

EFFECT OF PRESSURE AND TEMPERATURE
ON LATTICE PARAMETERS
OF NEPHELINE

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ON LATTICE PARAMETERS
OF NEPHELINE

By

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SCOPE AND CONTENTS: An experimental investigation was made involving the synthesis of nepheline ($\text{NaAlSi}_3\text{O}_8$) under varying conditions of temperature and a water pressure of 20,000 psi. The average lattice parameter $20\bar{2}2 - 21\bar{3}0$ for each synthesized charge was obtained using X-ray diffraction methods. It was found that the results of individual runs provided an erratic lattice parameter variation with temperature in the range 500° to 800°C . However, a least squares curve indicates that no change in lattice parameters in the low-nepheline polymorph occurs with temperature of formation, for 95 percent probability.

Abstract

MacKenzie (1957) from X-ray studies showed that variation in lattice parameter in synthetic albite was related to conditions at the time of crystallization. Similar work conducted by the author on synthetic nepheline indicates that no change in the cell parameter $20\bar{2}2 - 21\bar{3}0$ occurs with increase of temperature from 500° to 800°C . Thus, it is believed no lattice parameter variation is observable in the low-nepheline polymorph when using quenching techniques. This conclusion agrees with G. Donnay (1956b). Correlation of variation with pressure was not attempted in this study, and all nephelines were synthesized at 20,000 psi.

A survey of the literature shows that there are many different causes for lattice parameter variation in nepheline.

Acknowledgements

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I. INTRODUCTION

Nepheline is one of a group of minerals with the approximate composition $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$ (according to Buerger, Klein, and Hamburger, 1947), and being a prominent feldspathoid a knowledge of its manner of formation is desirable in understanding the origin of the alkalic rocks. The studies of this mineral have been primarily concentrated upon its relationship to other minerals within a closed system and within a magma; this relationship can be seen diagrammatically in figure 1.

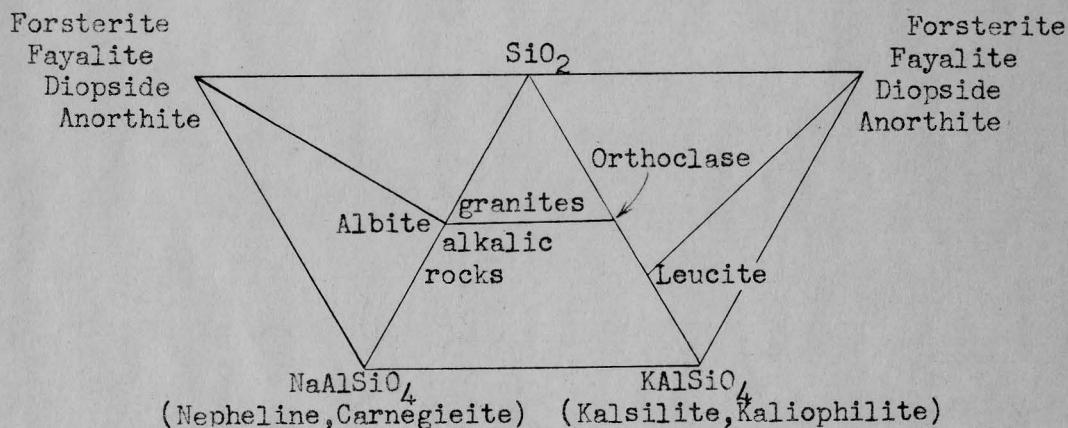


Figure 1. Diagram showing relations of eight simple systems to petrogeny's "residua" system, after Schairer and Bowen (1956).

Six polymorphs¹ of nepheline are known to form under the conditions of excess water and atmospheric pressure. High carnegieite (isometric) crystallizes from the liquidus at

¹A polymorph is a chemical compound that crystallizes in more than one crystal class.

1526°C to 1248°C, however, it may persist into the nepheline field and invert to a metastable triclinic form - low carnegieite - at approximately 690°C. High nepheline (orthorhombic) crystallizes from 1248°C to approximately 900°C when it inverts to the common hexagonal form of low nepheline which is stable to about 440°C. The nepheline hydrates, I and II, are both orthorhombic with probable stability fields of 330° - 375°C and 375° - 440°C respectively. The chemical difference between the two hydrates is that nepheline hydrate I contains twice as much water as nepheline hydrate II, and nepheline hydrate I has a more open framework structure than nepheline hydrate II (Barrer and White, 1952).

MacKenzie's (1957) investigation into the modifications of albite initiated the programme of research upon which this thesis is based. Nepheline was chosen because it bears some chemical similarity to albite, exists in a high and low temperature form, and is not difficult to synthesize. It is to be expected that the lattice parameter variation, if any, with changes in temperature and pressure will be small. For example, Smith and Sahama (1954) obtained consistent results for the $K/(K + Na + Ca)$ content of any natural nepheline simply by measuring the lattice parameters. Because this method is accurate to approximately 1.5 percent, then other factors determining lattice parameter variation must be small. Evidence that there is no variation in cell parameters comes from the work of G. Donnay (1956b) who measured the cell parameters of 10 synthetic nephelines of composition $NaAlSi_3O_8$ synthesized

at atmospheric pressure and at temperatures on both sides of the transition from low to high nepheline. She reported that there was no appreciable cell variation in either polymorph. However, MacKenzie (1957) found that the lattice parameter shift was slight for albite, and it is likely to be similarly small for other minerals such as nepheline. Smith and Tuttle (1957) thought that small changes in the low-nepheline polymorph occurred due to difference in temperature of formation of the nepheline.

The present thesis presents a pressure temperature study on the low-nepheline polymorph. A pressure of 20,000 psi was chosen since it was within the range of the experimental equipment and also would presumably give some indication of relations at depth within the earth. The temperature range chosen for study was 500° - 800°C and was controlled by the lower limit of nepheline stability on the one hand and on the other hand, by the temperature of failure of the pressure vessel used.

The results of this investigation, which effectively cover the low-nepheline polymorph stability range at 20,000 psi, support Donnay's (1956b) statement that no significant lattice parameter change occurs in the low-nepheline polymorph.

II. SOME PREVIOUS NEPHELINE STUDIES

In order to aid future research workers and to provide a general background for readers of this thesis, some previous nepheline studies are reviewed at this time. Each subsection described below presents a phase of nepheline investigation. Since some chemical studies on nepheline indicate that cell variation depends upon the presence or absence of certain elements, a review of these studies is apropos also.

1. Transitional Studies On Nepheline

Lemberg, in 1888, using glasses produced by fusing natural nepheline, was apparently the first person to discover the possibility of two modifications of nepheline. Lemberg heated the glasses of dubious chemical composition, at atmospheric pressure, to approximately 200°C in the presence of excess water, then observed the results optically. However, Thugutt is better known for finding different modifications of nepheline. He synthesized a hydrated nepheline (Thugutt, 1892) by dissolving 16.8 grams NaOH in 105 cubic centimeters of water, and having this solution react with 35 grams of kaolin at approximately 200°C for an unstated time. However, no identifying physical data were given for the nepheline hydrate. Two years later Thugutt (1894) fused the previously prepared nepheline hydrate and obtained the high temperature form of nepheline which was called soda anorthite at that time.

The name soda anorthite referred to the high temperature

complexly twinned modification of nepheline until Washington and Wright (1910) renamed it carnegieite after the founder of the Geophysical Institute in Washington, D.C. These authors postulated that solid solution of a triclinic metastable form of nepheline with the plagioclase feldspars explained the chemical abnormality in a mineral they were studying. The crystal system, twinning laws, cleavage, and hardness of the mineral were those of a plagioclase, and optical work indicated a plagioclase of andesine composition. However, the chemical analysis of the mineral showed excess calcium and aluminium with a deficit of silica if the material actually was andesine. Therefore, they assumed another mineral to be present in solid solution with a plagioclase to account for this anomaly, and chose a triclinic high temperature modification of nepheline. They named this modification carnegieite in order to escape the connotation of feldspar genesis contained in the term "soda anorthite".

Bowen (1912b), in the first precise work in the nepheline system, established the nepheline-carnegieite inversion to be 1248°C and the melting point for pure synthetic carnegieite to be 1526°C at atmospheric pressure. The establishment of carnegieite's true symmetry as isometric, with one or more (?) metastable inversions to a twinned low temperature form occurring at approximately 690°C and 225°C (doubtful) was made by Bowen and Greig (1925). A nepheline hydrate investigation

was carried out by Lagorio (1940), who studied the nepheline hydrate of Lemberg ($5\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$) and delineated crystal forms, crystal system, and interfacial angles. He found that the crystals when heated to 115°C were able to resorb water upon cooling, and as the mineral was different from any known zeolite he proposed the name "lebergite" for it.

Work by Tuttle and Smith (1952), in their investigation of the KAlSiO_4 - NaAlSiO_4 system, brought to light a new orthorhombic polymorph of nepheline which they named high-nepheline. This study was carried out at the Geophysical Institute in Washington, D.C., and because it is mentioned in their annual report, details are lacking. A more complete description of this polymorph was given by Smith and Tuttle (1957). Two nepheline hydrates (I and II), along with many other minerals, were synthesized and stability fields determined at atmospheric pressure in an excess of aqueous NaOH solution by Barrer and White (1952). The addition of aqueous NaOH solution to gels of mineral compositions lowered the temperature of the stability fields for the minerals studied and greatly enhanced crystallization, but provided very little, if any, data which could be used in the study of the origin of nepheline and its relationship to a magma. However, the determination of the crystal symmetry and approximate stability fields of the nepheline hydrates with scanty observations on their internal structure is important as it is the only published detailed information about these phases to date. Sand, Roy, and Osborn (1957) in a study of the system Na_2O - Al_2O_3 - SiO_2 - H_2O determined the border

between the stability fields of low-nepheline and nepheline hydrate to be 460°C at 15,000 psi. These authors further mention that they conform to Barrer and White's (1952) designation of the nepheline hydrates. However, Barrer and White designate the high temperature nepheline hydrate as II and the low temperature nepheline hydrate as I, whereas Sand, Roy, and Osborn designate the high temperature form as I. A further complication is that Barrer and White's low temperature nepheline hydrate I pattern conforms closely to Sand, Roy, and Osborn's high temperature nepheline hydrate I. This peculiarity is not mentioned nor is it explained by Sand, Roy, and Osborn. Further investigation, therefore, in the low temperature aqueous part of the nepheline system seems to be necessary; especially now that a superfluity of terms appears to be developing in the fields of the nepheline hydrates. Confirmation and delineation of the terms lebergite, nepheline hydrate I, and nepheline hydrate II are needed.

2. "Solid-Solution" Studies On Nepheline

It was discovered in the very early 1900's that natural nepheline did not appear to have a consistent chemical formula, but rather that silica, potassium, and calcium frequently appeared in excess of the chemical formula accepted for nepheline.

(1) Silica Studies

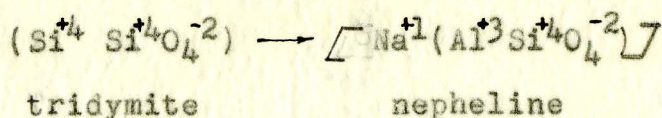
Foote and Bradley (1911), in their studies of solid solution² in minerals, thought that the excess silica in

²It is usual to think of solid solutions in terms of "molecules" or "components", although it is known that solid solutions occur by ionic adjustment in a mineral structure.

nepheline was due to a form of solid solution. They proposed that the silica was taken up by the nepheline in a manner analogous to salt dissolved in a beaker of water. The excess silica would not take part in the formation of nepheline, but would exist there in some unknown manner. Schaller (1912) was the first to propose that three isomorphous molecules were present forming nepheline; namely, NaAlSiO_4 , KAlSiO_4 , and $\text{NaAlSi}_3\text{O}_8$. Bowen (1912a) on the basis of experimental work on synthetic nephelines agreed with Schaller on the three components forming nepheline. He proved experimentally that the excess silica present in nepheline was in solid solution and most probably in the form of albite. However, he believed that the conditions favorable for albite to saturate nepheline were unattainable in nature and that the natural nephelines were probably never saturated with albite (i.e., silica). Foote and Bradley (1912) disagreed with Bowen (1912a) and attempted to show that there was a definite silica saturation limit in nepheline. Clarke (1914) agreed with Schaller (1912) and Bowen (1912a) in principle, but thought that the excess silica was due to the existence of a polymorphic variety of albite having the composition $\text{Na}_3\text{Al}_3(\text{Si}_3\text{O}_8)_3$. His view was that the replacement of the SiO_4 molecule by the Si_3O_8 molecule was fairly common among the silicates. The theory of Clarke and Schaller on the substitution of Si_3O_8 groups for SiO_4 groups, was disproved by Wherry (1923) who showed that volume relationships would not allow this substitution to occur.

Bowen (1917) performing experimental work in the $\text{NaAlSi}_3\text{O}_8 - \text{KAlSi}_3\text{O}_8$ system believed that complete solid solution occurred between these molecules. He concluded from this that $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 were the fundamental molecules of natural nephelines. However, he also pointed out that experimental work (Bowen, 1912a and 1912b) indicated that plagioclase entered into solid solution with nepheline; the albitic plagioclase explaining the excess silica, and the anorthitic plagioclase the calcium present in numerous analyses. Therefore, he thought nepheline should be represented by four components: $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , $\text{CaAl}_2\text{Si}_2\text{O}_8$, and $\text{NaAlSi}_3\text{O}_8$. Evidence for silica forming a solid solution in natural nepheline was shown by Bowen (1922), when he demonstrated that nepheline acted as a desilicating agent upon diopside.

Cherbuliez and Rosenberg (1928) found that when a mixture of nepheline and quartz was heated in the range $900^\circ - 1000^\circ\text{C}$ there was a decrease in conductivity at any one constant temperature. This proved that the two minerals reacted to form one homogeneous compound, and showed that silica is "soluble" in nepheline. Bannister (1931) agreed with Schiebold (1930) that the excess silica present in nepheline was due to nepheline being derived from the tridymite structure along the lines:



A study, revealing that silica was soluble to 15 percent in nepheline at atmospheric pressure, was performed by Greig and Barth (1938). Shand (1939), from a study on staining feldspathoids, noticed that zoned nephelines containing lime and/or potash were stained homogeneously, but that nephelines containing excess silica (albitic nephelines) were zonally stained. He attributed this to solid solution of albite in nepheline resulting in an alteration of silica-rich and silica-poor zones.

Barth and Kvalheim (1947), in a paper written in 1944, found that spectrographic analysis of a tridymite-like mineral from Antarctica revealed a content of 5.2 percent nepheline. The authors knew silica to be soluble to 15 percent in nepheline (Greig and Barth, 1938), and presumed that nepheline was soluble in tridymite as well, therefore, incomplete solid solution occurred in the system $\text{NaAlSiO}_4 - \text{SiO}_2$. The authors proposed the name "christensenite" for the solid solution members in the series, nepheline - tridymite. However, since this series also includes albite, the term "christensenite" includes three separate mineral species. Also, these minerals participate in extensive solid solutions with other minerals, and the use of the term "christensenite" to delineate part of these solid solutions appears superfluous. MacKenzie (1953), in his investigation of the nepheline - albite - water system, found that (p. 119) "the limit of nepheline solid solutions richer in silica than NaAlSiO_4 was ... about $\text{Ne}_{75}\text{Ab}_{25}$ at 750°C "

and 14,500 psi water pressure. This amounted to a 10 percent increase over Greig and Barth's (1938) result in the 'dry' system at atmospheric pressure.

Eitel (1954), in his review of the physical chemistry of the silicates, outlined a process which he believed explained excess silica in most nephelines. That is, tridymite lamella lying parallel to the basal pinacoid in the nepheline structure, or as otherwise stated, SiO_4 groups isomorphously replacing AlO_4 groups within nepheline. No elaboration accompanied mention of this process. Hahn and Buerger (1955), in their detailed discussion on the structure of nepheline, stated that incomplete replacement of silicon atoms by aluminium atoms accounted for the excess silica found in the nephelines. This view is the antithesis of Eitel's (1954) idea as stated above.

At present it appears that several agencies may cause excess silica to be present in nepheline. There is little doubt that limited solid solution of albite and/or tridymite can occur in nepheline, and also that these solid solutions could cause excess silica to be present. Hahn and Buerger's (1955) idea of incomplete substitution of atoms with the tridymite structure would also account for some excess silica. It therefore appears probable that all of the aforementioned causes of excess silica are operative and that excess silica in nepheline is a result of any one or a combination of these.

(ii) Potassium and calcium studies

Bowen (1912b) discovered experimentally that $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite) was soluble up to 35 percent by weight in solid solution in nepheline at atmospheric pressure. Becke and Hirsch (1925) described some natural zoned nephelines supporting Bowen's experimental evidence that $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ formed solid solutions. The following year they discussed the crystals in greater detail giving further chemical analyses (Becke and Hirsch, 1926). Trömel (1930) demonstrated from synthesis and X-ray work on nepheline that the replacement of sodium by calcium in valence proportions depended upon the spreading of the oxygen lattice by aluminium. Eitel, Herlinger, and Trömel (1930) confirmed Trömel's (1930) work and pointed out that X-ray studies on the two end members, $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 , made it very doubtful that these two compounds formed a complete isomorphous series as Bowen (1917) had stated. This has since been proved correct (see Tuttle and Smith, 1952).

One of the most detailed and comprehensive studies on nepheline and its relationship to chemical composition was that of Bannister (1931). He established that the volume of the unit cell and refractive index increased proportionally with the number of potassium atoms present. This increase was rather erratic (see figure 2b). He also inferred that calcium would produce an effect similar to that of potassium. Thus, variation in sodium, potassium, and/or calcium content of the unit cell may explain the recorded differences in lattice

parameters of natural nephelines. Calcium could not of course increase the cell dimensions as much as potassium due to its smaller size. Foster (1942) found that from 5 to 10 percent of CaSiO_3 (wollastonite) would participate in solid solution in nepheline at atmospheric pressure. Buerger, Klein, and Hamburger (1947) found that chemical analyses supported the thesis that potassium substitutes for sodium and that the ideal formula of nepheline should be $\text{KNa}_3\text{Al}_4\text{O}_{16}$. Goldsmith (1949), in an experimental study in the system $\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$, showed that in the stability field of nepheline, nepheline can absorb at least 60 percent CaAl_2O_4 in solid solution at atmospheric pressure. Juan (1950) also demonstrated that nepheline can not exist in a pure state in the presence of lime compounds.

Therefore, it is seen that a few minerals and compounds, notably kaliophilite and lime compounds, participate in partial solid solution with nepheline, and probably could explain other recorded deviations besides silica from the theoretical formula $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$ of Buerger, Klein, and Hamburger (1947). The variation of cell dimensions primarily depends upon the presence or absence of certain elements (potassium and calcium) or compounds as is seen in figure 2. It is probable that results obtained using pure synthetic nepheline would not be valid in a study of the compositionally complex natural nephelines. However, the understanding of the complex nephelines must arise from an understanding of the simple pure synthetic nephelines.

3. Structural Studies On Nepheline

Buerger, Klein, and Hamburger (1947) successfully approximated the nepheline structure and showed that Schiebold (1930) was correct in his idea that the structure of nepheline was based upon the tridymite structure with half the silicon atoms replaced by aluminium atoms, and with alkali atoms placed in the voids of the open high tridymite structure to satisfy the valency requirements. Chemical analyses lent support to the thesis that the true formula for ideal nepheline should be $KNa_3Al_4Si_4O_{16}$. The 1947 paper was expanded and clarified by Buerger, Klein, and Donnay (1954). Hahn and Buerger (1955) published the most detailed and refined account of the structure of nepheline to date. They found that their nepheline was very slightly non-centrosymmetric with a space group $P6_3$. They also found that oxygen atoms departed considerably from spherical symmetry, and thought that this represented strong thermal motion. It was found that rotational collapse occurred, which reduced $3/4$ of the voids in the nepheline structure and increased $1/4$ of the voids. These two void sizes became filled with potassium, sodium, and a few calcium atoms until the valency requirements were met.

G. Donnay (1955a) observed that there are two compositions in nepheline where high order transitions occur: namely, at $x = 1/4$, and $x = 2$ (where x = the number of potassium atoms per unit cell). The two transition points divide the compositional range $NaAlSiO_4 - KAlSiO_4$ into three segments, for which she

proposed the term 'subphases'. She also pointed out that the nepheline Hahn and Buerger (1955) used was situated on the transition border $x = 2$ and, therefore, was under internal stress which might account for some of their oxygen atoms being displaced from the threefold axes.

Recently, Sahama (1958) found one sample of natural nepheline which showed, from a single crystal X-ray investigation, that the unit cell we are accustomed to (e.g., $a_0 = 10.0\overset{\circ}{\text{A}}$, $c_0 = 8.4\overset{\circ}{\text{A}}$) is in reality a pseudocell and the true nepheline cell has dimensions of $a_0 = 17.4\overset{\circ}{\text{A}}$, $c_0 = 76.0\overset{\circ}{\text{A}}$. The true cell is also hexagonal with the a -axes at angles of 60° and 120° to one another. However, the extra reflections of the true cell were too weak to allow determination of the space group. Since all other nepheline studies use the old cell dimensions and the new values have not as yet been corroborated, the measurements in the present study were taken between lattice planes defined using the old values for the unit cell of nepheline.

From the present state of knowledge, nepheline appears to be derived from the tridymite structure with aluminium atoms substituting for half of the silicon atoms. Sodium and potassium atoms, and/or calcium atoms fill voids produced by rotational collapse of the tridymite structure, and satisfy the valency requirements produced by the substitution of aluminium for silicon. Hahn and Buerger (1955) state that disorder occurs in their nepheline, with 12 of the 16 tetrahedra in the unit

cell being disordered with respect to the silicon and aluminium atoms.

4. Cell Variational Studies On Nepheline

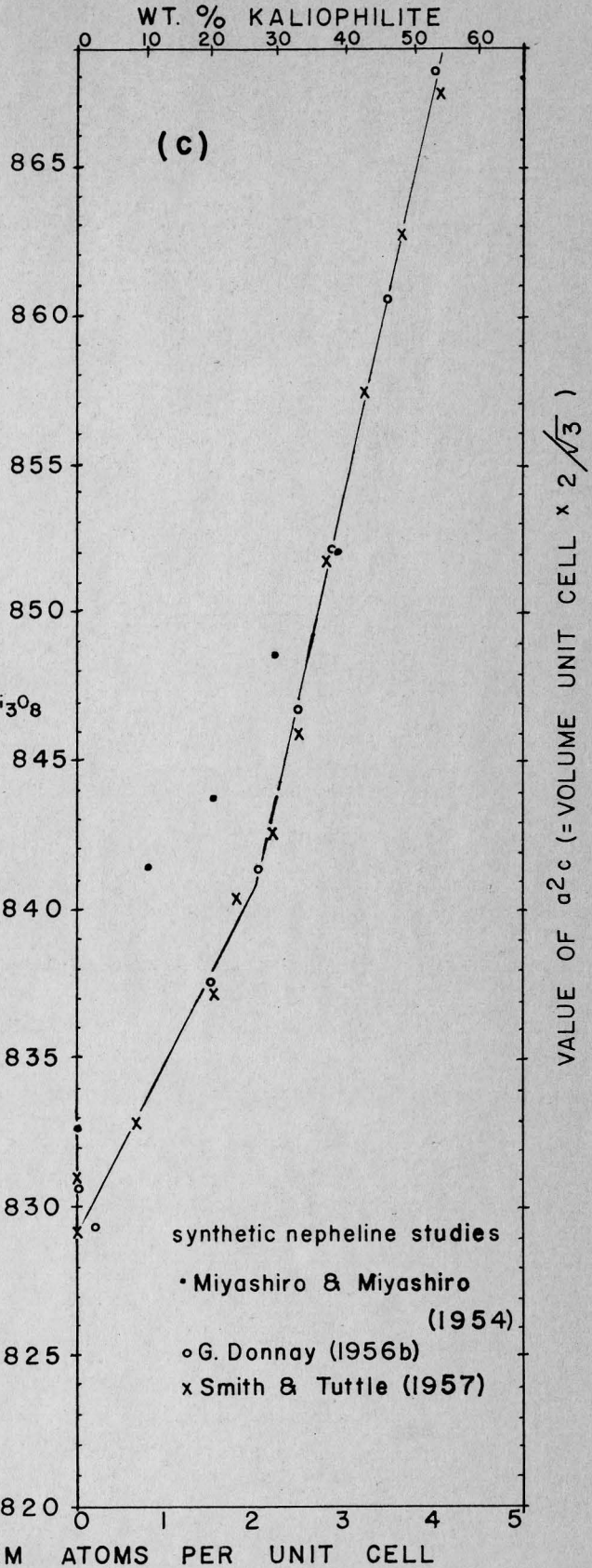
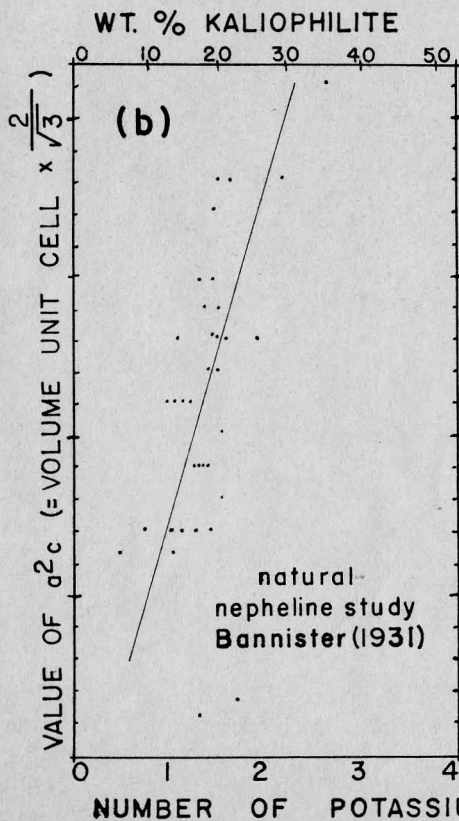
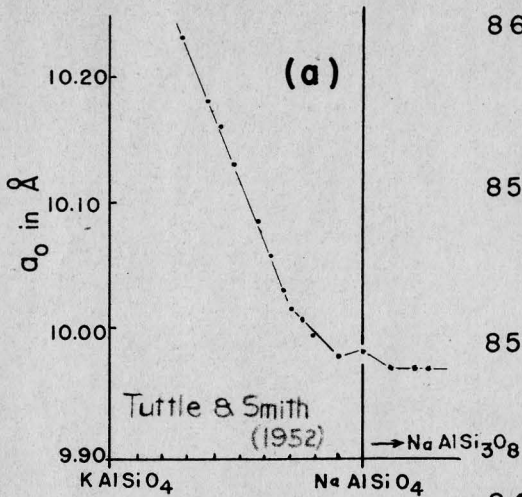
Bannister (1931) was the first person to conduct a cell dimension variational study on nepheline. He correlated the cell dimensions with change in composition, and found that the cell dimensions increased with addition of potassium to the unit cell. This is seen in figure 2b, and as can be seen the correlation was not very good. Tuttle and Smith (1952) found as Bannister (1931) had that the cell dimensions of nepheline vary with composition. However, they also mention that temperature causes a variation in cell volume. The results of their work are presented in figure 2a. Miyashiro and Miyashiro (1954) prepared mixtures in varying proportions of NaAlSiO_4 , KAlSiO_4 , $\text{CaAl}_2\text{Si}_2\text{O}_8$, and SiO_2 . Part of their results are presented in figure 2c, and as can be seen these results do not agree very well with later investigations. In addition to the increase in unit cell and lattice parameters with composition, they found that excess anorthite and silica decreased cell edge a_0 and increased cell edge c_0 .

G. Donnay (1955b), in a study of solid solution in the system $\text{NaAlSiO}_4 - \text{CaAl}_2\text{O}_4$, found that double substitution (calcium for sodium and aluminium for silicon) caused variation with composition in cell sizes. This indicates that calcium might cause variation in cell sizes in nepheline. She also found that omission solid solution caused no variation in cell dimensions in pure synthetic nepheline. The following

FIGURE 2

(a) Diagram showing change in a_0 with composition in nepheline.

(b & c) Diagrams showing change in a^2c with composition in nepheline.



year (G. Donnay, 1956a), she implied that substitution-omission solid solution also occurred in nepheline, but little affected cell dimensions. In the same report, but in another article (G. Donnay, 1956b), she utilized information obtained from synthesizing 10 pure nephelines at different temperatures and for different lengths of time, and concluded that there was no observable cell variation in the polymorphs of nepheline. A further discussion of this paper is left to the interpretation of results where it is compared with the results of the present study.

Smith and Tuttle (1957) found that the lattice parameters for pure synthetic nepheline prepared hydrothermally were the same after 3 hours as after 34 hours at 4000 psi. This indicated that lattice parameters might be independent of the time required for synthesis of nepheline. The variations of lattice parameters a_0 and c_0 for nepheline-kalsilite solid solutions were given, and anomalous results were found for pure synthetic nepheline. Some of their results are presented in figure 2c. It was found that lattice parameters of synthetic nepheline varied slightly among different specimens and that (p. 302-303) "to some extent these variations are related to the thermal history of the samples." The cause for these variations was not known, but Smith and Tuttle put two hypotheses forward (p. 303): "first, order-disorder between the silicon and aluminium ions and secondly the presence of H^+ ions in the lattice perhaps as OH^- replacing O^{2-} ."

Mackenzie (1957, p. 513) stated:

that the differences between high- and low-temperature forms of both sodium and potassium feldspar are principally due to different degrees of order in the distribution of Al and Si atoms ... although the possibility that slight chemical differences may be partly responsible for the lattice variations cannot be completely ruled out.

Thus, minor lattice parameter variations in any one silicate polymorph would appear to be primarily caused by different kinds or degrees of order-disorder in the silicate network. It is the principal aim of this study to differentiate between Donnay's (1956b) and Smith and Tuttle's (1957) conclusions on the amount of lattice parameter variation with temperature of formation in synthetic nephelines.

III. EXPERIMENTAL METHODS

1. Description of Apparatus

The apparatus used in this study is the usual pressure and temperature synthesis equipment common in pressure-temperature laboratories in North America. The essential components of the experimental apparatus consist of an air-driven pump unit to supply pressure, a pressure vessel or "bomb" to contain the pressure along with the charge to be synthesized, and a controlled furnace to supply the temperature required.

(i) The air-driven pump

The pump used was manufactured by the Sprague Engineering Corporation of Gardena, California under the model number S-216C-300. The principle of operation of this pump is quite simple. Utilizing the principle of differential areas, laboratory air was introduced onto a large area piston at low pressure in order to develop high pressure by forcing a small area piston against a small volume of fluid, in this case, water. Thus, a water pressure is formed. This water pressure depends upon the surface areas of the two pistons. Therefore, if the upper or air surface of the piston has a surface area 300 times greater than the lower surface, and laboratory air is supplied at 100 psi, the resulting water pressure developed is 30,000 psi. The model used (S-216C-300) had an input to

output ratio of 1 : 335, and maintained a set output pressure to within 700 psi. The pump used broke down several times during the experimental period, ruining several runs. Whether these breakdowns were due to mechanical or operational faults could not be determined, however, all known precautions were taken during the operation of the pump. The pressure supplied by the pump was conducted by high pressure tubing to the pressure vessel.

(ii) The pressure vessel

Several bombs have been developed for use in pressure-temperature systems over the last 60 years. However, the best design and the type used in this study was developed by Tuttle (1949). This bomb is machined from "Stellite 25", an alloy of cobalt, chromium, and tungsten, which provides a highly temperature and pressure resistant bomb. The dimensions of the bombs used were $1\frac{1}{4}$ inches outside diameter x $\frac{3}{8}$ inch inside diameter x 12 inches in length. A bomb of these dimensions would fail under a pressure of 20,000 psi at approximately 900°C when used for prolonged periods of time (e.g., over 2 days). A sketch of this bomb type and the manner in which it was utilized in the experimental apparatus is shown in figure 3. Temperature was supplied to the bomb by a controlled cylindrical furnace.

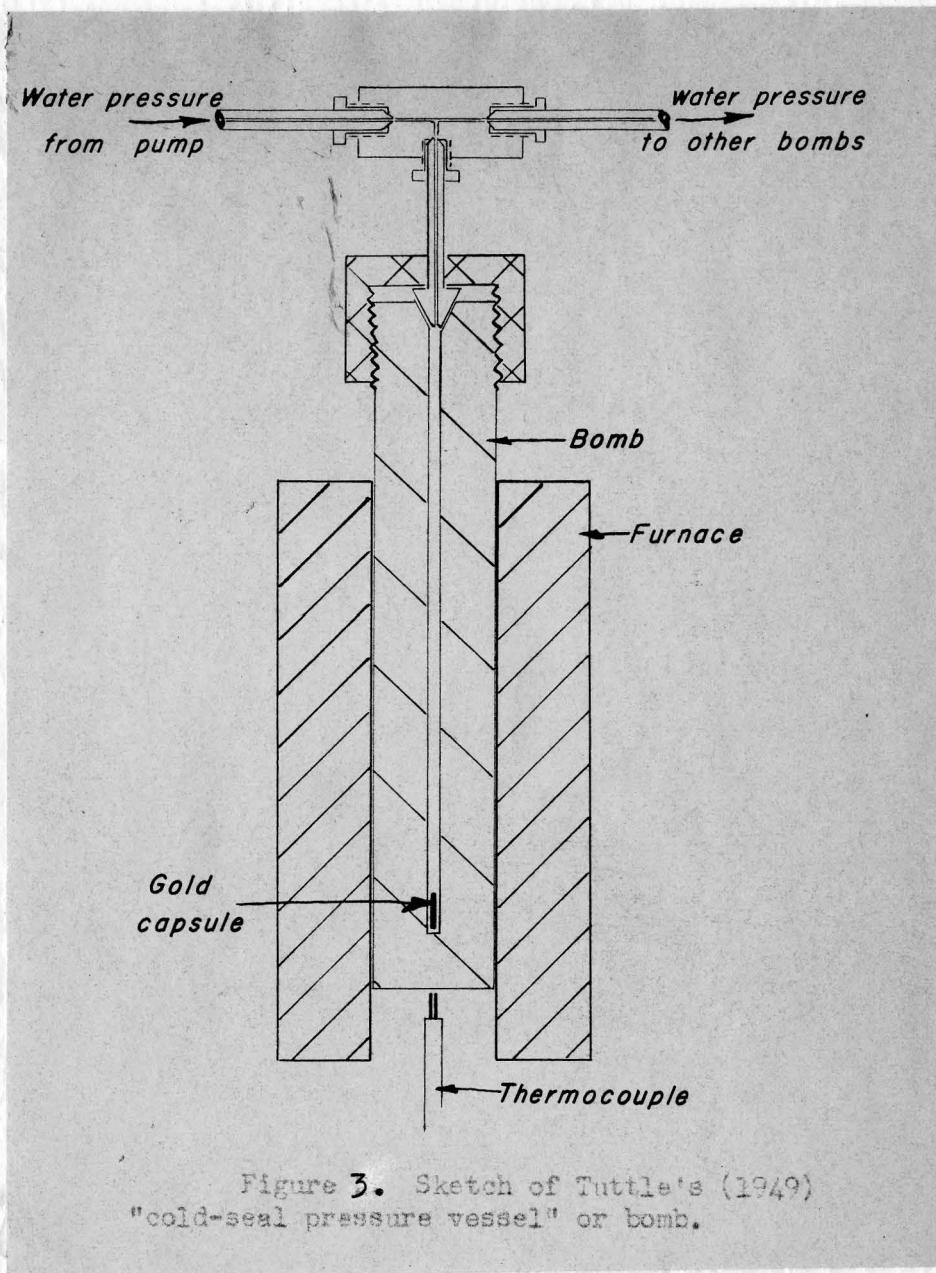


Figure 3. Sketch of Tuttle's (1949) "cold-seal pressure vessel" or bomb.

(iii) The temperature apparatus

The equipment used to supply and control the temperature for any one bomb was as follows: a "Hevi-Duty" furnace, a chromel-alumel thermocouple, and a Bristol Indicating Millivoltmeter Pyrometer Controller, Model 478L.

The furnace, sold under the trade name "Hevi-Duty", was

manufactured by the Ideal Furnace Company. The furnace was of the ordinary cylindrical type with an inside diameter equal to the outside diameter of the bomb, and was capable of producing temperatures up to the limit of the controller which was 1100°C . The heating element consisted of heavy duty nicrome wire backed with asbestos insulation. The furnace would be improved through the use of a metal clamp to facilitate closing of the furnace around the bomb.

Each controller was supplied with its own thermocouple and since the controllers were not correctly calibrated, a working curve of actual versus recorded temperature had to be established for each controller and its thermocouple. These working curves are believed accurate to $\pm 10^{\circ}\text{C}$. More precise equipment should be used to control temperature in any further pressure-temperature lattice parameter studies.

Each thermocouple consisted of a positive wire of chromel (an alloy of approximately 90 percent nickel and 10 percent chromium) and a negative wire of alumel (an alloy of approximately 95 percent nickel, 5 percent aluminium, manganese, and silicon). The wires used were No. 8 AWG. Due to the high nickel content of this type thermocouple wire and its large diameter, it is resistant to oxidation and can be used to record temperature from 0° to 1250°C . Utilizing the thermocouple, the controller was able to maintain temperatures from room temperature to 1100°C .

The apparatus as used in this study consisted of four controllers, thermocouples, furnaces, and bombs. These could

all be run concurrently under the same pressure, while the temperature for each bomb could of course be individually controlled.

2. Preparation for Runs

(i) Sample Preparation

The formation of a dry mixture of the composition NaAlSiO_4 was accomplished by mixing αSiO_2 , $\gamma\text{Al}_2\text{O}_3$, and Na_2SiO_3 together by weight in molecular proportion: $\text{Na}_2\text{O} \cdot \text{SiO}_2$, 43% : $\gamma\text{Al}_2\text{O}_3$, 36% : αSiO_2 , 21%. αSiO_2 and $\gamma\text{Al}_2\text{O}_3$ were used because they are highly reactive components. The αSiO_2 and $\gamma\text{Al}_2\text{O}_3$ were prepared separately by heating spectrographically pure silicic acid and aluminium chloride in furnaces at the appropriate temperatures to achieve the required transformations. The Na_2SiO_3 was prepared from $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$. Since this compound is deliquescent, accurate weighing of portions was difficult. In order to overcome this difficulty the water was evaporated off in a drying oven and the compound was weighed out as Na_2SiO_3 .

After the three powders had been weighed out in the correct proportions to form NaAlSiO_4 , they were placed in an hour-glass mixer and mixed until the powder became homogeneous. The fact that nepheline was easily synthesized from the mixture used would indicate that the mixing was adequate, and that the Na_2SiO_3 used did not contain a significant amount of H_2O .

(ii) Sealing of Sample

In order to synthesize nepheline under known conditions, the starting material and excess water were placed in gold cylinders which were then sealed and weighed. The method used is one which was described by Yoder in a personal communication to the author. 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 fused shut in a carbon arc. Distilled water, in excess of the amount of mixture to be used, was then placed in the bottom of the cylinder by means of a capillary tube. The powdered mixture was then added and the top edge and inside lip of the cylinder cleaned with a cotton swab. A pair of flat-faced pliers was used to crimp shut 4 - 6 mm. of the cylinder and the crimp then peened tightly closed. The crimped end of the cylinder was then placed in a small vise whose jaws were approximately 1 mm. thick and the vise tightened. It was found that shearing of the gold occurred if too much pressure was exerted and that care was needed when tightening the cylinder in the vise.

The vise was then placed in a direct current electrical system as shown in Figure 4.

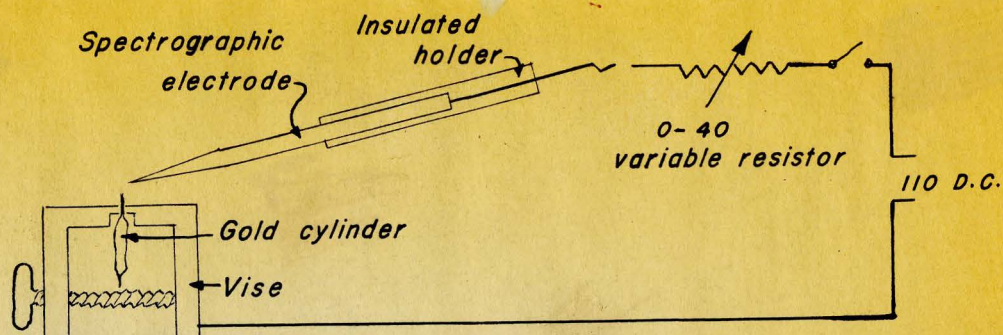


Figure 4. Sketch after Yoder (personal communication) of the welding circuit used to seal the gold cylinders.

The resistor was set at about 20 ohms, the circuit was closed, and the cylinder welded. Welder's goggles were necessary during this process. Upon completion of welding, the cylinder was removed and examined under a binocular microscope (35x) for any defects. If there were none, the cylinder was then weighed and placed in one of the bombs available.

(iii) Starting of Run

The bombs were tightened and inserted into the pressure circuit in the laboratory. Each run consisted of four bombs, each bomb containing a single cylinder. An arbitrary temperature and a pressure of 20,000 psi were then applied to each bomb for the length of the experiment.

3. Quenching of Runs

The method of quenching is important since the formation of any metastable phases must be prevented. Several methods were tried before the equipment was renovated, but

they were only moderately successful. However, the quenching procedure used for the last half of the experiments was quite successful. This method consisted of removing the furnace and thermocouple, and simply raising a cold bucket of water over the bomb. The pressure in the system was maintained during the quenching process so that the gold cylinders would not burst. When the bombs had been quenched, they were removed from the pressure system and opened. The cylinders were then removed and weighed to determine if they had come open during the run. A new set of gold cylinders was then inserted in the bombs for another run.

4. X-ray Determination of Lattice Parameters

In order to X-ray the synthesized nepheline, the powder was removed from the gold cylinders and ground. Care was taken to grind all the runs to the same grain size in order to minimize any error introduced by varying grain size. Benzene was added to the synthesized mineral(s) in the mortar to facilitate grinding. The ground powder was run upon a Norelco High Angle Diffractometer to determine the phases present. The machine was set to oscillate between 22.5° and 30.0° 2θ since this interval contained the peaks $20\bar{2}1$, $21\bar{3}0$, and $20\bar{2}2$ which were found suitable for measuring lattice parameter shift. At least six patterns were run over this interval and the distances between peaks were then measured upon the Norelco Film Illuminator and

Measuring Device. These measurements are accurate to ± 0.0008 of an inch. However, the thickness of any one line is 0.02 inches and the line width can vary up to 0.005 inches. The changes in lattice parameter were thus measured directly on the six chart patterns, averaged, and then plotted upon a graph (see figure 5, and table 2). It is thought that averaging of the six values reduced any measuring error to less than $0.005^\circ 2\theta$.

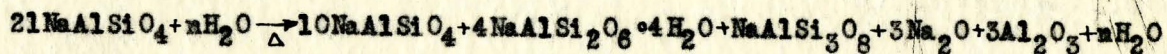
The diffractometer settings used were scanning rate, $1/4^\circ 2\theta$ per minute; chart speed, $1/8$ inch per minute; rate meter scale factor, 4; multiplier, 1; and time constant, 4.

5. Problems Encountered and Sources of Error

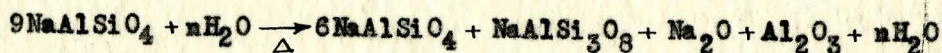
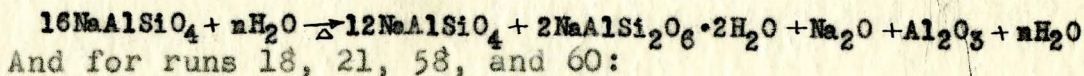
A number of problems were encountered during the experiments. First, the Norelco diffractometer gave varied readings for the lattice parameters; the average error for 95 percent probability being $\pm 0.012^\circ 2\theta$. Second, the Fisher pyrometers were not correctly calibrated and a set of correction curves had to be constructed so that one could determine the temperature of the bombs. These curves are believed accurate to $\pm 10^\circ\text{C}$. Third, several small leaks occurred in the pressure system, causing pressure variation in the runs. However, this variation was not greater than ± 700 psi from the set pressure value of 20,000 psi. Fourth, the pump which was used did not maintain the necessary pressure on all the runs, thus causing the gold cylinders to burst from their high internal pressure. Fifth, because Yoder's method of sealing the gold tubes was not used until the very end of the

experimental period, runs which had leaked or absorbed water during the experiment had to be included in the results. Since this has had to be done, then the problem of leaching needs to be considered.

Hydraulic fluid may enter a capsule either at the beginning of a run due to faulty sealing of the capsule, or at the end of a run when the pressure is dropped for quenching. However, in runs of 96 hours duration since run 19, the pressure was maintained until the bombs were quenched and, therefore, the capsules could not burst. Thus, almost all the capsules leaked because of faulty sealing allowing the hydraulic fluid to be in contact with the synthetic nepheline for the duration of the run. The fluid affected the charges and, judging from the results of the runs, Na_2O and Al_2O_3 probably were leached away. The following equations could illustrate some of the reactions which might have occurred during the experimental period. For runs 17, 22, and 55:



For runs 53 and 56:



Although it is improbable that Na_2O and Al_2O_3 both dissolved at equal rates, the general relationship is seen whereby both soda and alumina might have been leached out of the charge, leaving an excess of silica over the limits of solid solution which might react with the nepheline present to form analcite and/or albite. All the phases present after synthesis had occurred could not be determined, but the presence of artificial noselite and/or sodalite proves that SO_3 and/or NaCl were added to a few of the charges in some manner. The sulphur may have come from the oil used to lubricate the pump; for each time the hydraulic fluid was drained after a run, oil was noticeably present and could have acted upon any charge whose cylinder was insufficiently sealed. The NaCl present in four of the 53 charges might have come from careless handling of the tools used to place the charge into the gold cylinders. The preparation of charges took place in the pressure-temperature laboratory where the room temperature frequently exceeded 80°F . This is a good illustration of why laboratory methods should be carried out carefully and under the cleanest conditions possible. Further reference is made to sources of error in the section entitled "Interpretation of Results".

IV. RESULTS

In order to determine which peaks might be suitable for use in measuring lattice parameter shift, an X-ray powder diffraction pattern was run and indexed on a natural nepheline from Brevik, Norway (McMaster University collection number, M 681). The indexed powder pattern of this natural nepheline appears in table 1. The peaks $20\bar{2}1$, $21\bar{3}0$, and $20\bar{2}2$ were chosen for measuring cell dimension changes because of their strong intensity, and because these peaks were found useful in measuring cell dimensional variation in nepheline by other workers (e.g., Smith and Sahama, 1954; G. Donnay, 1956b; and Smith and Tuttle, 1957).

Nepheline was synthesized in 53 runs to determine the variation of 2θ in $20\bar{2}2 - 21\bar{3}0$ and $21\bar{3}0 - 20\bar{2}1$ with temperature of formation. These runs were then quenched and analysed using X-ray diffraction. Of the 53 samples, 28 consisted of pure nepheline only. The other 25 contained other mineral(s) besides nepheline. The results of each run and the conditions under which each charge was synthesized are listed in table 2. Figures 5a and 5b show the effect of temperature of formation upon $\Delta 20\bar{2}2 - 21\bar{3}0$. Early in the investigation it was seen that $\Delta 21\bar{3}0 - 20\bar{2}1$ was too erratic to establish any trend in lattice parameter variation with temperature.

TABLE 1

INDEXED POWDER PATTERN OF A NATURAL NEPHELINE

Material: McMaster collection No. M-681, containing 32.5 ± 1.8 K/(K+Na+Ca)
 Method: Smear mount, no internal standard, $\text{CuK}\alpha$
 Lattice parameters: hexagonal, $a_0 = 10.08\text{\AA}$, $c_0 = 8.46\text{\AA}$

'd' spacing	2θ	Obs. $\sin^2\theta$	Calc. $\sin^2\theta$	Indices
4.37	20.3	.0311	.0312	20 $\bar{2}$ 0
4.23	21.0	.0332	.0332	0002
3.88	22.9	.0394	.0395	20 $\bar{2}$ 1
3.82	23.3	.0407	.0410	10 $\bar{1}$ 2
3.30	27.0	.0545	.0546	21 $\bar{3}$ 0
3.04	29.33	.0641	.0644	20 $\bar{2}$ 2
2.90	30.8	.0705	.0702	30 $\bar{3}$ 0
2.60	34.5	.0879	.0878	21 $\bar{3}$ 2
2.51	35.7	.0939	.0936	22 $\bar{4}$ 0
2.42	37.2	.1017	.1014	31 $\bar{4}$ 0
2.37	38.0	.1060	.1059	20 $\bar{2}$ 3
2.32	38.75	.1101	.1097	31 $\bar{4}$ 1
2.18	41.5	.1255	.1248	40 $\bar{4}$ 0
2.14	42.3	.1302	.1293	21 $\bar{3}$ 3
2.11	42.9	.1337	.1328	0004
2.09	43.2	.1355	.1346	31 $\bar{4}$ 2
2.05	44.2	.1415	.1406	10 $\bar{1}$ 4
2.00	45.45	.1493	.1482	32 $\bar{5}$ 0
1.94	46.75	.1574	.1565	32 $\bar{5}$ 1
1.91	47.5	.1622	.1638	41 $\bar{5}$ 0
1.90	48.0	.1654	.1640	20 $\bar{2}$ 4
1.85	49.2	.1733	.1721	41 $\bar{5}$ 1
1.81	50.55	.1823	.1814	32 $\bar{5}$ 2
1.77	51.5	.1888	.1874	21 $\bar{3}$ 4
1.72	53.32	.2013	.1996	40 $\bar{4}$ 3
1.70	53.85	.2051	.2033	50 $\bar{5}$ 1
1.65	55.85	.2194	.2184	42 $\bar{6}$ 0
1.64	56.0	.2204	.2189	33 $\bar{6}$ 1
1.63	56.6	.2248	.2264	22 $\bar{4}$ 4
1.61	57.3	.2298	.2282	50 $\bar{5}$ 2
1.57	58.85	.2415	.2418	51 $\bar{6}$ 0
1.48	62.95	.2727	.2750	51 $\bar{6}$ 2
1.46	63.65	.2782	.2777	30 $\bar{3}$ 5
1.45	64.4	.2840	.2853	33 $\bar{6}$ 3
1.44	64.95	.2884	.2891	60 $\bar{6}$ 1
1.39	67.5	.3087	.3089	31 $\bar{4}$ 5
1.38	68.00	.3127	.3125	52 $\bar{7}$ 1
1.33	70.95	.3369	.3354	61 $\bar{7}$ 0
1.33	71.15	.3386	.3374	52 $\bar{7}$ 2
1.32	71.50	.3422	.3434	33 $\bar{6}$ 4
1.32	71.75	.3435	.3437	61 $\bar{7}$ 1

TABLE 2

EXPERIMENTAL RESULTS*

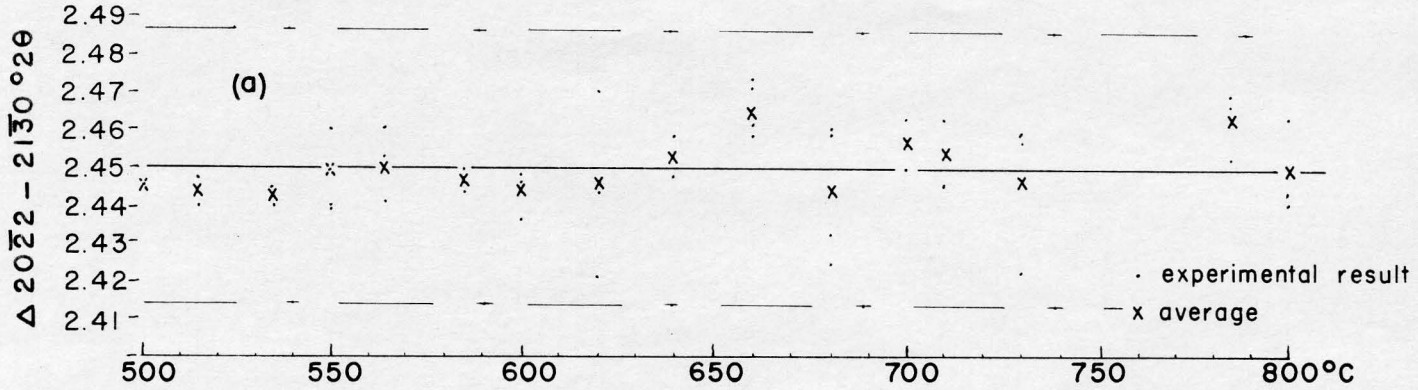
Run No.	Wt. before Run in gms	Wt. after Run, gms.	Hrs.	Temp. °C.	2022-2130 in °2θ	Phases Present
10	.6957	.6958	95	650	2.464 ± .020°	Ne
11	.6701	.6701	95	625	2.506 ± .015	Ne + Ab + ?A
12	.6910	.6911	95	640	2.486 ± .019	Ne + Ab + ?A
13	.6374	.6460	95	660	2.462 ± .007	Ne + ?B
15	.6680	.6722	95 ¹	700	2.451 ± .011	Ne + ?B
16	.6883	.6912	95 ¹	710	2.446 ± .024	Ne
17	.6869	.6927	95 ¹	500	2.445 ± .009	Ne+Anal + Ab
18	.7106	.7196	95 ¹	550	2.438 ± .008	Ne + Ab
20	.6737	.6836	96	565	2.461 ± .025	Ne
21	.5790	.5576	96	585	2.451 ± .012	Ne + Ab
22	.4847	.5132	96	600	2.437 ± .013	Ne + Ab + Anal
23	.5768	.5511	96	680	2.425 ± .007	Ne + Ab + ?B
24	.8044	.8687	96	565	2.454 ± .007	Ne
25	.6778	.6649	96	585	2.448 ± .006	Ne
26	.6948	.6934	96	600	2.447 ± .009	Ne
27	.7745	.7701	96	680	2.433 ± .012	Ne
28	.5523	.5523	96	680	2.459 ± .007	Ne + Nos or Sod
29	.7790	.7777	96	565	2.442 ± .011	Ne
30	.8053	.8053	96	585	2.444 ± .016	Artif. Nos + Ne
31	.6770	.6717	96	600	2.448 ± .009	Ne + Nos or Sod
32	.6499	.6410	96	680	2.460 ± .009	Ne
33	.6286	.6286	96	550	2.460 ± .006	Ne + Nos or Sod Ab
34	.7984	.8190	96	620	2.444 ± .009	Ne + ?C
35	.7288	.7288	75?	640	2.465 ± .013	Ne
36	.6610	.6687	96	660	2.474 ± .013	Ne
41	.6364	.6376	96	550	2.440 ± .016	Ne
42	.6891	.6655	96	620	2.470 ± .002	Ne
43	.7388	.7379	96	640	2.448 ± .009	Ne
44	.8206	.8041	96	660	2.471 ± .005	Ne
45	.7700	.8...	62 ¹	550	2.466 ± .013	Ne
46	.7609	.7251	62 ¹	620	2.449 ± .009	Ne
47	.7770	.7948	62 ¹	640	2.471 ± .020	Ne
48	.7804	.7303	62 ¹	660	2.451 ± .009	Ne
49	.6861	.6637	96	550	2.450 ± .011	Ne
50	.7276	.7079	96	620	2.422 ± .014	Ne
51	.7088	.6822	96	640	2.457 ± .012	Ne

TABLE 2 -- Continued

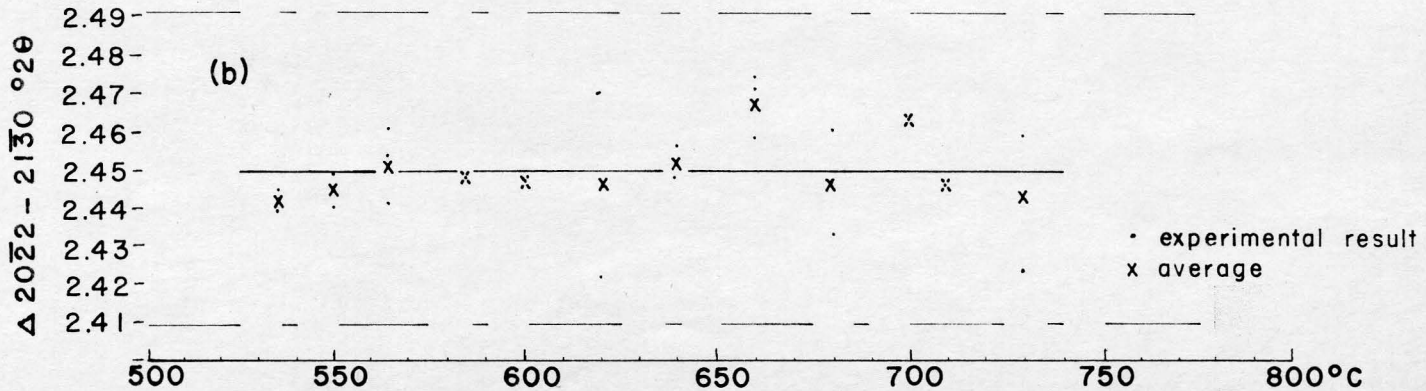
52	.7250	.6902	96	660 ^o	2.458 ± .006	Ne
53	.6440	.6356	96	515	2.448 ± .014	Ne + Anal
54	.6317	.6100	96	535	2.445 ± .012	Ne
55	.6300	.6117	96	515	2.440 ± .012	Anal + Ne + Ab
56	.6337	.6136	96	535	2.445 ± .011	Ne + Anal
57	.6220	.5741	96	700	2.463 ± .017	Ne
58	.6278	.6022	96	710	2.463 ± .015	Ne + Ab
59	.6121	.5848	96	730	2.459 ± .016	Ne
60	.6416	.6110	96	785	2.467 ± .011	Ne + Ab
62	.6285	burst	93 ¹ / ₂	800	2.441 ± .008	Ne + ?D
63	.6218	.6069	93 ¹ / ₂	730	2.457 ± .013	Ne + ?B
64	.6279	.6243	93 ¹ / ₂	785	2.469 ± .009	Ne + ?B
65	.6225	.5744	96	800	2.444 ± .005	Ne + ?Anal?
66	.6060	.5666	96	800	2.464 ± .019	Ne + ?B
67	.6229	.5940	96	730	2.423 ± .025	Ne
68	.6171	.5721	96	785	2.453 ± .012	Ne + ?B
73	.5850	.5850	96	535	2.440 ± .010	Ne

*All runs at 20,000 psi.

FIGURE 5



Graph showing variation in $20\bar{2}2 - 21\bar{3}0$ with temperature ($^\circ\text{C}$) for all hydrothermal four day runs at 20,000 psi.



Graph showing variation in $20\bar{2}2 - 21\bar{3}0$ with temperature ($^\circ\text{C}$) for runs yielding pure nepheline only at 20,000 psi.

V. INTERPRETATION OF RESULTS

In pure synthetic nepheline, the $\Delta 20\bar{2}2 - 21\bar{3}0^02e$ for individual runs shows an apparent erratic increasing and decreasing with rise in temperature. An elementary study of order-disorder in crystals, shows the relationship between the internal (or total) energy of a crystal and temperature to be gradual. Specifically, the characteristic feature of any type of order-disorder transformation is an ever increasing rate of disorder with temperature increase. This is illustrated in figure 6.

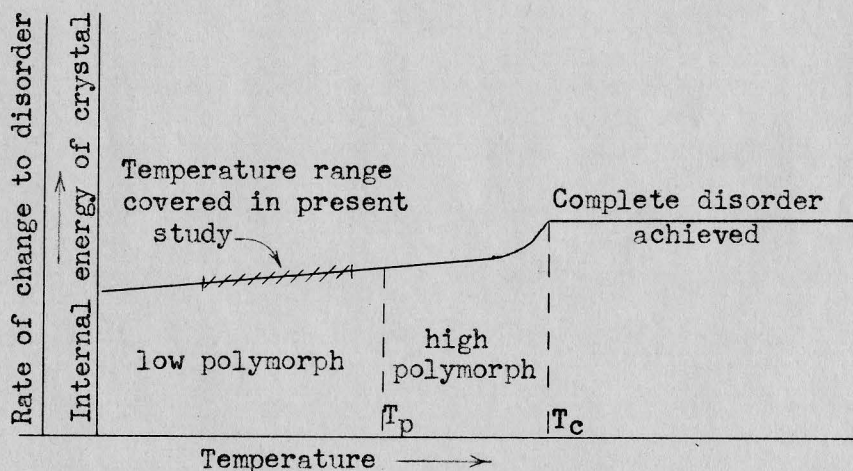


Figure 6. Diagram illustrating the relationship between temperature and the internal energy of a polymorphic crystal, based on Buerger (1949). T_p = polymorphic transition temperature. T_c = critical temperature where disorder becomes complete.

Presumably interchange disorder and distortional disorder occur in nepheline (e.g., see, Buerger, 1949; Hahn and Buerger, 1955; and Donnay, 1955a). Interchange disorder

only concerns the interchanging of aluminium and silicon atoms; which is achieved through increase of temperature. Increase of temperature can also cause a gradual transition and distortion of some mineral structures. This is distortional disorder, and can be visualised as occurring in the following manner. At low temperatures the linked polyhedra of the network structures slump to acquire lower internal energy through increased coordination. An increase in temperature increases the tendency of the polyhedra to rotate or swing. Thus, at any particular temperature, a probability exists that one of the polyhedra may obtain enough rotational energy to drag with it some of its adjacent polyhedra. Therefore, a portion of the structure becomes reversed with respect to the average remainder of the structure. With further increase of temperature more and more such centres of disordered polyhedra occur until the crystal becomes completely disordered as shown in figure 6. Since an increase of lattice parameter is directly related to the internal energy of the crystal, a graph of lattice parameter versus increasing temperature should show the same relationship as figure 6, other things being equal, in a crystal in which disorder transformation occurs. In the temperature range of the study, 500° - 800°C , we are only concerned with one polymorph of nepheline in which the disordering transformations described above have been reported in the literature. Therefore, a graph of cell dimension variation versus temperature increase should give rise to a relationship

similar to the shaded area in figure 6, if cell dimension variation is "frozen" in the nepheline structure on quenching.

Utilizing the method of least squares or linear regression analysis, a statistically based line for figure 5a and 5b was drawn. The equation $\bar{Y} = A + B(X - \bar{X})$ holds for the experimental data; where \bar{Y} = mean value of $\Delta 20\bar{2}2 - 21\bar{3}0^\circ 2\theta$, A = value of \bar{Y} for a corresponding value of \bar{X} on the line, B = slope of the line, X = any one experimental temperature, and \bar{X} = mean value of all experimental temperatures. Solution of this equation for figure 5a yields:

$$\bar{Y} = 2.4501^\circ 2\theta + 0.000037^\circ 2\theta (X - \bar{X}),$$

and for figure 5b: $\bar{Y} = 2.4505^\circ 2\theta + 0.000025^\circ 2\theta (X - \bar{X})$.

For figure 5a, 95 percent confidence limits for the value of \bar{Y} are $\pm 0.0032^\circ 2\theta$, and for the slope of the line are $\pm 0.000036^\circ 2\theta$. For figure 5b, 95 percent confidence limits for the value of \bar{Y} are $\pm 0.0054^\circ 2\theta$, and for the slope of the line are $\pm 0.000086^\circ 2\theta$. Comparison of the equations shows that the slopes of the lines are negligible in comparison with the mean values of $20\bar{2}2 - 21\bar{3}0^\circ 2\theta$ obtained by quenching pure synthetic nephelines between 500° and 800°C . Comparison also shows that the mean value of $20\bar{2}2 - 21\bar{3}0^\circ 2\theta$ is the same within experimental error for both figure 5a and 5b. Therefore, crystallization of other minerals in proximity with nepheline does not appear to affect the lattice parameter of nepheline. From the statistical analyses, the conclusion can be drawn that the value of the low-nepheline polymorph lattice parameter $20\bar{2}2 - 21\bar{3}0^\circ 2\theta$ is $2.450 \pm 0.005^\circ 2\theta$ for the temperature range 500° to 800°C . The dashed lines in figure 5a and 5b

are the limiting values of $20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ for 99.75 percent confidence in pure synthetic nepheline. Although none of the plotted values of $20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ lie outside the dashed lines in figure 5a and 5b, a review of the factors influencing $20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ seems appropriate here. Factors which may cause a variance in $20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ are variation in: (1) water pressure; (2) duration of experiment; (3) temperature of runs; (4) disorder; (5) original chemical components through addition of new material; (6) temperature of sample at time of X-ray diffraction; (7) diffractometer response, goniometer speed, and/or chart speed; (8) leaching; (9) initial grain size of the charge; or (10) through crystallization of other components besides nepheline during a run.

(1) Water pressure and (2) duration of experiment were kept relatively constant and should not have caused any variations. (3) At any one particular temperature, the fluctuation was not more than $\pm 10^{\circ}\text{C}$ on the surface of any one bomb. Therefore, temperature should be regarded as a constant as well since the thickness of the bomb should smooth out nearly all temperature fluctuation. (4) The author did not find any case in the literature where disorder in any one polymorph varies other than uniformly, nor is there reason to suppose that it should vary otherwise. The points in figure 5 should lie upon a varying line if disorder has affected $\Delta 20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ in quenched synthetic nepheline. (5) There can be no doubt

that addition of matter to the starting material has occurred as runs 28, 30, 31, and 33 testify. However, none of these runs gave values of $20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ which lie off the curve in figure 5a except possibly run 33. Therefore, it must be concluded that, although excess chemicals were present in these runs, it appears that they had little, if any, effect upon the lattice parameters. (6) Although the temperatures at which X-ray diffraction patterns are run affect lattice parameters, the slight variation of room temperature during the running of the X-ray patterns introduces a negligible effect. As has been shown in (3) the temperature for any vertical group of values in figures 5a and 5b was kept constant as well. (7) The X-ray diffractometer used was new and similar machines have given accurate readings for other investigators. Also, whenever the machine was checked using the silicon standard a good degree of accuracy was obtained. Thus, it is unlikely that the diffractometer response, the goniometer speed, or the chart speed varied to an extent to cause a few erratic values. (8) The opportunity for leaching has occurred in almost every run, and probably caused albite and analcite to crystallize with nepheline in some charges. It is not to be expected that the few runs which are erratic are the result of leaching which affected nearly every run; however, this possibility should not be completely ignored. (9) The initial grain diameter used in all the charges was fairly uniform, and averaged 0.0005 inches. The limiting

grain diameters observed microscopically were 0.0015 and 0.0001 inches. MacKenzie (1957), in a study of the effect of the grain size of starting material on lattice parameters of synthetic albite, found that $\Delta 131 - \bar{1}\bar{3}1$ for a grain size less than 0.003 inches was $1.908^{\circ}2\theta$ while $\Delta 131 - \bar{1}\bar{3}1$ for an average grain size of 0.0008 inches was $1.900^{\circ}2\theta$. Thus, for a variation of 0.0022 inches in grain diameter MacKenzie found a corresponding variation of $0.008^{\circ}2\theta$ in lattice parameter. The variation of grain diameter in this study is 0.0014 inches and even a $0.010^{\circ}2\theta$ variation is not enough to bring all the values obtained into coincidence with the curve in figures 5a and 5b. Since the starting material used in this study was different than MacKenzie's, a strict comparison should not be made between the two. However, the composition and crystallization fields are similar and it is thought that the variation in cell dimensions due to variable grain size of the starting material was not pronounced enough to account for all the aberrations.

(10) Lastly, changes in lattice parameters of artificial nepheline due to simultaneous crystallization of the other components is negligible as seen from comparison of figure 5a and 5b.

G. Donnay (1956b) found that all pure synthetic nephelines acquired the same lattice parameters when allowed to cool slowly, and that when pure synthetic nepheline was formed above 1000°C and quenched it acquired another uniform set of lattice parameters. From these facts she made the statement (p. 239),

In contradistinction to albite, which exhibits a unique stable crystalline form for each temperature ..., nepheline shows only two forms.

She also performed a study of $\Delta 20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ with temperature at atmospheric pressure in a heating camera. The results of her investigation showed that as the temperature increased so did $20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$, which means lattice parameters a_0 and c_0 increased too. The amount of her increase in $20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ was $0.032^{\circ}2\theta$ for the temperature range $500^{\circ} - 800^{\circ}\text{C}$. If upon quenching a run this increase was "frozen" in the nepheline structure it should result in a relationship where $\Delta 20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ increased with temperature. That a change in lattice parameter can be "frozen" in a crystal structure was shown by MacKenzie (1957). However, in the present investigation the curve in figure 5b is a horizontal straight line within the limits of error of the experiment. The anomaly at 660°C is unexplainable. Therefore, this study supports G. Donnay's (1956b) statement that polymorphs of synthetic nepheline have the same lattice parameters throughout their stability ranges.

VI. CONCLUSIONS

Experimental investigation of synthetic nephelines under 20,000 psi water pressure has revealed within the limits of error no general increase in lattice parameters from 500° - 800°C. Thus, no evidence was found to corroborate the existence of order-disorder, which several investigators claim occurs in nepheline (e.g., see, Buerger, 1949; Hahn and Buerger, 1955). Also the nature of the curve in figure 5b tends to disprove one suggestion by Smith and Tuttle (1957) that replacement of O^{2-} by OH^- might cause variation of lattice parameters in synthetic nepheline with temperature of formation. It is expected that this replacement would probably cause some variation in lattice parameters with temperature whereas this study indicates that no change occurred.

An examination of the probable causes within the experimental method for departure of lattice parameter values from the least squares curve of $\Delta 20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$ versus temperature was made, and no satisfactory explanation for the discrepancies was found. However, if more accurate equipment was used a better correlation might be obtained.

APPENDIX

Determination of Linear Regression Analysis*

The equation required for a linear regression analysis is:

$\bar{Y} = A + B(X - \bar{X})$. This equation will yield a straight line when solved using the present data; where \bar{Y} = mean value of $\Delta 20\bar{2}2 - 21\bar{3}0^{\circ}2\theta$, A = value of \bar{Y} for a corresponding value of \bar{X} on the line, B = slope of the line, X = any one experimental temperature, and \bar{X} = mean value of all experimental temperatures.

If \bar{Y}_X denotes our estimate of the mean Y when X is given we have: $\bar{Y}_X = \bar{Y} + B(X - \bar{X})$. Therefore, \bar{Y} can be taken as the value of A for the value of \bar{X} . The solution of B depends upon the relationship:

$$B = \frac{\sum X_i Y_i - \frac{\sum X_i \sum Y_i}{n}}{\sum X_i^2 - \frac{(\sum X_i)^2}{n}}$$

The values required in the solution of the equation, $\bar{Y} = A + B(X - \bar{X})$, for figure 5a and 5b are:

For figure 5a

n = 44, where n = no. observations
 $\sum X_i Y_i = 69080.415$
 $\sum X_i Y_i = 3038994.76$
 $\sum X_i^2 = 18397850.0$
 $(\sum X_i)^2 = 794676100.0$
 $\bar{Y} = 2.54009$

For figure 5b

n = 22, where n = no. observations
 $\sum X_i Y_i = 33770.04$
 $\sum X_i Y_i = 742893.58$
 $\sum X_i^2 = 8716850.0$
 $(\sum X_i)^2 = 189888400.0$
 $\bar{Y} = 2.45050$

Solution of the equation $\bar{Y} = A + B(X - \bar{X})$ requires that the values for A and B be found, for figure 5a:

$$A = \bar{Y} = \frac{\sum Y}{n} = \frac{107.804}{44} = 2.54009^{\circ}2\theta$$

*Method and equations from: Dixon, W.J. and Massey, F.J. (1951) Introduction to Statistical Analysis. 1st ed. Toronto: McGraw-Hill Book Co.

$$B = \frac{69080.415 - \frac{3038994.76}{44}}{18397850.0 - \frac{794676100.0}{44}} = \frac{69080.415 - 69068.062}{18397850.0 - 18060820.4} = 0.00003665^{020}$$

For figure 5b:

$$A = \bar{Y} = \frac{53.911}{22} = 2.45050^{020}$$

$$B = \frac{33770.04 - \frac{742893.58}{22}}{8716850.0 - \frac{189888400.0}{22}} = \frac{33770.04 - 33767.89}{8716850.0 - 8631290.9} = 0.00002513^{020}$$

Formulae for computing error for A and B with 95 percent confidence limits are:

$$A \pm t_{95} \frac{S_{y \cdot x}}{n}$$

$$B \pm t_{95} \frac{S_{y \cdot x}}{S_x n - 1}$$

The values required in the solution of the equations are: $t_{95} = 1.68$ for figure 5a, and 1.72 for figure 5b, where $t_{95} = t$ value for 95 percent confidence limits and $n-2$ degrees of freedom.

$S_{y \cdot x} = 0.0124399$ for figure 5a, and 0.014221 for figure 5b, where $S_{y \cdot x} =$ the standard error of estimate.

$S_x = 88.532$ for fig. 5a; 63.830 for fig. 5b.

Solutions of 95 percent confidence limits for A and B.

For figure 5a:

$$A \pm (1.68) \frac{0.0124399}{6.6333} = A \pm 0.0032^{020}$$

$$B \pm (1.68) \frac{0.0124399}{88.532(6.5574)} = B \pm 0.000036^{020}$$

For figure 5b:

$$A \pm (1.72) \frac{0.014221}{4.6904} = A \pm 0.0054^{020}$$

$$B \pm (1.72) \frac{0.014221}{63.830(4.5826)} = B \pm 0.000086^{020}$$

Because the slopes of the lines (the B's) are negligible the value of A can be considered equal to \bar{Y} for any value of X. Thus, the line for figure 5a and 5b is a horizontal straight line at $20\bar{2}2 - 21\bar{3}0^{020} = 2.540^{020}$.

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