKα
Filter – Ni
Standard – Quartz
Sample No.– A29s

Wischnewite
Radiation – CuKα
Filter – Ni
Standard – Quartz
Sample No.– B36b

d	Intensity (Visual)	d	Intensity (Visual)
4.66	25	4.71	50
3.673	100	3.929	25
3.259	100	3.672	60
2.919	10	3.257	100
2.737	15	3.012	20
2.614	35	2.756	25
2.576	20	2.643	10
2.418	20	2.605	10
2.103	15	2.436	10
2.015	5	2.351	7
1.872	5	2.191	5
1.749	5	2.030	5
1.582	5	1.765	5 (diff.)
1.500	5	1.604	5 (diff.)
1.454	5	1.507	5
		1.416	5
		1.294	5
		1.153	5

V. DISCUSSION OF RESULTS

The present investigation of synthetic cancrinites in the temperature range 200° to 800°C., and at water pressures between 10,000 and 30,000 psi, indicates that of the six end-member formulae of the group proposed by Winchell and Winchell (1951) at least three do not synthesize a cancrinite type of mineral under the conditions of this investigation. The fact that these minerals synthesized to members of the sodalite family indicates that there is a possible relationship between the cancrinite and sodalite groups. Because of failure to synthesize some of Winchells' cancrinites, and because some of the compositions have been modified, it is suggested that the nomenclature of the cancrinites be revised.

In addition, this investigation indicates that there is considerable variation in the fields of synthesis and cell dimensions of cancrinite with compositional variation. Solid solution measurements demonstrate that a limited solid solution is possible between some end-members of this family.

The experimentally determined stability curves probably represent metastable equilibrium as some of the reactions were not reversed. The general problems of metastable equilibrium in experimentally determined systems, and their bearing on the cancrinite stability fields presented in this thesis, are discussed in the first sections of this chapter.

1. Problems of Equilibrium

The fields of synthesis and boundary curves presented in Chapter IV are believed to represent conditions of metastable equilibrium. The conditions required for experimental mineral synthesis to take place under equilibrium conditions have been discussed by Fyfe (1960), who has shown that the ease with which equilibrium is reached depends on (a) the free energies of the starting materials compared to the free energy of the resulting mineral and its dissociation products in the region of the equilibrium temperature; (b) the grain size of the starting materials; and (c) the ability to quench the experimentally formed phases. The only proof of equilibrium however, is the reversing of the reaction. Some of these conditions are considered for the cancrinite stability curves.

A phase or assemblage of phases is stable only if the free energy of the phase assemblage is lower than any equivalent phase or assemblage. At the equilibrium temperature therefore, the equilibrium phase will have the lowest free energy. Thermodynamic data on cancrinites are insufficient to determine whether the phases are stable. Considerations of the starting materials however, do indicate that these have relatively high free energies of formation, as at least two of them, α- cristobalite and γ- alumina, are known to be metastable at the temperatures and pressures used in this investigation. This indicates that there is a possibility that they will not react to give the most stable phase but merely another metastable assemblage. Unfortunately it is necessary to use these highly reactive starting materials because the more stable oxides have such a low free energy that they probably will not react to form the desired products in a reasonable time. The possibility of using less reactive constituents in the synthesis of cancrinites was not investigated in the present thesis.

In theory, an equilibrium boundary between assemblages can be established by converting one assemblage to another by infinitesimal changes in pressure or temperature from the values given by the boundary curves. In practice, it is usually necessary to change these conditions considerably, due to the sluggishness of reactions near equilibrium conditions. It was found impossible to reverse the reaction in the davynes by lowering the temperature as much as 250°C. (see stability data on D74). However, in the system natrodavyne proper one run was reversed over a temperature range of 300°C. (see F-IIIx). This inability to reverse the reactions is considered as evidence that some of the curves may not represent stable equilibrium.

Fyfe (1960) also considers the grain size of the starting materials to be important in the synthesis of equilibrium assemblages, excessively fine materials having large surface energies. Throughout this investigation the grain size of the starting materials was fairly uniform at - 200 mesh and probably did not increase the free energies of these materials. The last condition for proof of equilibrium, the ability to quench the experimentally formed phases, was thought to be fulfilled in this investigation, although impossible to check.

The evidence indicates that the stability curves determined in this investigation may represent metastable equilibrium. Absolute proof of metastable equilibrium cannot be established until more thermodynamic data are available. It is also possible that by lowering the temperature more than 250°C. and increasing the reaction time, reversibility would occur for the davynes. The success of this experiment however, would only indicate that the equilibrium boundary curve lay somewhere between broad temperature limits.

2. Problem of Analcite at Low Temperatures

Analcite was detected at low temperatures in several of the systems investigated. This analcite field was only delineated in one system, the bisulphate nosean ($3NaAlSiO_4.NaHSO_4$), and extends from 475°C. at 10,000 psi to 525°C. at 23,000 psi. In determinations of the fields of synthesis of cancrinite proper, analcite was detected at temperatures up to 250°C. in the closed system, in the hydroxy-cancrinite system analcite is still present at 450°C. at a water pressure of 20,000 psi; and in the sulphatic cancrinites analcite is present at 300°C. between 10,000 and 20,000 psi. These temperatures are not necessarily the upper limit of the stability of analcite but merely represent the upper temperature limit at which analcite was detected in this investigation. Only minor analcite was detected in the bicarbonate davyne system, and no analcite in the davyne proper and natrodavynes, although very few experiments were run with these compositions in low temperature environments.

It could not be definitely established whether the analcite or the cancrinite were metastable, as both products were observed in the X-ray diffractograms. In the cancrinite system, two runs (59 and 60) were allowed to run for over 400 hours, but still contained peaks of both of these minerals, and in addition the main calcite peak. Another run (63) was "seeded" with a small amount of natural cancrinite, but also produced cancrinite, analcite and calcite peaks. Possibly experiments of much longer duration would have proved whether cancrinite or analcite was the metastable phase, or whether this is an equilibrium assemblage on a univariant line.

In the case of cancrinite proper, the following theoretical equations can be postulated to explain this analcite:-

(i) 1 cancrinite mix + nH_2O ⟶ 1 analcite + 1 nepheline

+ 1/2 $Na_2O.Al_2O_3$ + 1 calcite ⟶ 1 cancrinite.

(ii) 1 cancrinite mix + nH_2O ⟶ 1 analcite + 1/3 cancrinite

+ 2/3 calcite + 1/2 $Na_2O.Al_2O_3$ ⟶ 1 cancrinite.

(iii) 1 cancrinite mix + nH_2O ⟶ 1 analcite + 1 nepheline

+ 1/2 $CaAl_2O_4$ + 1/2 Na_2CO_3 + 1/2 calcite ⟶ 1 cancrinite.

Of these three equations the second one seems most likely, as no nepheline could be detected in any of the X-ray patterns containing analcite. No $Na_2O.Al_2O_3$ was detected in these patterns. The absence of $Na_2O.Al_2O_3$ is very possible as this compound is very soluble in water and therefore may be removed in solution when the capsule is opened.

A similar equation can be formulated for hydroxy-cancrinite viz:-

1 hydroxy-cancrinite mix + nH_2O ⟶ 1 analcite + 1/3 hydroxy-cancrinite + 2/3 $Ca(OH)_2$ + 1/2 $Na_2O.Al_2O_3$. ⟶ 1 hydroxy-cancrinite.

No $Ca(OH)_2$ or $Na_2O.Al_2O_3$ were detected in the X-ray patterns.

The field of analcite in the bisulphate nosean composition was well established over the pressure range 10,000 to 23,000 psi. The likely equation for this metastable analcite is

1 bisulphate nosean mix + $nH_2O \longrightarrow$ 1 analcite + 1/3 bisulphate nosean + 1/2 $Na_2O.Al_2O_3$ + 2/3 $NaHSO_4 \longrightarrow$ 1 bisulphate nosean.

Examination of the X-ray patterns containing analcite indicated that both analcite and bisulphate nosean were present in the temperature range 400° to 450°C. In this range $NaAlSO_4$ is also a possible product, but was difficult to detect as the main $NaHSO_4$ peak occurs in the same position as the main analcite peak. With the exception of one run at 350°C., no nepheline was detected, and it is possible that at this temperature the nepheline and the $NaHSO_4$ had not combined to form bisulphate nosean.

3. Identification of Products

In all experiments in hydrothermal synthesis there is an uncertainty in the composition of the phases produced. This problem is a serious one that cannot be readily solved, as it is usually impossible to chemically analyze the small amounts of synthesized phases, and hence prove that the reactions predicted have in fact occurred. For example, it is not possible to say that the cancrinites synthesized on the low temperature side of the reaction curves actually have the composition stated. It is theoretically possible that the hydroxide radical has entered the structure in place of oxygen or some other anion, and it is possible also that CO_2 does not enter into the phase but exists as a gas and is lost as soon as the capsule is opened. This, of course, is also true of syntheses on the high temperature side of the reaction curves. However, one is used to the difficulty of identifying products on the high temperature side of the reaction curves, and consequently fails to recognize that this is also a real problem on the low temperature side.

All products synthesized have been examined microscopically and by X-ray diffraction methods. In the cancrinite proper composition two runs were made without water but merely in a CO_2 atmosphere and no major difference could be detected between cancrinites synthesized in this fashion and those synthesized under water pressure. In addition a cancrinite has been synthesized in which the carbonate radical has been replaced by a hydroxide radical. These hydroxy cancrinites have slightly different d spacings and cell dimensions from cancrinite proper, synthesized in the presence of excess water.

The possibility of the hydroxide radical entering the structure of natrodavynes in place of the carbonate radical was investigated by synthesizing a cancrinite composed of nepheline mixture and approximately 6N sodium hydroxide solution. This cancrinite is presumably similar to the "basic cancrinite" synthesized by Barrer and White (1952) using coprecipitated gels. It is significant that this sodium hydroxide cancrinite had uniformly higher d spacings than either natrodavyne or bicarbonate natrodavyne. The d spacings of the sodium hydroxide cancrinite as well as those for natrodavyne and bicarbonate natrodavyne are presented in Table 5.1. If the carbonate and bicarbonate radicals of the natrodavynes are replaced by the hydroxide radical it would be expected that their d spacings would be similar to those of the sodium hydroxide cancrinites. The results shown in Table 5.1 indicate that this is not the case, and therefore strongly support the contention that the low temperature natrodavynes actually have carbonate and bicarbonate compositions.

TABLE 5.1

d Spacings for Synthetic Natrodavyne, Bicarbonate Natrodavyne and Sodium Hydroxide Cancrinite

Radiation – CuKα
Filter – Ni
Standard – Quartz

Natrodavyne $3NaAlSiO_4.Na_2CO_3$ F40x		Bicarbonate Natrodavyne $3NaAlSiO_4.NaHCO_3$ F3		Sodium Hydroxide Cancrinite $NaAlSiO_4.xNaOH$	
I (visual)	d	I (visual)	d	I (visual)	d
50	6.36	40	6.33	-	-
65	4.69	75	4.68	80	4.70
15	4.15	-	-	-	-
-	-	15	3.837	-	-
70	3.663	-	-	80(diff.)	3.672
-	-	75	3.397	-	-
100	3.234	100	3.234	100	3.252
-	-	10	2.996	-	-
-	-	10	2.874	-	-
-	-	-	-	15	2.816
50	2.747	50	2.741	35	2.758
10	2.628	25	2.622	30	2.634
-	-	30	2.584	30	2.589
15	2.515	10	2.516	15	2.566
5	2.426	25	2.422	15	2.431
20	2.264	10	2.239	-	-
7	2.172	10	2.172	5	2.184
5	2.113	7	2.112	-	-
-	-	-	-	15	2.096
15	2.021	-	-	-	-
5	1.977	-	-	-	-
5	1.883	10	1.880	5	1.886
7	1.804	15	1.803	-	-
10	1.758	15	1.757	7	1.763
5	1.705	10	1.702	-	-
10	1.590	15	1.590	5	1.593

Further evidence of carbonate composition is given by consideration of natural cancrinites. From chemical analyses and limited structural determinations of these cancrinites, it appears that CO_2 readily enters the cancrinite structure.

For these reasons the author feels reasonably confident that the compositions of the various phases are as stated. Assuming the compositions of the synthesized phases are as stated, the problem of identification of the phases formed from the starting materials and of the dissociation products by X-ray methods requires some consideration. The synthetic cancrinites formed from their constituent oxides, carbonates, hydroxides and sulphates gave X-ray patterns which in the majority of runs, consisted of the pure cancrinites. These were proved to be the pure products by determination of their d spacings and corresponding cell dimensions. In a few cases, it was found impossible to index and assign cell dimensions to a few of the minor peaks. The d spacings of these peaks were checked with the d spacings of several likely components and no correlation was found. These extraneous peaks, usually of low intensity, possibly represent some unidentifiable phase. From X-ray considerations, it appeared that the starting materials had reacted to produce almost 100 per cent yields of cancrinite.

Investigation of the dissociation products of davyne proper and bicarbonate davyne showed that the dissociation product consisted only of nepheline, even in the closed system. The apparent disappearance of K_2CO_3 and $KHCO_3$ as revealed in the X-ray pattern can be explained in several ways. First, in the case of $KHCO_3$, which melts at approximately 200°C. at atmospheric pressure, the $KHCO_3$ may be present as a glass at the high temperature of dissociation and therefore not appear in the X-ray pattern. Second, both K_2CO_3 and $KHCO_3$ are fairly soluble in water, and may be removed in solution when the capsules are opened. Third, the K_2CO_3 and $KHCO_3$ may not appear on the X-ray pattern because the intensity of peaks is dependent on the scattering factors of the atoms which in turn depend on the atomic numbers of the atoms. Thus, it is possible that K_2CO_3 and $KHCO_3$, having relatively much lower atomic numbers than the three nepheline molecules, would have less intense peaks than the nepheline. Each of the possibilities mentioned above was examined experimentally.

The second possibility was examined experimentally by synthesizing a davyne proper containing 42 weight per cent K_2CO_3 in excess of the stoichiometric proportions required by the formula (see stability data on D87 x E). The ratio of water to powder in this sample was one to four. When this mixture was taken above the dissociation temperature, only nepheline was detected in the X-ray pattern, indicating that even the excess K_2CO_3 was probably soluble in water at these temperatures.

The third possibility was tested by X-raying a mixture of natural nepheline and K_2CO_3 in the same proportions as the davyne formula. This produced a diffractogram containing peaks of nepheline and K_2CO_3. This may indicate that the disappearance of the K_2CO_3 in the breakdown products of davyne proper is due to the solubility of K_2CO_3. The formation of K_2CO_3 as a glass is unlikely as K_2CO_3 does not melt at atmospheric pressure, until approximately 800°C.

The first possibility could not be tested by X-ray methods. Optical examination of the dissociation products of bicarbonate davyne indicated that glass might be present. Unfortunately the synthetic products, both above and below the dissociation temperatures of all the systems investigated, were poorly crystallized and not amenable to optical examination. Some products synthesized just below the boundary curves revealed minor nepheline crystals in addition to some glass. This indicated that the dissociation takes place over a range of temperatures.

The problem of solubility of Na_2CO_3 and $NaHCO_3$ in the natrodavynes did not occur. The transformation products in these systems, as determined by X-ray methods, are discussed in a later section of this chapter.

4. Influence of Time of Reaction on Products

The length of the experimental runs is interesting for two reasons. First, the time required to synthesize cancrinites, and second, the influence of reaction times on the breakdown curves of these minerals.

The average length of the experiments was six to seven days (144 to 168 hours) and depended on the water pressure used, longer time being required at lower pressures. This time was found to be sufficient to give a reasonably good product for X-ray identification. The minimum time used was 48 hours and the maximum time 520 hours. The minimum time gave a good product, indicating that cancrinites can probably be synthesized in a few hours. The longer experiments did not alter the stability curves, nor did they promote the breakdown of cancrinite proper. This shows that within the limits used in this study, time is not an important parameter.

5. Influence of Composition on Stability Fields

Of the five carbonate and bicarbonate cancrinites synthesized, it was found that the davynes containing potassium carbonate and bicarbonate dissociated at the lowest temperatures; the natrodavynes containing sodium carbonate and bicarbonate transformed at a temperature approximately 150°C. higher than the potassium cancrinites; and lastly, the calcium carbonate cancrinite did not dissociate at the upper temperature limit of this study. In addition, neither the sulphate nor hydroxide end-members dissociated at a temperature of 800°C.

Analcite occurred, particularly in the opened capsules, at low temperatures in most of the systems, but the limits of this field were not fully determined for the various cancrinites.

6. Influence of Composition on Cell Dimensions

The determinations of cell dimensions of the various synthetic cancrinites from powder patterns were not as accurate as would have been obtained with single crystal methods. These dimensions, although subject to considerable variation caused by the mathematical complexities of the method of Nelson and Riley (1945), do indicate a definite variation in cell volumes (where volume is $0.866a^2c$) with composition. The spread in volumes on each determination did not exceed 2 per cent and in many cases was lower.

Of the carbonate and bicarbonate cancrinites, the davynes containing potassium have the largest cell volumes, the sodium cancrinites (natrodavynes) have intermediate cell volumes, and the common calcium cancrinites (cancrinite proper) have the smallest cell volumes. The addition of sulphate, in the form of $NaHSO_4$ to cancrinite proper in the correct proportion for sulphatic cancrinite does not alter the cell volume. This is to be expected as sulphatic cancrinite contains a large proportion of the cancrinite molecule. The substitution of the hydroxide radical for the carbonate radical in the hydroxy-cancrinites also produces only a slightly smaller cell volume. The cell dimensions and corresponding cell volumes of the synthesized cancrinites are given in Table 5.2.

TABLE 5.2

Cell Dimensions and Cell Volumes

of Synthetic Cancrinites

Name	a(Å)	c(Å)	Cell Volume ($0.866a^2c$)
Cancrinite proper	12.59	5.17	710
Davyne proper	12.73	5.18	727
Bicarbonate davyne	12.73	5.20	730
Natrodavyne proper	12.67	5.18	720
Bicarbonate natrodavyne	12.67	5.16	717
Sulphatic cancrinite	12.59	5.18	711
Hydroxy-cancrinite	12.60	5.14	707
Microsommite	12.59	5.14	706

A consideration of Table 5.2 shows that the major changes in cell volumes are produced by variations in the cations rather than by the carbonate, sulphate and hydroxide radicals. If the cancrinites have framework type structures with large open spaces, capable of accommodating the potassium, sodium and calcium ions combined with the acid radicals, it is reasonable that the davynes would 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 the natrodavynes have a larger cell volume than cancrinite proper, as calcium and sodium have similar ionic radii. A complete explanation of variation in cell volume with composition cannot be given until the structure of cancrinites is more definitely established.

7. High Temperature Products in the Natrodavynes

The high temperature product in the natrodavynes consisted of a mineral resembling the nosean-hauyne group. There are two possible explanations to account for this product. First, that the transition represents polymorphism from a hexagonal low natrodavyne to a cubic high natrodavyne. Second, that the transition product represents a "basic-nosean", such as has been synthesized by Barrer and White (1952). This possibility can be represented by the equation:-

$$1 \text{ natrodavyne} + nH_2O \xrightarrow{600^\circ C.} 1\tfrac{1}{2} \text{ "basic-nosean"} + CO_2$$

$$\text{i.e. } 3NaAlSiO_4.Na_2CO_3 + nH_2O \xrightarrow{600^\circ C.} (1\tfrac{1}{2}Na_2O.1\tfrac{1}{2}Al_2O_3.3SiO_2.2NaOH)$$
$$+ CO_2$$

This second possibility was investigated by synthesizing a mineral of the composition of nepheline + NaOH. This produced a nosean-hauyne-type mineral, but with different d spacings from the nosean-hauyne-type mineral produced by the regular natrodavyne compositions. A comparison of the d spacings of high natrodavyne, high bicarbonate natrodavyne and this "basic nosean" is given in Table 5.3. The fact that the d spacings of this "basic nosean" differ from those of the high temperature natrodavynes indicate that polymorphism exists in natrodavynes. As mentioned in a previous section of this chapter, the composition nepheline + NaOH, synthesized at low temperatures, produced a cancrinite-type pattern but with different d spacings from the natrodavynes (Table 5.1)

This indicates that polymorphism also exists in the composition nepheline + NaOH, producing at low temperatures a sodium hydroxide cancrinite, and at high temperatures a "basic-nosean". The exact transition boundary for sodium hydroxide cancrinites transforming to "basic-noseans" was not established but lies between 400° and 700°C. at a water pressure of 15,000 psi.

TABLE 5.3

A Comparison of d Spacings of High Natrodavyne Proper, High Bicarbonate Natrodavyne and "Basic-Nosean"

High Natrodavyne Proper F21x ($3NaAlSiO_4.Na_2CO_3$)		High Bicarbonate Natrodavyne F31 ($3NaAlSiO_4.NaHCO_3$)		"Basic-Nosean" ($NaAlSiO_4.xNaOH$)	
I (visual)	d	I (visual)	d	I (visual)	d
70	6.38	30	6.40	40	6.40
10	4.64	-	-	5	4.67
100	3.676	100	3.676	100	3.687
10	3.206	-	-	-	-
25	2.848	25	2.852	40	2.860
35	2.600	40	2.603	75	2.608
5	2.496	-	-	-	-
10	2.404	5	2.406	15	2.415
10	2.250	-	-	15	2.256
20	2.120	20	2.125	40	2.127
-	-	-	-	5	1.927
20	1.764	7	1.765	20	1.771
7	1.587	5	1.589	15	1.598
5	1.498	5	1.499	10	1.506
5	1.461	5	1.460	15	1.465

The type of polymorphism involved in the natrodavynes is not exactly known. It is possibly dilatational polymorphism, caused by slight displacements of the atoms, but breaking no chemical bonds. This type of polymorphism is achieved by a simple differential dilatation in which the structure expands along one axis and contracts at right angles to this axis. Gossner and Mussnug (1930) have shown that the hauyne structure, which is similar to nosean, can be changed to the cancrinite structure by dilatation of one of the cube diagonals. Dilatational polymorphism is also characterized by its rapidity and reversibility. The boundary curves for these natrodavynes are well defined, indicating rapid transformation. One attempt to reverse the reaction in the system natrodavyne proper was successful between 700° and 400°C. at a water pressure of 15,000 psi. It is not known whether dilatational high temperature polymorphs can be quenched.

8. Extent of Solid Solution in the Cancrinite Family

In this thesis no complete attempt has been made to delineate the various binary systems between the carbonate and bicarbonate end-members of the cancrinite family. It was assumed that a plot of change in cell volume with composition would give a straight line for ideal binary solid solution (Zen, 1956). The assumption was also made that the parameter $2\theta_{(10\bar{1}1 \text{ quartz} - 21\bar{3}1 \text{ cancrinite})}$ was a measure of cell volume. This was proved to be correct, as experiments showed that a plot of change in volume versus composition gave curves of the same shape as the 2θ versus composition curves. Using these assumptions, tests were made to see whether there was solid solution between the end-members. In the event that no complete solid solution was observed, no further experiments were undertaken.

The results of solid solution measurements indicate that solid solution in the cancrinite family is possibly very limited, and that in none of the five cases investigated is complete solid solution observed.

The end-members, cancrinite-natrodavyne proper and cancrinite-bicarbonate natrodavyne show similar types of curves (see Figures 4.13 and 4.14), each having a distinct break at 50 weight per cent cancrinite, but being approximately linear between both end-members and this break. No reasonable explanation for the irregularity in this curve can be given without further experimentation. The end-members, davyne proper-natrodavyne proper (see Figure 4.15) indicate possible solid solution between 25 and 75 weight per cent davyne. This is an unexpected range for solid solution to occur in, but a determination of actual cell volumes plotted against composition gave a similar type of curve. The end-members, bicarbonate davyne-bicarbonate natrodavyne (see Figure 4.16) show that solid solution may exist between 50 and 100 weight per cent bicarbonate natrodavyne. Finally, the end-members, cancrinite proper-bicarbonate davyne (see Figure 4.17) indicate that solid solution is possible between 50 and 100 weight per cent cancrinite proper. The reasonably smooth curve between zero and 50 weight per cent cancrinite proper cannot be explained.

The evidence of solid solution between the cancrinites as determined from these measurements, must be regarded merely as a preliminary investigation for theoretical and practical reasons. Theoretically, ideal binary solid solution should produce a linear, or at least a smooth, curve with no sharp breaks. From structural considerations it is most unlikely that solid solution would occur at intermediate compositions, and not at the end portions of the diagrams. However, this situation has been found to be true for davyne proper-natrodavyne proper, and has been verified by plotting cell volumes against composition. In practice the straight lines determined may extend further than shown. This would be possible if a solvus had been realised, and would produce two phases; one of a major composition, the other of minor composition that might not be recognized. The possibility of a solvus being realized in these systems is unlikely, due to the sluggishness of unmixing in silicates.

9. Relationship between the Cancrinite and the Sodalite Families

A consideration of the chemical composition and geological environment of the cancrinite and sodalite mineral families suggests that there is some relationship between them. Chemically, these families are similar in that they are composed of nepheline molecules plus chloride and sulphate salts; geologically they often occur together in alkalic rocks. This investigation further suggests that there is a strong similarity between the two families and may indicate that carbonate varieties of the sodalite family are feasible at high temperatures, as has been discussed in the section on polymorphism of natrodavynes.

In 1916, Larsen and Steiger, reporting the first occurrence of sulphatic cancrinite, suggested that a complete range of minerals might exist between the carbonate cancrinites and the sodium sulphate nosean. This observation has been to some extent confirmed in the case of synthetic minerals in this composition range.

Mixtures of the cancrinite proper molecule ($3NaAlSiO_4.CaCO_3$) and the bisulphate nosean molecule ($3NaAlSiO_4.NaHSO_4$) were synthesized in various proportions. It was found that compositions richer in sulphate than seven cancrinite to one nosean retained the characteristic peaks of the nosean pattern on the diffractograms, while in compositions richer in carbonate than this seven to one ratio there were the characteristic cancrinite peaks and no nosean peaks on the diffractograms. This indicates that, at the single temperature and pressure at which this phenomena was investigated, the cancrinite molecule can accommodate approximately 23 weight per cent of the bisulphate molecule. Similar results were obtained for a mixture of the davyne proper molecule ($3NaAlSiO_4 \cdot K_2CO_3$) and the sulphate nosean molecule ($6NaAlSiO_4 \cdot Na_2SO_4$). Investigations of the composition between hydroxy cancrinite molecule ($3NaAlSiO_4 \cdot Ca(OH)_2$) and the hypothetical calcium sodalite molecule ($3NaAlSiO_4 \cdot CaCl_2$) showed that compositions richer in the chloride than four hydroxy-cancrinite to one hypothetical calcium sodalite produced characteristic sodalite peaks on the diffractograms, while compositions richer in the hydroxide molecules produced peaks characteristic of the hydroxy cancrinite. This indicated that the hydroxy cancrinite molecule can accommodate approximately 51 weight per cent of the calcium sodalite molecule.

These results do not indicate that complete solid solution exists between the sodalite and cancrinite families, at the temperatures and pressures used in this investigation as peaks of both cancrinite and sodalite could be detected in the sodalite-rich fields. Complete solid solution however, is unlikely between minerals belonging to different crystal systems.

The experimental results presented here are insufficient to definitely establish the relationships between these two families, but do indicate a great similarity between them. One notable difference however, is that the synthetic sodalites appear to be higher temperature minerals than synthetic cancrinites, as none of the sodalite family dissociate at the temperatures and pressures of this investigation. (Van Peteghem - oral communication).

10. Geologic Implications

The fact that the nine cancrinites with different compositions were synthesized is in agreement with the analysis of the literature that indicates natural cancrinite can have a wide range of composition. It is noteworthy that cancrinites rich in K_2O have not been recorded in the literature.

The experimental data and dissociation products show that cancrinites are moderately high temperature minerals, some of which are reaction products of nepheline and possibly calcite (or some other carbonate or sulphate). This is also in accordance with the fact that natural cancrinites are commonly found in close association with nepheline and calcium bearing rocks, and have been reported as "reaction rims" around nepheline grains (Pirsson and Washington (1907); Larsen and Foshag (1926)).

The presence of the nosean-type high temperature polymorph in natrodavynes has not been reported in the literature. It is possible however, that some of the noseans reported may actually be of carbonate composition. The fact that noseans are relatively rare, and that only a few analyses are available could easily result in carbonate noseans not being detected, as their optical properties and crystallographic features are very similar to the regular noseans.

The presence of analcite at low temperatures in the synthetic systems indicates that analcite can appear as a hydrothermal alteration product of cancrinite. This has not been reported in the literature, but analcite has been described as a possible secondary mineral after sodalite in the Kola Peninsula by Labuntzov (1927) who proposes the reaction:–

$$2(3Na_2Al_2Si_2O_8 . 4NaCl) + nH_2O = 3(Na_2Al_2Si_4O_{12} . 2H_2O)$$
$$+ 3(Al_2O_3 . nH_2O) + 4NaCl + 6NaOH$$

11. Justification of Revised Nomenclature on the Basis of Experimental Results

As a result of being unable to synthesize some of the cancrinite species proposed by Winchell and Winchell (1951), and the fact that the davynes and natrodavynes synthesized with either carbonate or bicarbonate radicals, each with slightly different cell dimensions, it seems justifiable to revise the nomenclature of the cancrinite group proposed in Table 1.1 of Chapter 1.

The term wischnewite with composition $3NaAlSiO_4 . (NaHSO_4 . NaOH)$ should be abandoned as it does not synthesize a cancrinite type mineral. The terms microsommite with composition $3NaAlSiO_4 . CaCl_2$ and sulphatic cancrinite with composition $3NaAlSiO_4 . CaSO_4$ are also undesirable for the same reason. It is possible that a considerable amount of $Ca(OH)_2$ added to both these compositions would synthesize a cancrinite mineral. This has been shown to be the case for microsommite, and it is therefore proposed that the term microsommite be restricted to a mineral of composition $4[3NaAlSiO_4 . Ca(OH)_2] + [3NaAlSiO_4 . CaCl_2]$. The term sulphatic cancrinite has been arbitrarily assigned to the mineral of composition $7[3NaAlSiO_4 . CaCO_3] + [3NaAlSiO_4 . NaHSO_4]$. The term cancrinite proper as used by Winchell and Winchell has been split into two terms, one referring to the pure carbonate composition $3NaAlSiO_4 . CaCO_3$ and designated cancrinite proper, the other referring to the composition lacking carbonate – $3NaAlSiO_4 . Ca(OH)_2$ and designated hydroxy cancrinite.

The end-members used in the present study will probably never be found in nature, but the revised terminology could be used for natural cancrinites on the basis of the predominant cation and acid radical present.

VI. SOME DATA ON NATURAL CANCRINITES

Four specimens of natural cancrinite were investigated in an attempt to correlate these natural cancrinites with their synthetic counterparts. These specimens consisted of a yellow cancrinite from Red Hill, New Hampshire; two specimens of cancrinite from the American Nepheline Company quarry at Blue Mountain, Methuen Township, Ontario, one a yellow cancrinite, the other a purplish-pink cancrinite; and the fourth a specimen of sulphatic cancrinite from the Allt a' Mhuillin quarry at Loch Borolan, Scotland. For the New Hampshire specimen the d spacings and field of stability were determined; for the other three specimens only the d spacings and cell dimensions were determined.

1. Red Hill, New Hampshire, Cancrinite

The Red Hill, New Hampshire, cancrinite is a typical lemon-yellow coloured specimen, with $n_{\omega} = 1.506$ and a very low birefringence. This cancrinite occurs associated with a nepheline-syenite forming part of the White Mountain Magma series described by Quinn (1937).

Several grams of this cancrinite were separated from the rock and crushed to pass 200 mesh. This material was then placed in capsules along with water, and an attempt made to find the field of stability of this mineral. It was found that, in the closed system, the sample did not dissociate at temperatures as high as 750°C. and at water pressures ranging from 10,000 to 37,000 psi. However at temperatures ranging from 525°C. at 10,000 psi to 650°C. at 37,000 psi, nepheline started to appear in the open systems. The data for these runs are given in Table 6.1, and the dissociation curve for the open system, drawn visually, is given in Figure 6.1.

TABLE 6.1

Experimental Data for Red Hill, New Hampshire, Cancrinite

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
2*	0.5744	0.6473	15,000	400	70	Cancrinite
3*	0.5916	0.6056	15,000	360	70	Cancrinite
6*	0.5881	0.5820	15-25,000	700	72	Nepheline
7*	0.6354	0.6312	15-25,000	650	72	Nepheline
8*	0.6316	0.6281	15-25,000	600	72	Nepheline
9	0.6074	0.6075	15,000	525	144	Cancrinite
10*	0.5786	0.5746	15,000	550	144	Cancrinite
11*	0.5311	0.5221	15,000	575	144	Cancrinite
12*	0.5985	0.6036	25-30,000	580	122	Cancrinite
13	0.6490	0.6490	25,000	610	122	Cancrinite
14*	0.6215	0.5550	25,000	650	122	Nepheline
15*	0.6123	0.6635	10,000	500	75	Cancrinite
16	0.6319	0.6319	10,000	540	75	Cancrinite
17*	0.6040	0.6276	10,000	520	75	Cancrinite and Nepheline ?
18*	0.6218	0.6630	10,000	600	92	Cancrinite and Nepheline
19*	0.6154	0.6585	10,000	625	92	Cancrinite and Nepheline
20*	0.6188	0.6500	10,000	600	168	Cancrinite and Nepheline
21*	0.6109	0.6237	10,000	625	168	Cancrinite and Nepheline
22*	0.6108	0.6111	10,000	645	168	Cancrinite and v. Minor Nepheline
23*	0.6110	0.6144	20,000	550	90	Cancrinite
24*	0.6140	0.6116	20,000	650	90	Cancrinite and v. Minor Nepheline
25*	0.6140	0.6147	15,000	675	92	Cancrinite
26*	0.6217	0.6197	15,000	650	66	Cancrinite

Table 6.1 (contd.)

No. of Run	Initial Weight (gms)	Final Weight (gms)	Water Pressure (psi)	Temperature (°C.)	Time (hrs.)	Phases
28*	0.6813	0.7060	20,000	725	119	Nepheline
29	0.6099	0.6097	20,000	650	119	Cancrinite
30*	0.6150	0.6167	20,000	700	119	Nepheline and v. Minor Cancrinite
31*	0.6013	0.6007	15,000	625	156	Cancrinite
32	0.6173	0.6172	15,000	650	156	Cancrinite and Nepheline
33*	0.5967	0.5985	15,000	575	326	Cancrinite
34	0.5849	0.5850	10,000	200	235	Cancrinite
35*	0.5944	0.5995	20,000	600	156	Cancrinite
36*	0.6093	0.6083	15,000	700	96	Cancrinite
				537	66	
				430	24	
				270	6	
				180	14	
37*	0.6121	0.6149	37,000	650	140	Cancrinite and Nepheline
38*	0.5992	0.5924	37,000	725	140	Cancrinite and v. Minor Nepheline

* – open system

No calcite was detected in the open systems at the higher temperatures, presumably having been leached from the capsules or having dissociated at high pressures. The nepheline in a few cases was very minor, which may indicate that in the open systems the breakdown

cancrinite = nepheline + calcite ?

takes place over a range of temperature in the open system. This reaction is observed under the microscope for many natural rocks. No investigation was made to detect analcite at low temperatures.

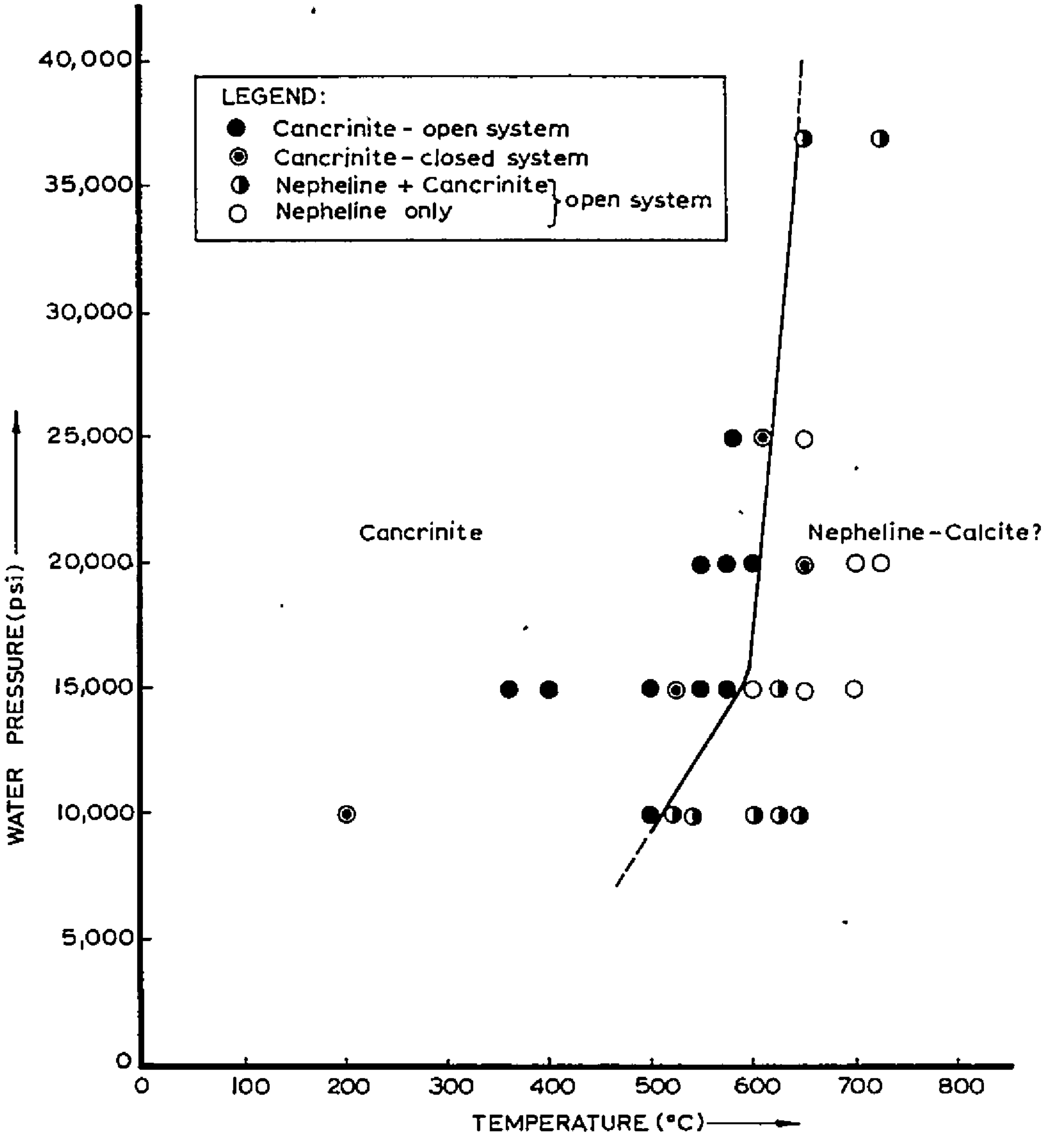
The d spacings and cell dimensions of the Red Hill cancrinite

FIGURE 6.1

Dissociation curve for natural cancrinite

from Red Hill, New Hampshire,

(mostly in open system, curve drawn visually)


LEGEND:
● Cancrinite - open system
◉ Cancrinite - closed system
◑ Nepheline + Cancrinite
○ Nepheline only
open system
Cancrinite
Nepheline - Calcite?
WATER PRESSURE (psi)
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
0
100
200
300
400
500
600
700
800
TEMPERATURE (°C)

were determined by the same methods used for the synthetic materials. Table 6.2 gives the d spacings and cell dimensions obtained for the unheated cancrinite, using in one case CuKα radiation, in the other case FeKα radiation.

TABLE 6.2

d Spacings and Cell Dimensions for Unheated Red Hill, New Hampshire, Cancrinite

CuKα Radiation λ = 1.5418Å Filter – Ni Standard – Quartz					FeKα Radiation λ = 1.9373Å Filter – Mn Standard – Quartz				
d	I (visual)	hk$\bar{i}$l	a	c	d	I (visual)	hk$\bar{i}$l	a	c
6.33	50	$11\bar{2}0$	12.63	–	6.28	70	$11\bar{2}0$	12.56	–
4.64	70	$10\bar{1}1$	(1)12.61	5.13	4.65	40	$10\bar{1}1$	(1)12.44	?
3.644	70	$30\bar{3}0$	12.62	–	3.639	90	$30\bar{3}0$	(1)12.62	–
3.213	100	$21\bar{3}1$	(1)12.61	5.13	3.211	100	2121	(1)12.62	5.10
3.022	5	$31\bar{4}0$	12.58	–	2.566	20	$00\bar{0}2$	–	5.18
2.965	5	$30\bar{3}1$	(2)12.68	5.04	2.415	20	$40\bar{4}1$	(2)12.61	5.18
2.731	40	$40\bar{4}0$	12.61	–	2.325	15	$20\bar{2}2$?	?	?
2.608	25	$31\bar{4}1$	(2)(3)12.66	5.04	2.150	10	$41\bar{5}1$	(2)12.00?	?
2.564	15	$00\bar{0}2$	–	5.13	2.089	20	$33\bar{6}0$	12.53	–
2.499	5	$32\bar{5}0$	12.58	–	2.012	5	$50\bar{5}1$	(2)12.61	5.18
2.408	5	$40\bar{4}1$	(3)12.59	5.14	1.867	5	$40\bar{4}2$	(3)12.59	5.11
2.150	15	$41\bar{5}1$	(4)12.54	5.12	1.792	10	$43\bar{7}0$	(3)12.59	–
2.090	20	$33\bar{6}0$	12.54	–	1.747	10	$52\bar{7}0$	12.60	–
2.010	5	$50\bar{5}1$	(4)(5)12.62	5.10	1.576	5	$44\bar{8}0$	12.61	–
1.867	5	$40\bar{4}2$	(5)12.62	5.10	1.491	5	$53\bar{8}1$	(4)12.58	5.19
1.789	5	$43\bar{7}0$	12.57	–	1.342	5	$44\bar{8}2$	(5)12.58	5.15
1.745	10	$52\bar{7}0$	12.58	–	1.319	5	4263	(5)12.58	5.15
1.577	10	$44\bar{8}0$	12.61	–	1.132	1	$5,5,\overline{10},2$ or $6,4,\overline{10},2$	(4)12.58	5.19
1.489	10	$53\bar{8}1$	(6)12.56	5.21					
1.447	10	$52\bar{7}2$	(6)12.56	5.21					
1.342	5	5053 or $44\bar{8}2$	(7)12.63	5.09					

Table 6.2 (contd.)

d	I (visual)	$hk\bar{i}l$	a	c	d	I (visual)	$hk\bar{i}l$	a	c
1.318	5	$42\bar{6}3$	(8)12.56	5.15					
1.212	5	6392	(7)12.63	5.09					
1.133	1	$6,4,\overline{10},2$ or $5,5,\overline{10},2$	(8)12.56	5.15					

(1) - numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation or by direct comparison of $\sin^2\theta$ calc. and $\sin^2\theta$ obs. values.

The calculations of the cell dimensions of this cancrinite from the diffractograms using both CuKα and FeKα radiation give a = 12.60Å ± .02Å (approximately) and c = 5.12Å (approximately). The plots of $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ versus a and c for CuKα are shown in Figure 6.2. The experimental data, d spacings and cell dimensions of the Red Hill cancrinite are very similar to the synthetic cancrinite, which might suggest a compositional similarity to the synthetic material.

2. <u>Blue Mountain, Methuen Township, Cancrinites</u>

(i) Yellow Specimen

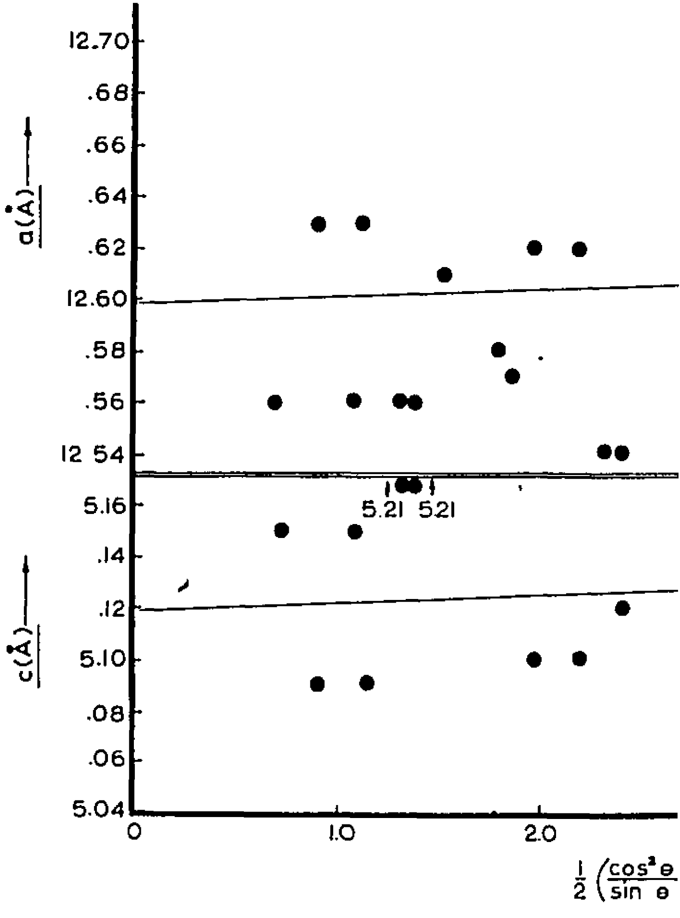
This specimen is an amber yellow cancrinite with average n = 1.506 (approximately) and occurs in a nepheline syenite rich in biotite. Samples of cancrinite from the same locality were described by Phoenix and Nuffield (1949).

The d spacings and cell dimensions of this cancrinite were determined in a similar manner to the other specimens and are shown in Table 6.3.

FIGURE 6.2

Cell dimensions versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$

for natural cancrinite from Red Hill, New Hampshire


a(Å)
c(Å)
12.70
.68
.66
.64
.62
12.60
.58
.56
12 54
5.16
.14
.12
5.10
.08
.06
5.04
5.21
521
0
1.0
2.0
½ (cos²θ / sin θ

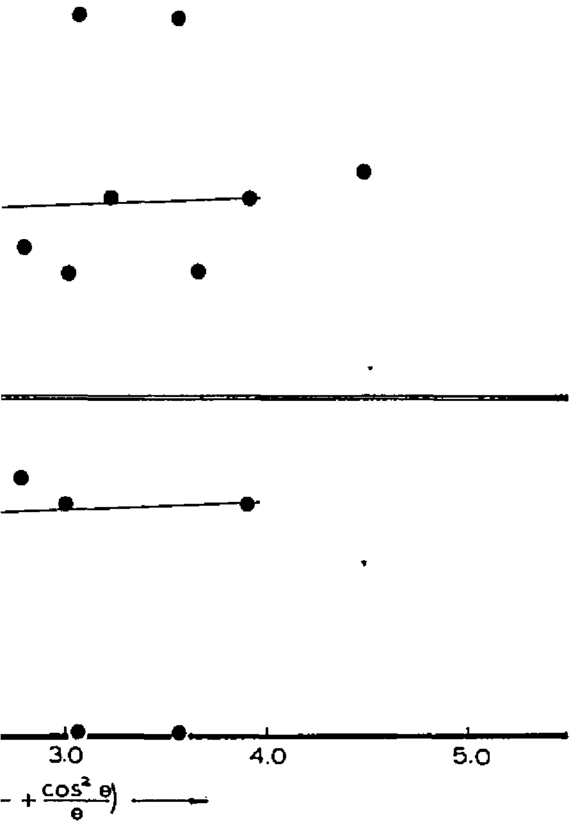

3.0
4.0
5.0
$- + \frac{\cos^2\theta}{\theta})$ ⟵

TABLE 6.3

Spacings and Cell Dimensions for Blue Mountain, Methuen Township, Cancrinite

Radiation - CuKα; λ - 1.5418Å; Filter - Ni; Standard - Quartz

Yellow Specimen					Pink Specimen				
d	I (visual)	$hk\bar{i}l$	a	c	d	I (visual)	$hk\bar{i}l$	a	c
6.31	30	$11\bar{2}0$	12.59	-	6.36	35	$11\bar{2}0$	12.72	-
5.46	5	$20\bar{2}0$	12.62	-	4.64	60	$10\bar{1}1$	(1)12.63	5.12
4.64	50	$10\bar{1}1$	12.59	5.14	4.14	12	$21\bar{3}0$	12.64	-
4.13	10	$21\bar{3}0$	12.62	-	3.639	100	$30\bar{3}0$	12.60	-
3.639	50	$30\bar{3}0$	12.60	-	3.220	100	$21\bar{3}1$	(1)12.63	5.12
3.215	100	$21\bar{3}1$	12.59	5.14	2.976	7	$30\bar{3}1$	(2)12.57	5.19
3.030	5	$31\bar{4}0$	12.62	-	2.730	60	$40\bar{4}0$	12.60	-
2.967	5	$30\bar{3}1$	12.59	5.14	2.606	50	3031	12.59	5.14
2.731	40	$40\bar{4}0$	12.61	-	2.562	20	0002	-	5.12
2.608	20	$31\bar{4}1$	(1)12.59	5.14	2.503	10	$10\bar{1}2$	(3)12.55	5.14
2.557	25	0002	-	5.11	2.410	45	$40\bar{4}1$	(2)12.57	5.19
2.408	15	$40\bar{4}1$	(1)12.59	5.14	2.250	20	$32\bar{5}1$	12.59	5.14
2.245	10	$32\bar{5}1$	(2)12.59	5.15	2.162	20	$41\bar{5}1$	(4)12.59	5.17
2.159	7	$41\bar{5}1$	12.59	5.14	2.100	80	$33\bar{6}0$	12.60	-
2.100	12	$33\bar{6}0$	12.60	-	2.009	10	$50\bar{5}1$	(4)12.59	5.17
2.010	5	$50\bar{5}1$	(3)12.72	5.13	1.868	12	$40\bar{4}2$	(3)12.55	5.14
1.867	10	$40\bar{4}2$	(3)12.72	5.13	1.791	12	$43\bar{7}0$		
							Or 3252	12.58	-
1.791	7	$32\bar{5}2$	(2)12.59	5.15					
1.745	7	$41\bar{5}2$	(4)12.60	5.11	1.746	12	$41\bar{5}2$	(5)12.67	5.10
1.693	5	$43\bar{7}1$	(4)12.60	5.11	1.577	20	$44\bar{8}0$	12.61	-
1.626	5	$33\bar{6}2$	(5)12.55	5.17	1.492	20	$31\bar{4}3$	(6)12.57	5.15
1.578	7	$61\bar{7}1$	(5)12.55	5.17	1.448	15	$52\bar{7}2$	(5)12.67	5.10
1.560	5	$51\bar{6}2$	(6)12.66	5.10	1.349	7	$54\bar{9}1$	?	?
1.492	12	$31\bar{4}3$	(7)12.59	5.14	1.325	10	3363	?	?
1.447	7	$52\bar{7}2$	(6)12.66	5.10	1.136	12	?	?	?
1.411	5	$32\bar{5}3$	(7)12.59	5.14	1.133	5	6283	(6)12.57	5.15
1.343	5	$54\bar{9}1$	(8)12.54	5.17					
1.320	10	4263	(8)12.54	5.17					

Table 6.3 (contd.)

d	I (visual)	$hk\overline{i}l$	a	c
1.249	5	$6,4,\overline{\underline{10}},0$	12.57	-
1.214	5	$6,\underline{4},10,1$	(9)12.57	5.13
1.186	5	$31\underline{4}4?$	?	?
1.151	5	5383	(9)12.57	5.13

( ) - numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation or by direct comparison of $\sin^2\theta$ calc. and $\sin^2\theta$ obs. values.

The a and c dimensions as obtained from a plot of $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ versus a and c (Figure 6.3) give an a value of 12.58Å ± .02Å (approximately) and a c value of 5.14Å ± .02Å (approximately). This agrees fairly well with the values of a = 12.60 Kx (a = 12.62Å) and c = 5.12 Kx (c = 5.13Å) obtained from Weissenberg photographs by Phoenix and Nuffield (1949).

(ii) Pink Specimen

This specimen occurs in the same rock sample as the cancrinite described above, but was not mentioned in Phoenix and Nuffield's paper. Under the petrographic microscope this sample is colourless and has average n = 1.509 (approximately).

The d spacings and cell dimensions of this specimen are given in Table 6.3, and a plot of $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ versus a and c dimensions in Figure 6.4. This graph gives approximately a = 12.58Å ± .02Å and c = 5.15Å ± .02Å.

These values are very similar to the cell dimensions obtained

FIGURE 6.3

Cell dimensions versus $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$

for natural cancrinite from Blue Mountain,

Methuen Township, Ontario (yellow specimen)

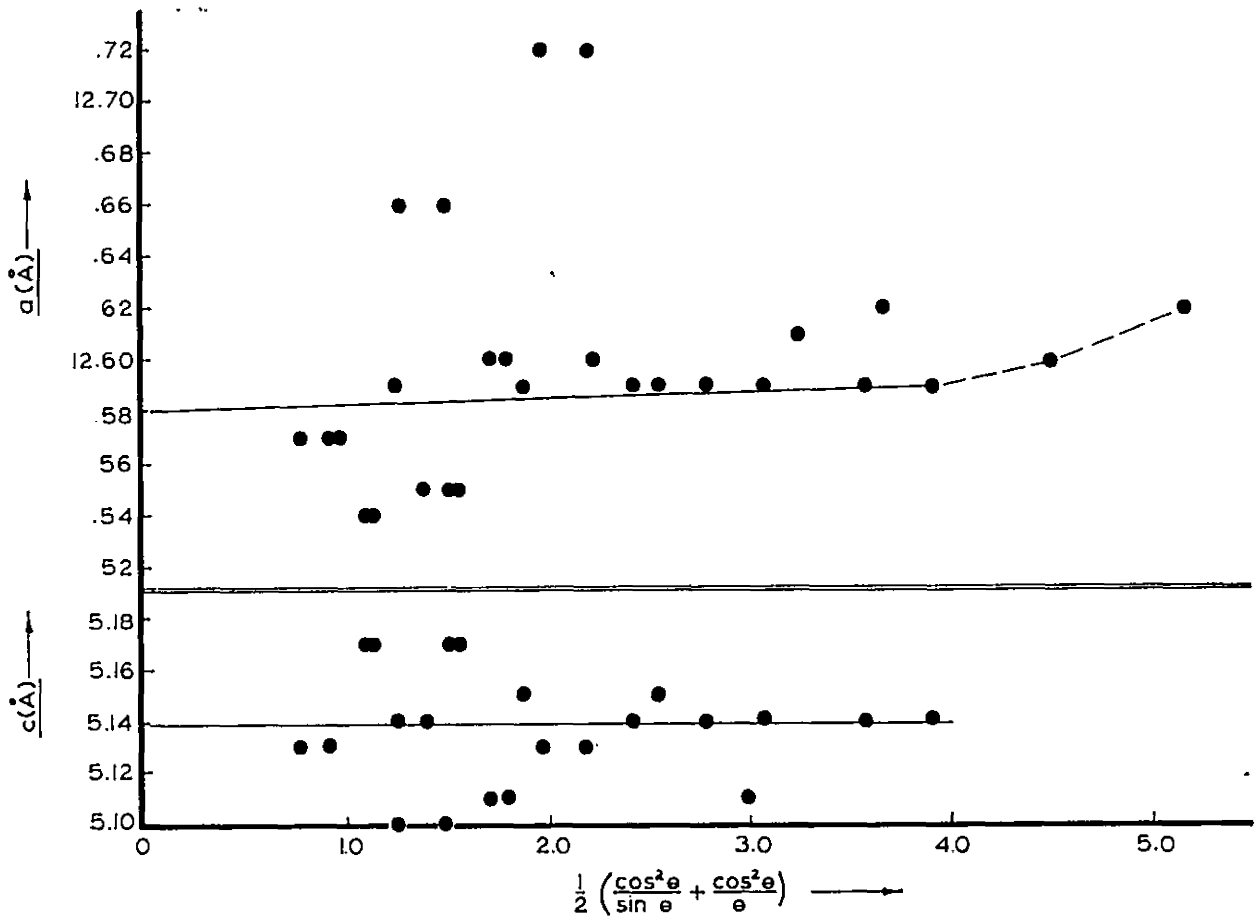
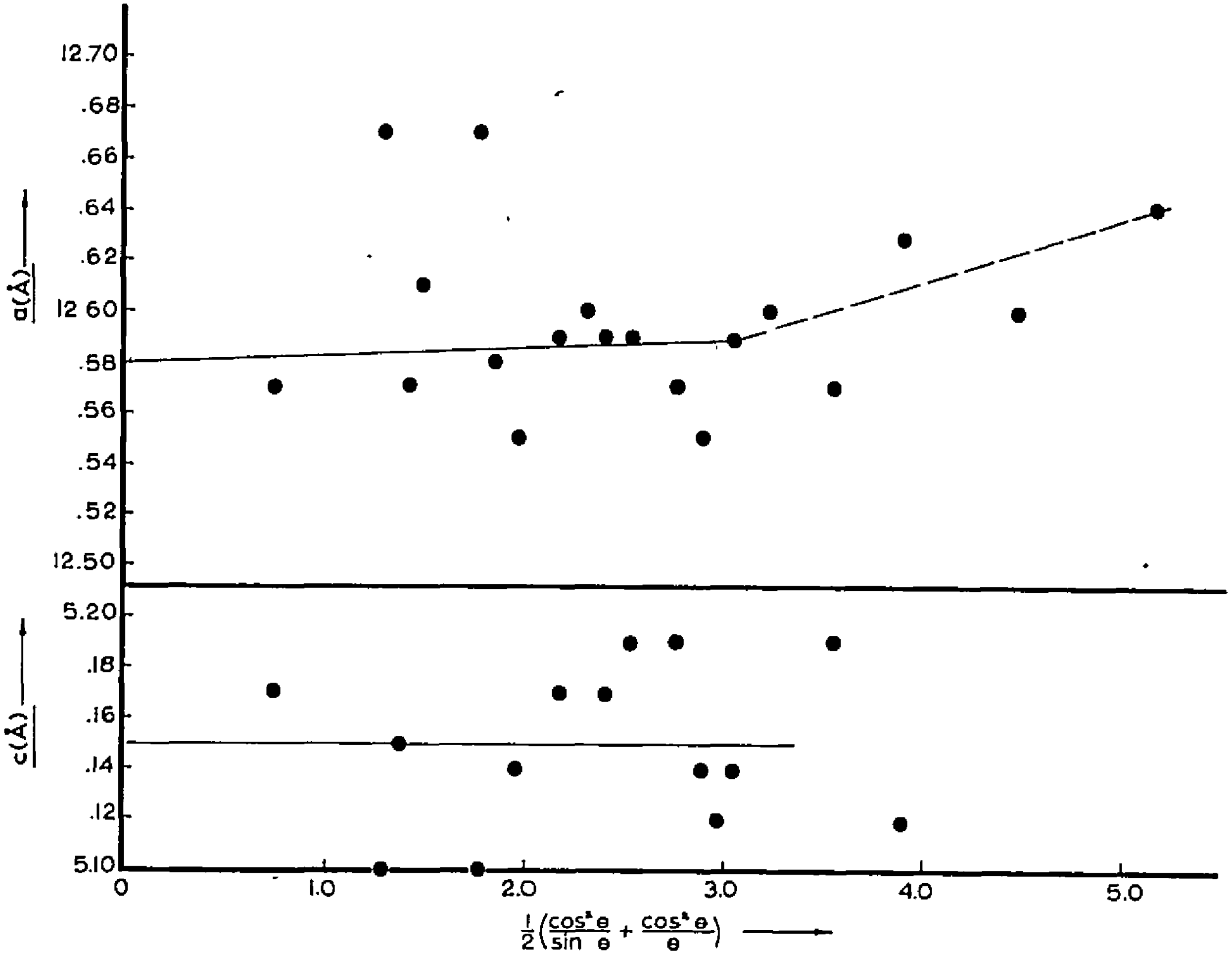

a(Å)
.72
12.70
.68
.66
.64
62
12.60
.58
56
.54
52
c(Å)
5.18
5.16
5.14
5.12
5.10
0
1.0
2.0
3.0
4.0
5.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

FIGURE 6.4

Cell dimensions versus $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ for natural cancrinite from Blue Mountain, Methuen Township, Ontario (pink specimen)


a(Å)
12.70
.68
.66
.64
.62
12 60
.58
.56
.54
.52
12.50
c(Å)
5.20
.18
.16
.14
.12
5.10
0
1.0
2.0
3.0
4.0
5.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

for the yellow sample, despite rather dissimilar physical characteristics. It was considered that the different colour of the samples might be caused by a variation in the trace element content of the two samples. Spectrographic analyses on both samples were kindly done by Mr. E. Cruft, the results of which are shown in Table 6.4. The semiquantitative spectrographic analyses of the Blue Mountain, Methuen Township, Ontario, cancrinites indicate that there is very little difference in trace element content between the yellow and pink specimens. The results were determined by visual comparisons of line intensities of the cancrinites with the intensities of the Spex Industries G-Standards. In both samples the trace elements were present in very minor amounts, and therefore the elements present are either major or are very low. The only difference in trace element content is in manganese, there being about ten times more manganese in the yellow specimen than in the pink one. It seems unlikely that this difference would account for the variation in colour between the two specimens.

TABLE 6.4

Semiquantitative Spectrographic Analyses of Blue Mountain, Methuen Township, Cancrinites

Percentage	Yellow Cancrinite	Pink Cancrinite
Major element > 1%	Al, Ca, Na, Si, (Fe)	Al, Ca, Na, Si, (Fe)
0.1 - 1.0%	(Fe)	(Fe)

Table 6.4 (contd.)

Percentage	Yellow Cancrinite	Pink Cancrinite
0.01 - 0.1%	(Mn)	-
0.001 - 0.01%	(Mn), Pb	Mn, (Pb)
0.0001 - 0.001%	Cu, Mg	Cu, (Pb), Mg
< 0.0001% (trace)	V, Cr, B, Ag, Co, W (very weak)	V, Cr, B, Ag, Co
Found, but not measured due to absence in G-standard or high CN	K, Ga	K, Ga
Looked for, but not detected	Ba, In, Rh, Au, P, Be, Sn, Ti, Ni, Ge, La, Sc.	Ba, In, Rh, Au, P, Be, Sn, Ti, Ni, Ge, La, Sc

Values in brackets were measured on more than one line and fall at the boundary of two composition groups.

Analyst - E. Cruft.

From considerations of the d spacings and cell dimensions of both the Blue Mountain cancrinites and the Red Hill cancrinite it appears that these natural specimens are similar and may represent fairly normal calcium carbonate cancrinites.

3. Sulphatic Cancrinite from Loch Borolan, Scotland

This specimen was kindly supplied by Professor F.H. Stewart of the University of Edinburgh. The sulphatic cancrinite is greyish-blue in colour and occurs in large cleavable masses in pegmatites and veins in borolanite (melanite-rich pseudoleucite syenite). This mineral is associated with melanite, orthoclase and dark mica, and with accessory calcite, sphene, zircon and orthite. The refractive indices, reported by Stewart (1941), are $n_\omega = 1.502$, $n_\epsilon = 1.497$.

The cell dimensions and d spacings obtained on this sulphatic cancrinite are given in Table 6.5. A plot of $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ versus a and c dimensions (Figure 6.5) yields an a dimension of 12.68 ± .02Å and a c dimension of 5.18 ± .02Å.

TABLE 6.5

d Spacings and Cell Dimensions of Sulphatic Cancrinite from Loch Borolan, Scotland

Radiation - CuKα; λ - 1.5418Å; Filter - Ni; Standard - Quartz

d	I (visual)	$hk\bar{i}l$	a(Å)	c(Å)
6.36	30	$11\bar{2}0$	12.72	-
4.70	45	$10\underline{1}1$	(1)12.63	5.20
3.666	60	$30\underline{3}0$	12.70	-
3.242	100	$21\underline{3}1$	(1)12.63	5.20
2.748	35	$40\underline{4}0$	12.69	-
2.626	25	$31\underline{4}1$	(2)12.72	5.26
2.592	25	0002	-	5.19
2.523	15	$32\underline{5}0$	12.70	-
2.427	30	$40\underline{4}1$	(2)12.72	5.26
1.872	15	$40\underline{4}2$	?	?
1.759	20	$41\underline{5}2$	(3)12.66	5.18
1.703	15	$43\underline{7}1$	(3)12.66	5.18
1.593	15	$21\underline{3}3$	(4)12.68	5.17
1.585	10	$44\underline{8}0$	12.68	-
1.502	15	$53\underline{8}1$	(4)12.68	5.17
1.486	10	$43\underline{7}2$	(5)12.75	5.17
1.352	15	$44\underline{8}2$	(6)12.68	5.18
1.328	15	$42\underline{6}3$	(5)12.75	5.17
1.300	5	5163	(7)12.63	5.20
1.268	5	$5,5,\underline{10},0$	12.68	-
1.244	5	$6,\underline{4},10,1$	(6)12.68	5.18
1.058	5	6064	(7)(6)12.68	5.18

Table 6.5 (contd.)

( ) – numbers in brackets refer to groups of a and c values solved simultaneously. Other values determined from a single equation or by direct comparison of $\sin^2\theta$ calc. and $\sin^2\theta$ obs. values.

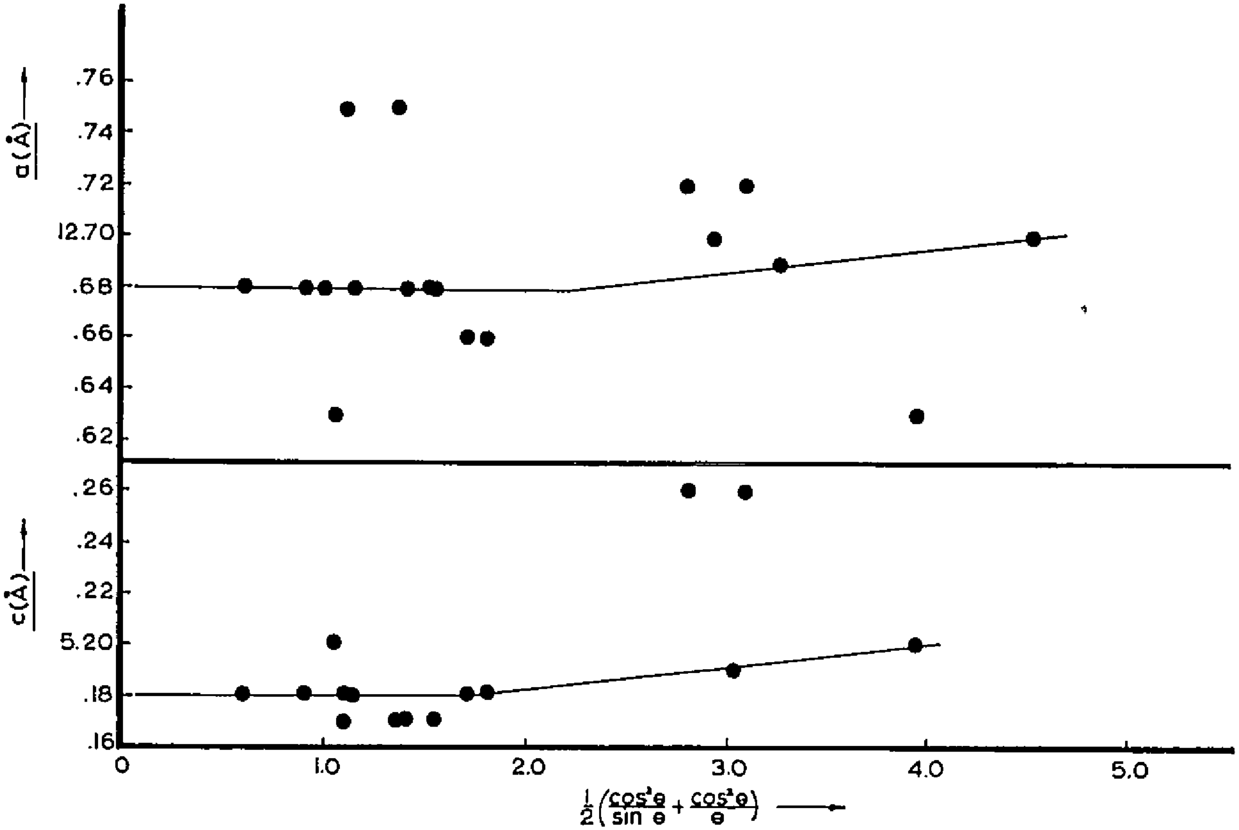
These larger cell dimensions indicate that this specimen is a different type of cancrinite from either the Red Hill or Blue Mountain minerals. These cell dimensions are also larger than those of the synthetic sulphatic cancrinite and probably reflect the difference in composition; the synthetic material having a much smaller sulphate to carbonate ratio and containing no potassium.

The d spacings of the sulphatic cancrinite synthesized according to the analyses of Stewart (1941) (see Table 4.18) did not correlate well with the d spacings obtained for the natural specimen, although there is a general similarity in d spacings between these samples. This may be caused by slight variations in composition between the synthetic specimen and the composition quoted by Stewart, or could be caused by difficulties in preparing synthetic mixtures from chemical analysis containing a fairly large number of components.

FIGURE 6.5

Cell dimensions versus $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$

for natural sulphatic cancrinite from Loch Borolan, Scotland


a(Å)
.76
.74
.72
12.70
.68
.66
.64
.62
c(Å)
.26
.24
.22
5.20
.18
.16
0
1.0
2.0
3.0
4.0
5.0
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

VII. SUGGESTIONS FOR FURTHER WORK

The present research on the cancrinite minerals has indicated that some future work on this family might be profitable. Investigation of the upper limits of stability of cancrinite proper, hydroxy cancrinite and sulphatic cancrinite should be undertaken, in addition to the relationship between the cancrinite and sodalite families; the substitution of other cations and acid radicals in the general cancrinite formula; the structure of cancrinite; and the overall problems of metastability in synthetic cancrinites. In this chapter, each of these problems will be considered briefly and an attempt made to show why the solution of these problems would clarify some of the work done in the present investigation.

Three of the eight synthetic cancrinite members investigated did not break down at temperatures of 800°C. It is likely that these synthetic cancrinites will dissociate at temperatures higher than 800°C., or by using catalysts at some temperature under 800°C. In the case of cancrinite proper, the addition of potassium and CO_2 as catalysts failed to promote dissociation. Therefore, investigation of the upper limit of stability should be undertaken using apparatus with a higher limit of temperature and water pressure. Such an investigation, patticularly for cancrinite proper, might give a better indication of the origin of cancrinites.

A definite relationship between the cancrinites and the sodalites is implied in the formula of Winchell and Winchell (1951) and has been to a limited extent verified in the research reported in this thesis. The extent of solid solution between cancrinite proper and sodalite, and between cancrinite proper and nosean, should be determined in order to definitely establish what limits of solid solution are possible between the two mineral groups.

The present investigation has also shown that a large number of cations and acid radicals can be substituted into the general cancrinite formula. Further work on the synthesis of cancrinites containing cations in the range of ionic radius close to potassium, sodium and calcium; and other acid radicals such as $SeO_4^{=}$, should be done.

One of the most profitable future studies on this mineral family would be a thorough determination of the structure of cancrinites. This would be most useful in the determination of the extent of solid solution between the different cancrinite end-members, in the correct representation of the cancrinite formula and in the distribution of cations between the nepheline and acid salt portions of the cancrinite formula.

Lastly, an investigation of the stability fields of synthetic cancrinites should be made using starting materials which are more stable than those used in the present study. This would enable the equilibrium stability fields to be more accurately established, as has been explained in the chapter entitled "Discussion of Results".

VIII CONCLUSIONS

Experimental investigation of synthetic cancrinites at temperatures of 200° to 800°C. and at water pressures between 10,000 and 30,000 psi indicates that cancrinites can be synthesized with a variety of different compositions. Some of the formulae of the cancrinite end-members proposed by Winchell and Winchell (1951), notably the pure sulphate and chloride end-members, synthesized members of the sodalite family. The failure to synthesize these end-members has resulted in the establishment of a new arbitrary nomenclature, in which the terms sulphatic cancrinite and microsommite have been used to represent cancrinite compositions containing minor sulphate and chloride respectively.

The curves determined in this thesis possibly represent metastable equilibrium. The temperature of dissociation of the carbonate cancrinites apparently depends upon the type of carbonate present. The potassium carbonate cancrinite (davyne) dissociates at 450° to 500°C. to nepheline and probably K_2CO_3; the sodium carbonate cancrinite (natrodavyne) transforms at 600° to 650°C. into a polymorph similar to nosean, and the calcium carbonate cancrinite (cancrinite proper) does not dissociate at a temperature of 800°C. The replacement of the bicarbonate ion for the carbonate ion does not appreciably alter these curves, nor does the replacement of the hydroxide ion for the carbonate ion in calcium carbonate cancrinites promote their dissociation. The composition represented by sulphatic cancrinite did not dissociate at 800°C. Analcite in addition to cancrinite, was detected at low temperatures in many of these compositions.

Determination of the cell parameters and cell volumes of the eight synthetic cancrinites indicates that in the carbonate and bicarbonate varieties the size of the unit cell also depends on the cation of the carbonate radical. The potassium carbonate and bicarbonate cancrinites (davynes) have the largest cell volumes, the sodium carbonate and bicarbonate cancrinites (natrodavynes) have intermediate cell volumes, and the calcium carbonate cancrinites (cancrinite proper) have the smallest cell volumes of the carbonate varieties. Hydroxy cancrinites, sulphatic cancrinites and microsommites have similar or slightly smaller cell volumes than cancrinite proper. The predominant control in the size of the cell volumes of synthetic cancrinites appears to be the cation attached to the carbonate, sulphate, hydroxide and chloride radicals, rather than the anionic radicals.

Limited investigation of the extent of solid solution between the carbonate end-members of the cancrinites indicates that complete solid solution between these end-members may not exist.

This investigation confirms that cancrinites have a complex chemistry. In addition the cell dimensions determined from the synthetic cancrinites are in good agreement both with those reported in the literature for natural cancrinites and with those determined on four specimens of natural cancrinite examined in this thesis.

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ERRATA

Page 11	For "alanyzed" read "analyzed"
Page 16	For "sighted" read "cited"
Page 33	For "cynlinders" read "cylinders"
Page 113	For "Mussnug" read "Mussgnug"