MELTING RELATIONS OF UNDERSATURATED ALKALINE ROCKS

FROM THE ILÍMAUSSAQ INTRUSION AND GRØNNEDAL-ÍKA COMPLEX SOUTH GREENLAND, UNDER WATER VAPOUR AND CONTROLLED PARTIAL OXYGEN PRESSURE

BY

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WITH 15 FIGURES AND 9 TABLES
IN THE TEXT

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1*

Abstract

As a continuation of a study reported by PIOTROWSKI and EDGAR (1970) on the melting and crystallization behaviour of undersaturated alkaline rocks from Greenland and elsewhere under different laboratory conditions, eight analysed rocks (5 from Greenland, 2 from Kenya and 1 from Tanzania) have been investigated at water vapour pressures up to 2070 bars; and two of the samples from the Ilímaussaq Intrusion, Greenland under conditions of controlled partial oxygen pressure at a total pressure of 1030 bars P_{H_2O}. The initial 1030 bar increment of P_{H_2O} decreases liquidus temperatures by 240–300° C compared to liquidus temperatures at one atmosphere pressure and for some samples alters the crystallization sequence. Lowering the P_{O_2} decreases liquidus temperatures by as much as 30° C at 1030 bars P_{H_2O} and for the samples investigated an aegirine-rich clinopyroxene replaces feldspar as the primary phase at the liquidus.

As in the previous study at one atmosphere pressure, rocks with a high agpaitic index have long melting intervals (300–460° C) at 1030 bars P_{H_2O}. The long melting intervals may be caused by the presence of higher proportions of volatiles, particularly Cl, F and H_2O, in the agpaitic rocks compared to miaskitic rocks. In an alkaline melt these volatiles are present in the liquid rather than the gaseous phase. During crystallization the volatiles act more or less independently of one another and are "fixed" in the sodium-rich minerals sodalite, eudialyte, arfvedsonite and villiaumite. The initial excess of alkalies in comparison to aluminium in agpaitic melts enhances the probability of such a process.

Results of experiments under different P_{O_2} conditions suggest that in initially undersaturated magmas low P_{O_2} conditions may favour a miaskitic differentiation trend whereas higher P_{O_2} will favour an agpaitic differentiation trend.

Melting and crystallization data obtained in the laboratory are generally in fair agreement with similar data obtained from field and petrographic observations.

INTRODUCTION

The study of the melting relations of igneous rocks provides some important information on the thermal and crystallization history of the magma. The studies of YODER and TILLEY (1962) and GREEN and RINGWOOD (1964, 1967) attest to the usefulness of this method. This approach is based on the assumption that crystallized or partly crystallized rocks may be treated as single bulk compositions in a multicomponent system and the course of crystallization can be followed in the usual way by the quenching method (SHEPHERD, RANKIN and WRIGHT, 1909; SCHAIRER in BOCKRIS, WHITE and MACKENZIE, 1959).

As part of a continuing study of the melting behaviour of undersaturated alkaline rocks from Greenland and elsewhere, the melting and crystallization relationships of eight analysed rocks have been investigated at water pressures of up to 2070 bars and under conditions of controlled oxygen pressure in an attempt to explain certain aspects of alkaline rock genesis.

PIOTROWSKI and EDGAR (1970) from the study of melting relations of alkaline rocks, mainly at one atmosphere, showed that the rocks with agpaitic[1]) tendencies and high volatile contents, had much longer melting intervals than rocks with miaskitic affinities. The preliminary results of SOOD and EDGAR (1967) and EDGAR, PIOTROWSKI and SOOD (1968) confirmed the existence of such a relationship under P_{H_2O} conditions. In the present study particular attention has been directed toward these rocks in an attempt to explain this phenomenon.

The rocks investigated are listed in Table I. Three are from the classical locality of agpaitic rocks, the Ilímaussaq Intrusion, South Greenland, two from the Grønnedal-Íka Complex, South Greenland, and the remainder, used for comparative purposes, from Kenya and Tanzania. All samples are believed to be of igneous origin (SØRENSEN, 1958, 1960; FERGUSON, 1964; EMELEUS, 1964; PULFREY, 1954), and were fresh or only very slightly altered.

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[1]) The definition of an agpaitic rock used in this paper is that of GERASSIMOVSKY (1956) i.e. a rock in which $\dfrac{Na_2O + K_2O}{Al_2O_3} \geq 1$ (as molecular proportions). Other definitions have been proposed by USSING (1912) and FERSMAN (1929, 1939). These are discussed by SØRENSEN (1960).

Table I. *List of Rocks*

Rock	No.	Locality	Donor	Reference
Naujaite	57041	Ilímaussaq Intrusion South Greenland	Prof. Dr. H. Sørensen Mineralogical Museum Copenhagen	Sørensen (1958)
Foyaite	57070	same	same	Sørensen (1958)
Lujavrite	57033	same	same	Sørensen (1958)
Foyaite	27113	Grønnedal–Íka Complex South Greenland	Dr. C. H. Emeleus University of Durham	Emeleus (1964)
Nepheline Syenite	58281	same	same	Emeleus (1964)
Phonolite	U 880	Sadiman Volcano Tanzania	R. W. Bartholomew Geol. Survey, Tanzania	Harkin (1960)
Foyaite	K 16	Ruri-Usaki Complex Kenya	Dr. M. J. Lebas Department of Geology Leicester University	Pulfrey (1954)
Nepheline Syenite	K 24	same	same	Pulfrey (1954)

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PETROGRAPHY AND CHEMISTRY

With the exception of the nepheline syenites (58281 and K 24) and the foyaite (K 16), the petrography of the rocks investigated has been discussed in detail in the previous paper (PIOTROWSKI and EDGAR, 1970, p. 8–15) and will not be repeated here. References to the geology and petrology of each of the areas from which the samples have been taken are given in Table I. Chemical, normative and modal analyses for each sample are given in Table II. Although the chemical and normative analyses for five of the rocks used in the previous study (PIOTROWSKI and EDGAR, 1970) are the same, there are slight differences in the modal analyses. This is due to an improved technique, using larger thin sections, which we believe permitted a more accurate estimation of the modal composition of these rocks, many of which are either too coarse-grained or too fine-grained to permit accurate analysis using standard (3 cm × 4 cm) slides. For each analysis a minimum of 2500 to 3000 points were counted using the method of CHAYES (1949). Some sections were stained using the technique of KEITH (1939) to distinguish nepheline from feldspar.

a) Petrography

58281 — Nepheline Syenite, Grønnedal-Íka Complex.

This is a coarse-grained, mesocratic, holocrystalline rock with large crystals of nepheline and feldspar (1–2 cm in length). Aegirine-augite, arfvedsonite, magnetite, sodalite, and natrolite and rare cancrinite, as alteration products, constitute the remaining minerals in the rock.

Microscopically, the rock shows hypidiomorphic granular texture. Subhedral alkali feldspars occasionally enclose small grains of nepheline. The feldspar is mainly microcline-microperthite, but small separate plates of albite are also seen. Some of the feldspars contain microlites of aegirine. Nepheline crystals are occasionally altered to natrolite and rarely to cancrinite. A few small sodalite grains associated with microlites of aegirine are contained in the nepheline crystals. Anhedral aegirine-augite contains inclusions of, and is commonly surrounded by, magnetite. The pyroxene is sometimes replaced by rims of pale-brown arfvedsonite, which in turn is commonly altered to a deep-brown biotite.

K 16 — Foyaite, Ruri-Usaki Complex, Kenya.

In hand specimen this is a fine — to medium-grained, densely cry-stalline rock with evenly distributed nepheline, feldspar and pyroxene.

In thin-section, the rock shows allotriomorphic granular texture. Nepheline, microcline, albite, aegirine, and hornblende with minor arf-vedsonite form the major constituents. Magnetite, zircon and apatite constitute the accessories. Nepheline occurs as irregular-shaped grains, partially altered to natrolite. The alkali feldspars are anhedral and show slight sericitization. Aegirine and aegirine-augite occur as small inclusions in the feldspars and also at the boundaries of the feldspar grains. The pyroxenes are mainly aegirine-augite, with a large X ∧ C extinction angle, and contain minor arfvedsonite intergrowths.

K 24 — Nepheline Syenite, Ruri-Usaki Complex, Kenya.

In hand specimen, this rock is fine- to medium-grained, dark-grey in colour with a few phenocrysts of nepheline and feldspar. In thin section, the texture is hypidiomorphic granular with soda-orthoclase and

Table II. *Chemical, Normative and Modal Compositions*

	Chemical Composition							
Oxides	57041[1])	57070[1])	57033[2])	58281[1])	27113[1])	U 880[2])	K 16[1])	K 24[1])
SiO_2......	47.05	50.59	52.96	55.45	51.50	50.42	52.75	43.90
Al_2O_3.....	21.34	17.09	15.52	16.03	16.80	20.60	17.15	18.07
Fe_2O_3.....	3.59	5.85	7.73	4.94	6.15	4.41	5.25	4.48
FeO	3.08	4.68	2.18	4.64	4.68	1.93	2.88	2.36
MgO......	0.03	0.38	0.02	0.98	1.04	0.53	1.30	1.36
CaO	2.68	1.94	0.88	3.74	4.53	5.92	4.43	9.68
Na_2O	14.43	10.04	11.60	5.82	7.56	7.73	5.04	8.58
K_2O	3.47	3.48	3.36	5.18	4.87	3.71	8.09	5.10
H_2O	1.03	4.38	3.04	0.90	1.04	3.38	1.24	0.59
CO_2	0.16	0.16	0.055	—	0.54	0.18	—	3.17
TiO_2......	0.27	0.42	0.32	1.12	0.17	0.54	0.96	0.92
P_2O_5......	0.09	0.17	0.013	0.60	0.11	0.09	0.16	0.56
ZrO_2......	0.36	0.15	1.11	0.066	0.13	—	0.064	0.092
S........	—	0.018	0.068	—	0.06	—	—	—
Cl........	2.57	0.206	0.016	—	—	—	—	—
MnO......	0.12	0.24	0.15	0.24	0.36	0.23	0.17	0.37
F	0.34[3])	0.30	0.72	—	—	—	—	—
Total	100.03	100.09	99.74	99.71	99.54	99.67	99.48	99.23

[1]) Analyst, K. Ramlal.

[2]) Analyses by Technical Services, Toronto, Canada.

[3]) Analyst, Dr. A. Mottana.

Table II (continued)

C.I.P.W. Norms

Minerals	57041	57070	57033	58281	27113	U 880	K 16	K 24
Or........	20.57	20.57	20.02	30.58	28.91	21.83	47.82	19.50
Ab	6.29	23.58	24.63	38.77	20.96	26.85	11.53	—
An	—	—	—	2.22	—	12.60	0.56	—
Lc........	—	—	—	—	—	—	—	8.28
Ne	45.44	24.42	19.60	5.68	20.73	18.81	16.76	34.93
Cor.......	—	—	—	—	—	—	—	—
Ac	10.63	12.94	22.18	—	4.16	—	—	7.39
Di........	8.29	5.58	1.46	15.43	12.06	2.84	7.13	10.57
Wo......	—	—	—	—	1.51	5.46	4.76	4.76
Hy......	—	—	—	—	—	—	—	—
Ol........	0.71	3.68	2.24	0.26	2.04	—	—	—
Mt	—	2.09	—	7.19	6.96	5.40	6.96	2.78
Hm	—	—	—	—	—	0.67	0.98	0.48
Il	0.61	0.76	0.61	2.13	0.30	1.02	1.98	1.67
Py	—	—	0.12	—	0.12	—	—	—
Ap	0.34	0.34	—	1.34	0.34	Tr.	0.34	1.34
Ct........	0.40	0.40	0.10	—	1.20	—	—	7.30
Zr........	0.55	0.37	1.65	0.18	0.18	—	0.18	0.18
NaCl	4.21	0.35	—	—	—	—	—	—
Na_2SiO_3(NS)	0.24	—	2.81	—	—	—	—	—
Fl........	0.70	0.63	1.48	—	—	—	—	—
Na_2CO_3(NC)	—	—	—	—	—	0.42	—	—

Modal Composition

	57041	57070	57033	U 880	58281	27113	K 16	K 24
Sodalite...........	40.1	—	—	0.8	—	—	0.8	1.0
Nepheline	12.7	33.7	13.2	32.1	15.8	32.0	14.5	30.8
Potassium feldspar (including perthite)	21.2	40.8	24.1	5.4	51.7	35.1	32.1	15.0
Albite	—	—	14.8	—	3.6	—	18.8	10.5
Pyroxene	17.5	14.2	26.1	13.4	10.4	22.4	30.3	29.0
Amphiboles	5.1	8.2	7.4	4.2	7.2	5.7	3.2	4.1
Eudyalite	3.4	—	10.9	—	—	—	—	—
Wollastonite.......	—	—	—	—	1.0	—	—	1.1
Biotite...........	—	2.0	—	—	—	2.4	—	—
Oxides...........	—	1.9	2.5	—	3.3	2.2	1.3	2.1
Ground mass	—	—	—	42.1	—	—	—	1.2
Leucite	—	—	—	1.0	—	—	—	—
Calcite...........	—	—	—	—	—	—	—	2.0
Alteration.........	—	—	1.0	1.0	5.2	1.2	—	3.2

albite forming large anhedral crystals poikilitically enclosing aegirine and less commonly nepheline. Nepheline occurs as idiomorphic crystals, altered to analcite along the fractures and occasionally containing some euhedral grains of sodalite. The pyroxenes, dominantly aegirine-augite, occur as small prisms often rimmed by aegirine and sometimes containing inclusions of diopside and wollastonite oriented along their borders. Hornblende and arfvedsonite form anhedral grains sometimes replaced by dark-brown to opaque biotite. Minor constituents are sodalite, zircon, magnetite, apatite and calcite.

b) Chemistry

Examination of the analyses of Table II shows that the samples investigated have a fairly wide range of composition. In the present study, we were particularly concerned with the differences between rocks with a high agpaitic index, reflected by their high $\dfrac{Na_2O + K_2O}{Al_2O_3}$, and the mias-kitic rocks in which this ratio is low. Using the definition of an agpaitic rock proposed by Gerassimovsky (1956), i.e. $\dfrac{Na + K}{Al} \geqslant 1$, five of the eight rocks (57041, 57070, 57033, 27113 and K 24) are agpaitic. The first three of these samples are from Ilímaussaq and two of them, the naujaite (57041) and lujavrite (57033), have large excess of alkalies to alumina. Previous workers (Sørensen, 1958; Ferguson, 1964) have shown that these rocks also tend to be enriched in certain volatiles, particularly Cl and F, and to be poor in CaO and MgO. The analyses indicate that the Ilímaussaq rocks do contain high Cl and F contents, and are poor in CaO and MgO. However, no definite relation between the content of the oxides and the agpaitic index can be established for these samples.

EXPERIMENTAL METHODS

a) Sample Preparation

Prior to the melting experiments, up to 5 kilograms of each sample were crushed in a mechanical grinder to pass through a 100 mesh sieve and then ground under acetone for two hours in a mechanical agate mortar. The resulting powder was thoroughly remixed and reduced in size by the method of "coning and quartering" to a 5–10 g sample. This sample was dried at 105° C for 1 hour and stored in a sealed container.

b) Apparatus

With the exception of runs done under controlled P_{O_2} conditions at total P_{H_2O} pressures, the apparatus and techniques used for identification of products is exactly the same as described by PIOTROWSKI and EDGAR (1970, p. 16–19). Remarks regarding the experimental procedure given by PIOTROWSKI and EDGAR also apply in the present study.

Two of the rocks used in the present study, the foyaite (57070) and lujavrite (57033) from the Ilímaussaq Intrusion, were investigated under controlled P_{O_2} conditions at a total water vapour pressure of up to 1030 bars using the solid buffer technique (EUGSTER, 1957). These samples were chosen because of their high total iron oxide content ((10.53 weight percent (57070) and 9.91 weight percent (57033)) in order to assess the effect of P_{O_2} on the melting temperature and crystallization sequence of these rocks in comparison to the results obtained at one atmosphere pressure and under unbuffered P_{H_2O} conditions.

c) Buffering Techniques

The theory of solid buffer assemblages to control P_{O_2} has been discussed by EUGSTER (1957, 1959) and EUGSTER and WONES (1962). The range of common buffers as functions of oxygen fugacities for various temperatures is shown in Fig. 1. Most igneous rocks probably form at partial oxygen pressures close to or within the magnetite stability fields (the area bounded by the hematite-magnetite and magnetite-wustite buffer curves of Fig. 1). Recently, CARMICHAEL and NICHOLLS (1967)
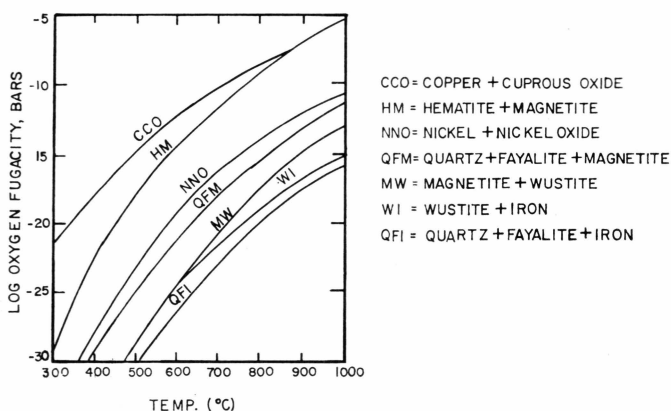
Fig. 1. Buffer equilibria as functions of oxygen fugacity and temperature. (After
Eugster and Wones, 1962).

have suggested that these conditions may not apply if the coexisting
liquid contains appreciable alkalies which increase the ferric/ferrous ratio.
This is probably the case with the two samples studied. However, because
of the presence of traces of magnetite in the unheated samples and the
difficulties in estimating the effect of excess alkalies in the liquid we have
chosen to investigate these rocks using hematite-magnetite buffer, repre-
senting the highest P_{O_2} at any total pressure and temperature where
magnetite is stable, and nickel-nickel oxide buffer assemblage lying well
within the magnetite stability field (Fig. 1).

Controlled P_{O_2} experiments were done using the double-tube tech-
nique described by Eugster (1957). Distilled water and the powdered
rock in the ratio of 1:10 by weight were sealed in a platinum tube and
placed in a larger gold tube containing excess water and the appropriate
buffer. The gold tube was then sealed and placed in an externally heated
cold-seal pressure vessel (Tuttle, 1949) and run at the desired P_{H_2O} and
temperature. Further details of the hydrothermal techniques can be
found in Piotrowski and Edgar (1970, p. 16). At the completion of the
run, both tubes were weighed to ascertain that the experiments had
taken place in a closed system. Both the charge and buffer were X-rayed
and examined under the petrographic microscope — the charge to deter-
mine the products of the run, the buffer to assure the effectiveness of
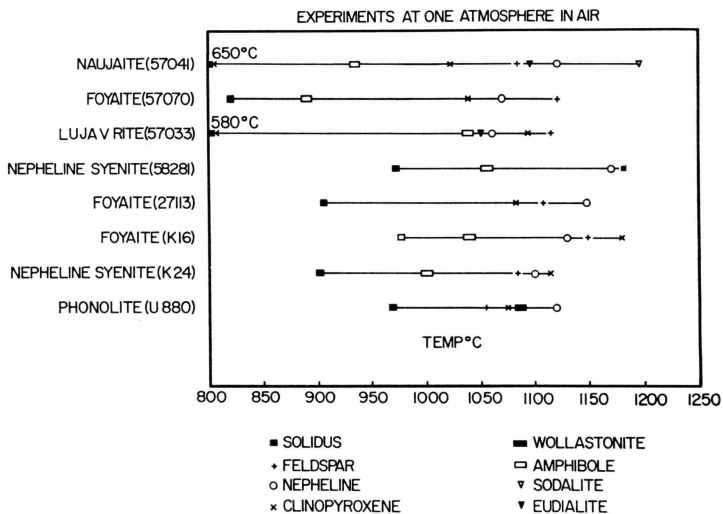the P_{O_2} control.

EXPERIMENTS AT ONE ATMOSPHERE IN AIR

Fig. 2. Melting relations at one atmosphere in air.

RESULTS

a) Experiments at One Atmosphere in Air

Three of the eight samples (58281, K 16 and K 24) had not previously been melted at one atmosphere in air. Data for these samples are given in Table III and shown in Fig. 2. For comparative purposes the melting and crystallization data for the five rocks used in the present study whose melting relations have been reported by PIOTROWSKI and EDGAR (1970) are also shown.

Samples 58281, K 16 and K 24 have liquidus temperatures of 1185, 1175 and 1120° C respectively, values comparable to those from the previous study of rocks of similar composition. As in the previous studies the primary crystalline phases (nepheline, feldspar and clinopyroxene) crystallize within 30–40° C below the liquidus. The melting intervals of these three samples are much smaller than those of the strongly agpaitic rocks from the Ilímaussaq Intrusion (Fig. 2 samples 57070, 57033 and 57041). The solidus temperatures given in Table III and Fig. 2 must be considered as only approximate because the beginning of melting is determined optically and it is very difficult to detect a few grains of glass in a largely crystalline product, particularly if some of the crystals are isotropic.

Table III. *Results of Experiments at One Atmosphere in Air*

(Only experiments indicating a phase change are listed).

Temp. (°C)	Time (hours)	Products[1])
58281 Nepheline Syenite, Grønnedal-Íka, Greenland		
1197	15	Gl.
1182	15	Gl. + Cpx. + Fp.
1165	20	Gl. + Cpx. + Fp. + Ne.
1076	24	Gl. + Cpx. + Fp. + Ne. + Am.
985	29$^1/_2$	Gl.? + Cpx. + Fp. + Ne. + Am.
970	30	Cpx. + Fp. + Ne. + Am.
Reversibility		
1200	16	Gl.
1165	26	Gl. + Fp. + Cpx.?
K 16 Foyaite, Kenya		
1182	18	Gl.
1170	18	Gl. + Cpx.
1150	24	Gl. + Cpx. + Fp.
1125	24	Gl. + Cpx. + Fp. + Ne.
1035	29	Gl. + Cpx. + Fp. + Ne. + Am.
960	31	Cpx. + Fp. + Ne. + Am.
Reversibility		
1190	18	Gl.
1155	28	Gl. + Cpx.
K 24 Nepheline Syenite, Kenya		
1125	28	Gl.
1120	28	Gl. + Cpx.
1100	27$^1/_2$	Gl. + Cpx. + Ne.
1090	27	Gl. + Cpx. + Ne. + Fp.
1002	32	Gl. + Cpx. + Ne. + Fp. + Am.
900	34	Cpx. + Ne. + Fp. + Am.
Reversibility		
1135	15	Gl.
1100	15	Gl. + Cpx.?

[1]) Abbreviations: Gl.-glass, Cpx.-clinopyroxene, Fp.-feldspar, Ne.-nepheline, Wol.-wollastonite, Am.-amphibole, Eud.-eudialyte, Sod.-sodalite, Bi.-biotite. Iron oxide is present in the runs but has not been included.

b) Experiments at One Atmosphere in Argon

Two of the three samples melted in air, foyaite (K 16) and nepheline syenite (K 28) with 8.30 and 6.84 weight percent total iron oxide respectively, have been melted at one atmosphere in argon. Results are shown in Table IV and plotted in Fig. 3, the latter including the results of
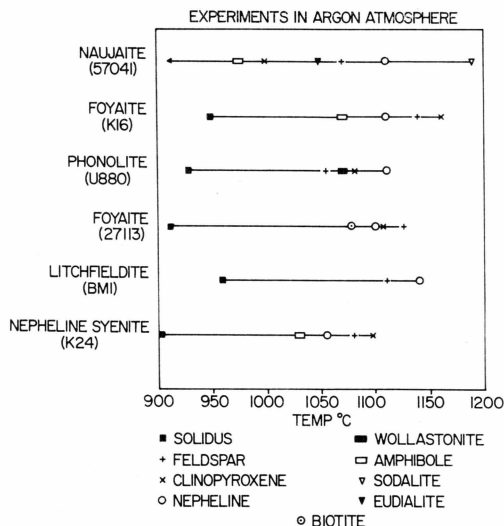

Fig. 3. Melting relations in an argon atmosphere.

Table IV. *Results of Experiments in Argon Atmosphere*
(Only experiments indicating a phase change are listed).

Temp. (°C)	Time (hours)	Products[1]
K 16 Foyaite, Kenya		
1185.	8	Gl.
1162.	10	Gl. + Cpx.?
1155.	11	Gl. + Cpx.
1145.	11$^1/_2$	Gl. + Cpx. + Fp.
1110.	12	Gl. + Cpx. + Fp. + Ne.
1070.	14$^1/_2$	Gl. + Cpx. + Fp. + Ne. + Am.
945.	20	Cpx. + Fp. + Ne. + Am.
K 24 Nepheline Syenite, Kenya		
1110.	12	Gl.
1095.	12	Gl. + Cpx.
1080.	12	Gl. + Cpx. + Fp.
1055.	12	Gl. + Cpx. + Fp. + Ne.
1030.	14	Gl. + Cpx. + Fp. + Ne. + Am.
900.	18	Cpx. + Fp. + Ne. + Am.

[1] Abbreviations are the same as in the footnote of Table III.
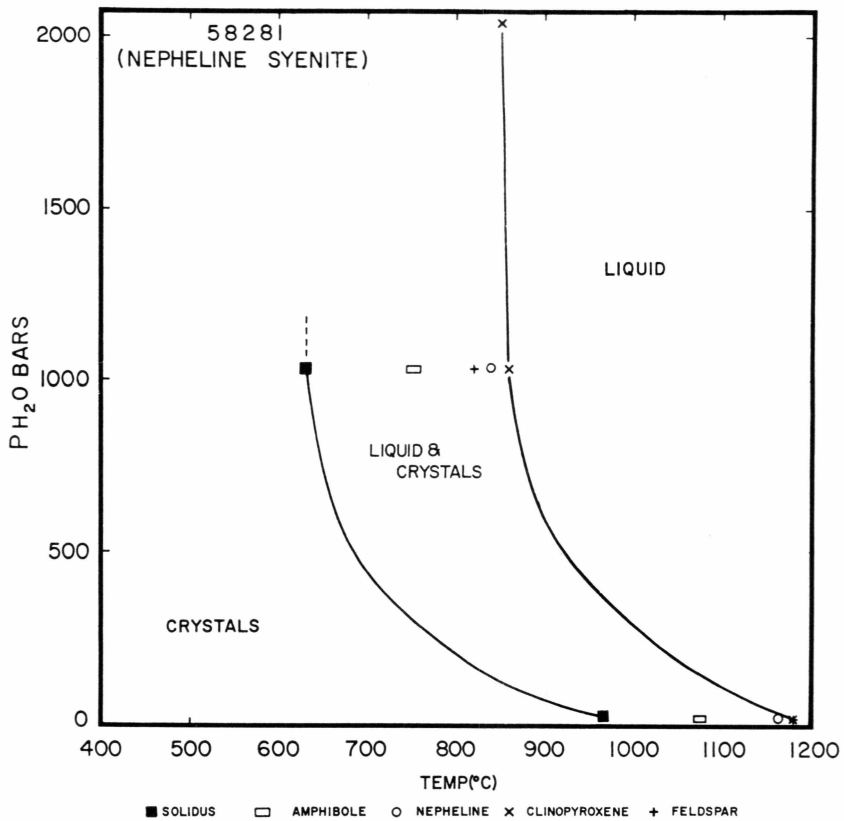   Magnetite is an ubiquitous phase in all runs.

Fig. 4. Melting relations for sample 58281 at water vapour pressures up to 2070 bars.
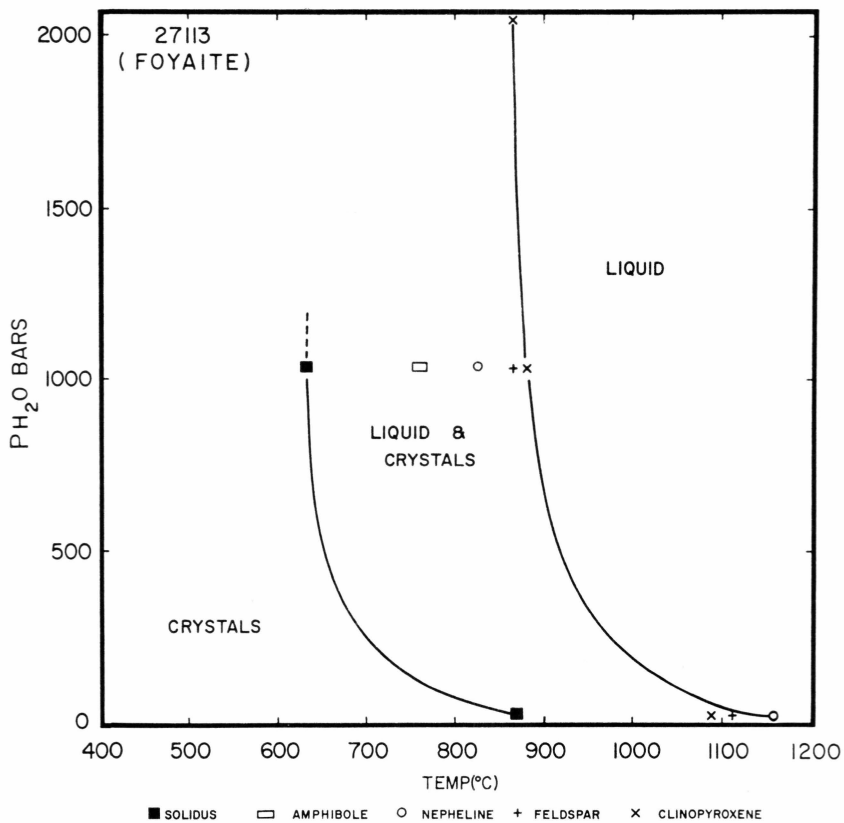

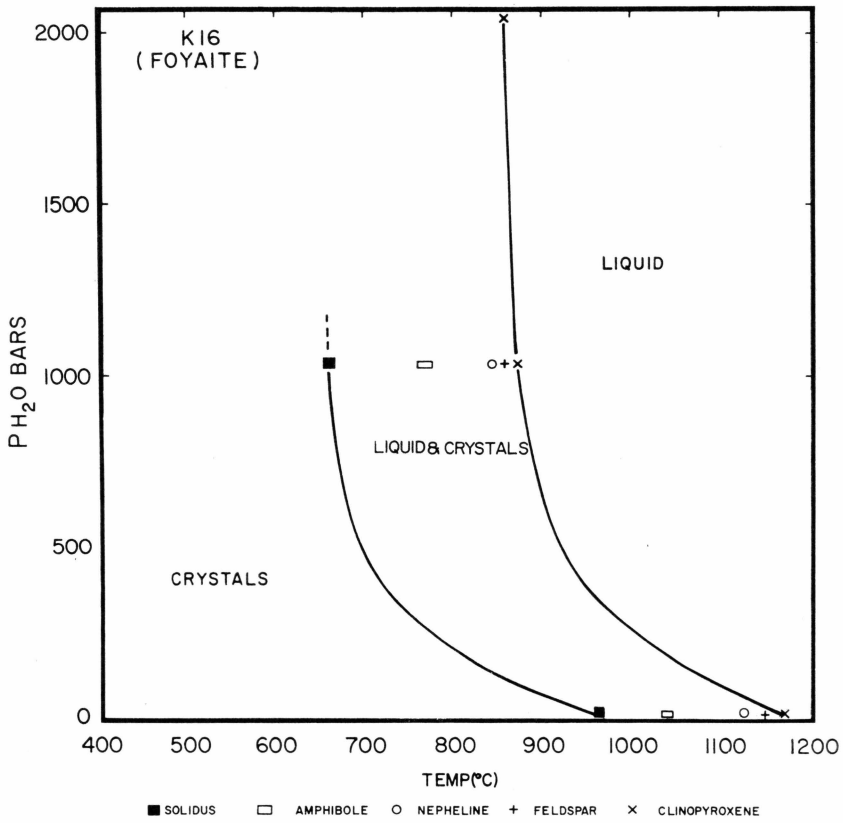Fig. 5. Melting relations for sample 27113 at water vapour pressures up to 2070 bars.

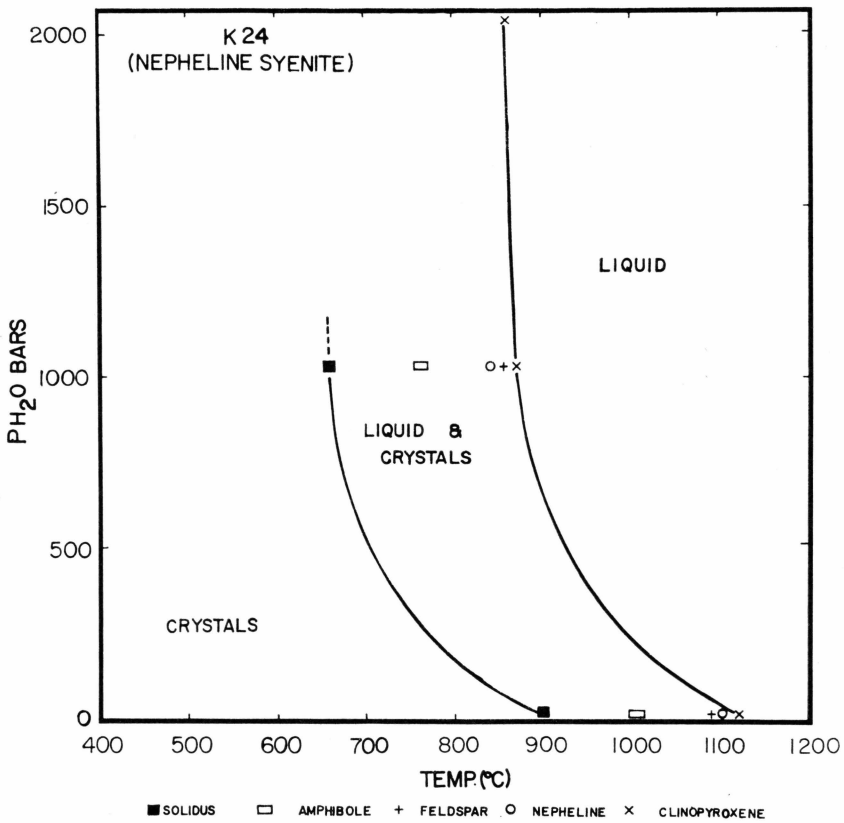Fig. 6. Melting relations for sample K 16 at water vapour pressures up to 2070 bars.

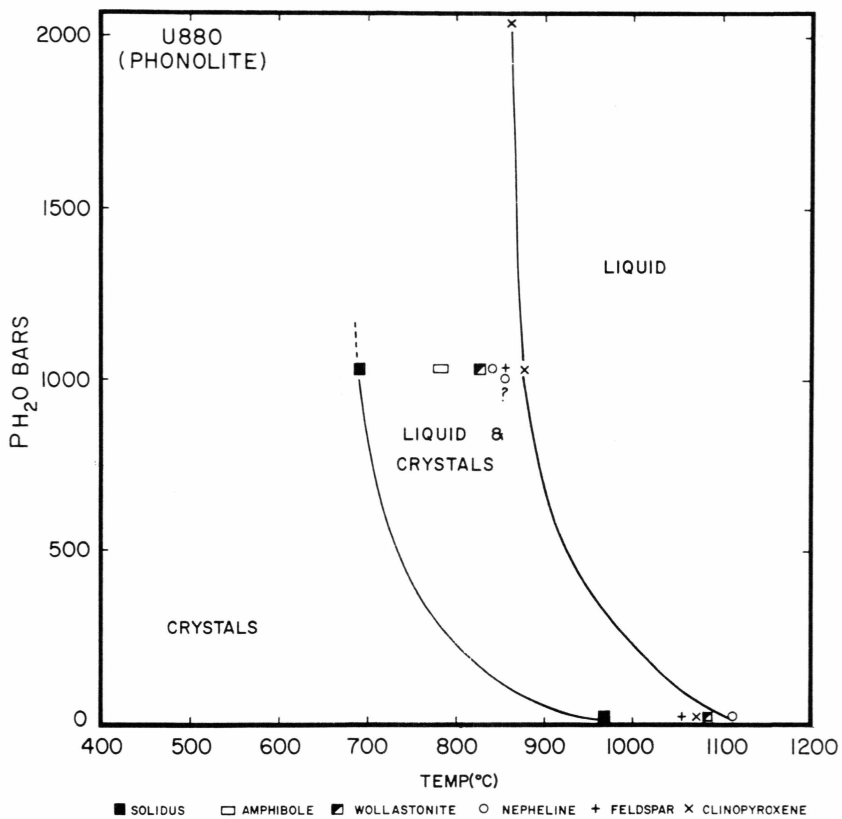Fig. 7. Melting relations for sample K 24 at water vapour pressures up to 2070 bars.

Fig. 8. Melting relations for sample U 880 at water vapour pressures up to 2070 bars.
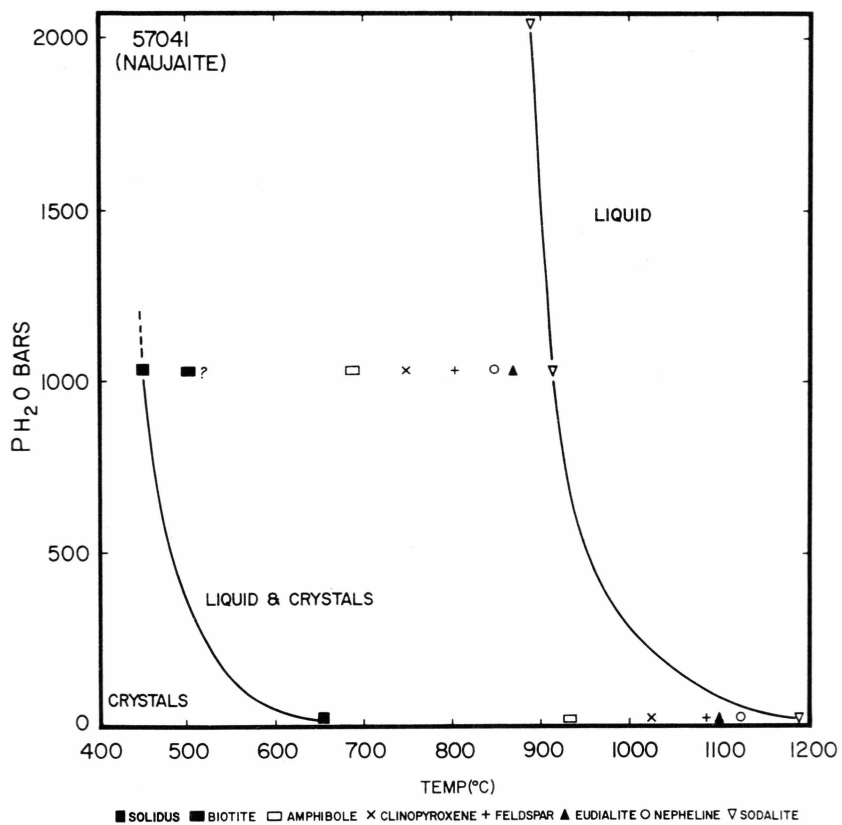

Fig. 9. Melting relations for sample 57041 at water vapour pressures up to 2070 bars.
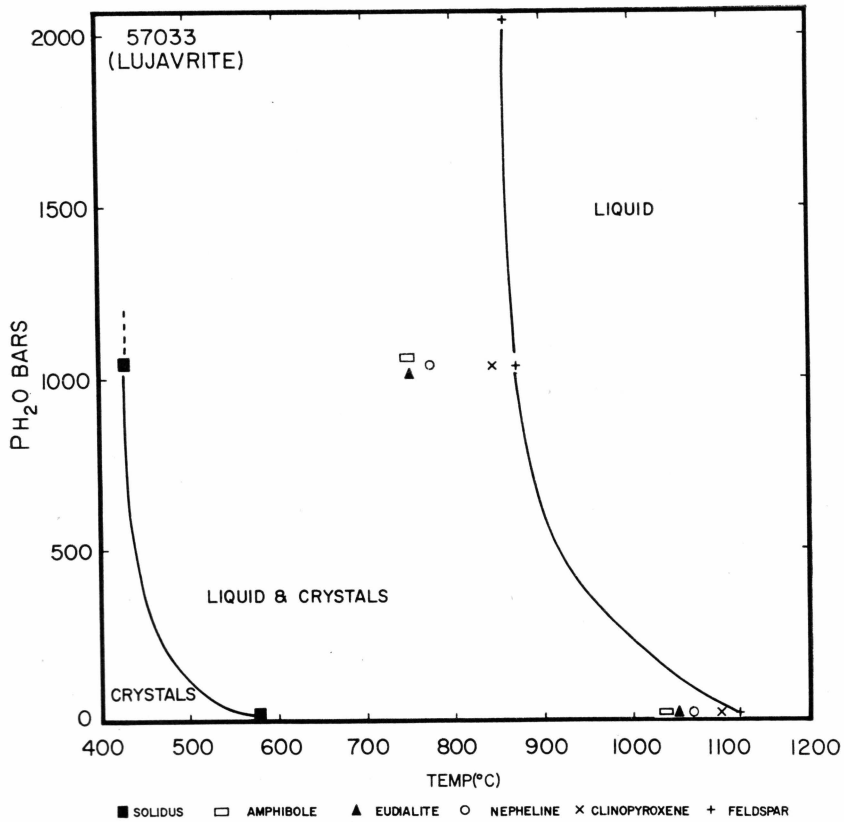
Fig. 10. Melting relations for sample 57033 at water vapour pressures up to 2070 bars.
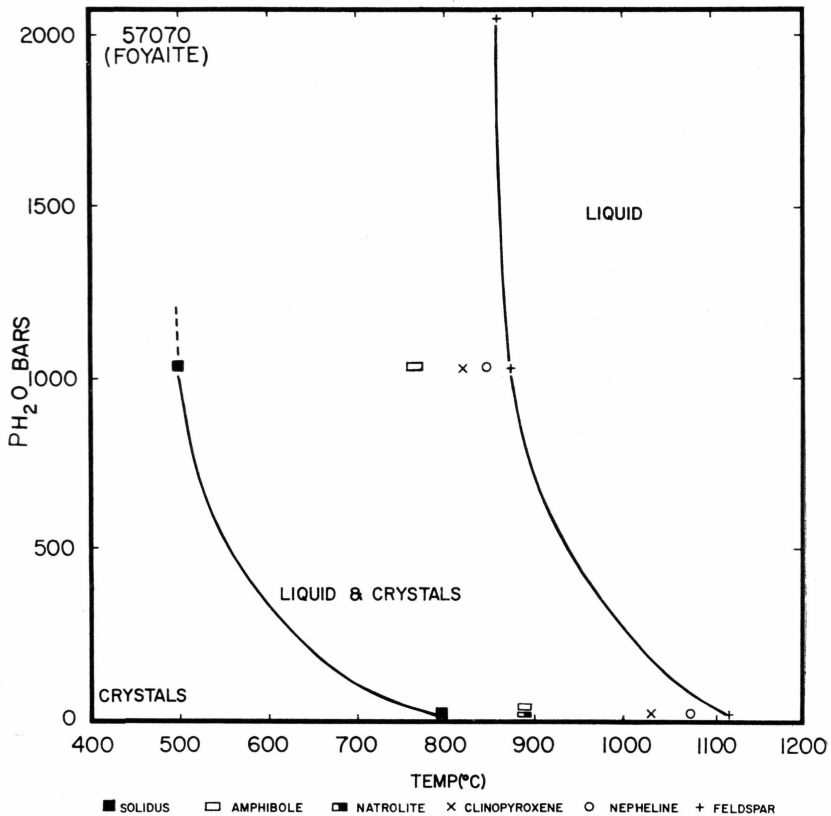

Fig. 11. Melting relations for sample 57070 at water vapour pressures up to 2070 bars.

U 880, 27113 and 57041 determined by Piotrowski and Edgar (1970). Although the exact partial oxygen pressure is not known in these experiments it is less than in the experiments at one atmosphere in air and is sufficiently low to prevent any magnetite in the sample oxidizing to hematite. As shown in Fig. 3 these conditions slightly lower liquidus temperatures in comparison to runs at atmospheric pressure in air. Tilley, Yoder and Schairer (1965) reported similar temperature lowering for basalts studied in a nitrogen atmosphere in comparison to their melting behaviour in air.

The lowering in melting temperatures under an argon atmosphere (Fig. 3) compared to those in air (Fig. 2) ranges from about 5° C to 25° C. Very approximately this lowering can be correlated with the total iron oxide content (Table II) in that samples with high iron oxide contents have greater lowering than those containing smaller amounts of total iron oxides.

The sequence of crystallization is slightly altered in some of the samples melted under the non-oxidizing (argon) conditions, and the amphibole in samples 57041, K 16 and K 24 crystallizes at a higher temperature under these conditions than at one atmosphere in air. The melting intervals are very similar under both conditions.

c) Experiments under Hydrothermal Conditions

Preliminary results of melting experiments and crystallization sequence for the Ilímaussaq samples (57041, 57070 and 57033) obtained by one of us (MKS) were included by Piotrowski and Edgar (1970) for comparative evaluations. The complete data for all the rocks are given in Table V and plotted on Figs. 4–8. For convenience the results of experiments on the Ilímaussaq rocks are given in Figs. 9–11.

At 1030 bars P_{H_2O} liquidus temperatures[1]) range from 875° C for nepheline syenite (58281) (Table V, Fig. 4) to 910° C for naujaite (57041) (Fig. 9). At 2030 bars P_{H_2O}, these temperatures are further lowered to 865° C and 890° C respectively. The slopes of the liquidus curves indicate that the first kilobar P_{H_2O} increment has a much greater effect in lowering temperatures than subsequent increments. The exact liquidus temperatures for foyaite (K 16) and nepheline syenite (K 24) could not be determined due to limitations in the strength of the externally heated pressure vessels used in this study. However, an estimated 95–98 percent glass was observed in K 16 at 885° C and at 875° C in K 24 at 1030 bars P_{H_2O}, indicating that these temperatures are very close to the true liquidus temperatures.

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[1]) Liquidus temperature is defined here as that temperatures at which the rock is completely melted *exclusive* of minor amounts of high melting minerals such as magnetite, corundum, etc.

Considering the diverse compositions of the rocks investigated, 25–35° C range of liquidus temperatures is remarkably small. There is, however, a very large range of melting intervals under hydrothermal conditions from 185° C for phonolite (U 880) to 460°C for naujaite (57041) .As discussed in a later part of this paper the length of melting interval can

Table V. *Results of Experiments Under Water Vapour Pressure*

(Only experiments indicating a phase change are listed).

Temp. (°C)	P_{H_2O} (bars)	Time (hours)	Products[1])
58281 Nepheline Syenite, Grønnedal-Íka, Greenland			
875...................	1030	72	Gl.
860...................	1030	80	Gl. + Cpx.
840...................	1030	100	Gl. + Cpx. + Ne.
820...................	1030	100	Gl. + Cpx. + Ne. + Fp.
750...................	1030	180	Gl. + Cpx. + Ne. + Fp. + Am.
630...................	1030	212	Cpx. + Ne. + Fp. + Am.
865...................	2070	14	Gl.
850...................	2070	28	Gl. + Cpx.
Reversibility			
885...................	1030	40	Gl.
850...................	1030	80	Gl. + Cpx.
27113 Foyaite, Grønnedal-Íka, Greenland			
895...................	1030	20	Gl.
885...................	1030	20	Gl. + Cpx.
875...................	1030	30	Gl. + Cpx. + Fp.?
840...................	1030	48	Gl. + Cpx. + Fp.
825...................	1030	60	Gl. + Cpx. + Fp. + Ne.
760...................	1030	120	Gl. + Cpx. + Fp. + Ne. + Am.
625...................	1030	160	Cpx. + Fp. + Ne. + Am.
870...................	2070	10	Gl.
855...................	2070	12	Gl. + Cpx.
K 16 Foyaite, Kenya			
885...................	1030	32	Gl. + Cpx.?
875...................	1030	60	Gl. + Cpx.
855...................	1030	60	Gl. + Cpx. + Fp.
845...................	1030	60	Gl. + Cpx. + Fp. + Ne.
760...................	1030	90	Gl. + Cpx. + Fp. + Ne. + Am.
660...................	1030	192	Cpx. + Fp. + Ne. + Am.
875...................	2070	10	Gl.
865...................	2070	15	Gl. + Cpx.

[1]) Abbreviations are the same as footnote accompanying Table III.
    Iron oxides are present in the runs but have not been listed.

Table V (continued)

Temp. (°C)	P_{H_2O} (bars)	Time (hours)	Products
K 24 NephelineSy enite, Kenya			
865.....	1030	40	Gl. + Cpx.
855.....	1030	60	Gl. + Cpx. + Fp.
840.....	1030	60	Gl. + Cpx. + Fp. + Ne.
750.....	1030	100	Gl. + Cpx. + Fp. + Ne. + Am.
640.....	1030	168	Cpx. + Fp. + Ne. + Am.
870.....	2070	12	Gl.
860.....	2070	12	Gl. + Cpx.
U 880 Phonolite, Tanzania			
890.....	1030	24	Gl.
880.....	1030	48	Gl. + Cpx.
850.....	1030	72	Gl. + Cpx. + Fp.
840.....	1030	80	Gl. + Cpx. + Fp. + Ne.
830.....	1030	90	Gl. + Cpx. + Fp. + Ne. + Wol.
780.....	1030	100	Gl. + Cpx. + Fp. + Ne. + Wol. + Am.
700.....	1030	120	Gl.? + Cpx. + Fp. + Ne. + Wol. + Am.
880.....	2070	15	Gl.
855.....	2070	20	Gl. + Cpx.
57041 Naujaite, Ilímaussaq, Greenland			
910.....	1030	8	Gl.
900.....	1030	10	Gl. + Sod.
865.....	1030	48	Gl. + Sod. + Ne.? + Eud.
845.....	1030	48	Gl. + Sod. + Ne. + Eud.
800.....	1030	56	Gl. + Sod. + Ne. + Eud. + Fp.
745.....	1030	72	Gl. + Sod. + Ne. + Eud. + Fp. + Cpx.
685.....	1030	168	Gl. + Sod. + Ne. + Eud. + Fp. + Cpx. + Am.
500.....	1030	336	Gl. + Sod. + Ne. + Eud. + Fp. + Cpx. + Am. + Bi.?
450.....	1030	400	Gl.? + Sod. + Ne. + Eud. + Fp. + Cpx. + Am. + Bi?
430.....	1030	400	Sod. + Ne. + Eud. + Fp. + Cpx. + Am. + Bi.?
890.....	2070	10	Gl.
880.....	2070	10	Gl. + Sod.
57070 Foyaite, Ilímaussaq, Greenland			
885.....	1030	48	Gl.
875.....	1030	48	Gl. + Fp.
865.....	1030	48	Gl. + Fp. + Ne.?
850.....	1030	48	Gl. + Fp. + Ne.
820.....	1030	72	Gl. + Fp. + Ne. + Cpx.
765.....	1030	96	Gl. + Fp. + Ne. + Cpx. + Am.
500.....	1030	320	Gl.? + Fp. + Ne. + Cpx. + Am.
475.....	1030	320	Fp. + Ne. + Cpx. + Am.
875.....	2070	10	Gl.
860.....	2070	10	Gl. + Fp.

Table V (continued)

Temp. (°C)	P_{H_2O} (bars)	Time (hours)	Products
Reversibility			
890.....	1030	24	Gl.
865.....	1030	24	Gl. + Fp.
57033 Lujavrite, Ilímaussaq, Greenland			
885.....	1030	36	Gl.
875.....	1030	50	Gl. + Fp.
845.....	1030	60	Gl. + Fp. + Cpx.
785.....	1030	80	Gl. + Fp. + Cpx. + Ne.?
765.....	1030	90	Gl. + Fp. + Cpx. + Ne.
750.....	1030	100	Gl. + Fp. + Cpx. + Ne. + Eud. + Am.
430.....	1030	400	Fp. + Cpx. + Ne. + Eud. + Am.
865.....	2070	$10^1/_2$	Gl.
855.....	2070	$10^1/_2$	Gl. + Fp.
Reversibility			
885.....	1030	36	Gl.
870.....	1030	36	Gl. + Fp.

be directly correlated with the agpaicity of the rock. For the Ilímaussaq rocks, the melting interval is shortened under P_{H_2O} conditions compared to the melting interval in experiments at one atmosphere. In contrast, the other rocks investigated showed greater melting intervals in experiments under P_{H_2O} conditions compared to the melting intervals under atmospheric conditions.

The results of the hydrothermal experiments may be summarized as follows:

i) The primary phase at the liquidus for all rocks, except 57041 in which sodalite is the primary phase (Figs. 4–11), is clinopyroxene or feldspar with the order of crystallization being feldspar-nepheline-clinopyroxene or clinopyroxene-feldspar-nepheline. For three of the samples, (58281, 27113 and U880) melting under P_{H_2O} conditions changes both the primary phase and the crystallization sequence in comparison to runs at atmospheric pressure (Fig. 2).

ii) Increasing the P_{H_2O} from 1030 to 2070 bars does not alter the primary phase at the liquidus.

iii) The temperature at which the primary phase appears for different compositions lies within a narrow range (870–910° C at 1030 bars P_{H_2O}).

iv) Amphibole is the last phase to crystallize in all samples although liquid remains well below the temperature of appearance of this phase, indicating changes in composition of both the liquid and crystalline phases down to the solidus temperature.

d) Hydrothermal Experiments under Controlled P_{O_2} Conditions

Two of the iron-rich specimens, foyaite (57070) and lujavrite (57033) from the Ilímaussaq Intrusion, were investigated under two different P_{O_2} conditions corresponding to the NNO[1] and HM[2] buffer assemblages at a total pressure of 1030 bars P_{H_2O}. Results are tabulated in Table VI and plotted on Fig. 12 as temperature against log P_{O_2} for a total pressure of 1030 bars P_{H_2O}.

Liquidus temperatures are lowered by 15° C and 20° C for foyaite (57070, Fig. 12) and lujavrite (57033, Fig. 12) respectively at the P_{O_2} of the HM buffer. With NNO buffer (representing a lower P_{O_2}), temperatures were lowered a further 5–10° C. The sloping dashed lines of Fig. 12 represent the changes in liquidus temperatures under the different P_{O_2} conditions. This temperature lowering, although only slightly greater than the temperature error of the experiments, is believed to be real, and is in agreement with the results obtained by Osborn (1963) and Fudali, Muan and Osborn (1962) for experiments with basalts.

Under controlled P_{O_2} conditions, clinopyroxene is the first phase to crystallize in both samples in contrast to feldspars which are the primary
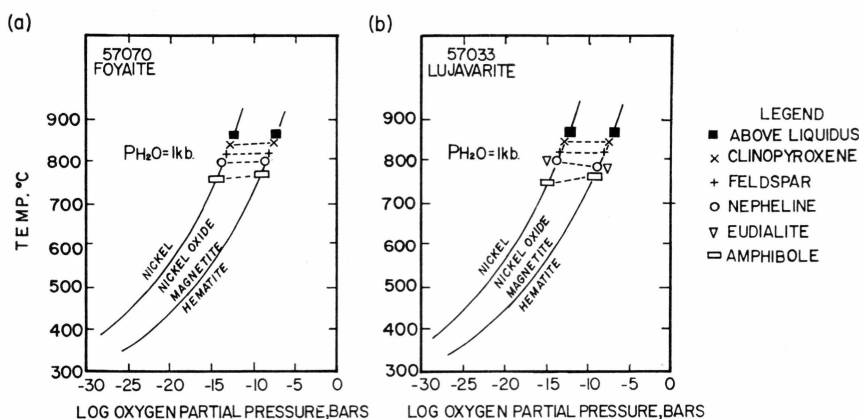

Fig. 12 a and b. Combined effect of water vapour and partial oxygen pressure on the crystallization sequence of agpaitic rocks from the Ilímaussaq Intrusion, South Greenland.

[1] NNO = Nickel-Nickel oxide.
[2]   HM = Hematite-Magnetite.

Table VI. *Results of Experiments Under Controlled P_{O_2} Conditions and at a Total Pressure of 1030 Bars P_{H_2O}*

(Only experiments indicating a phase change are listed).

Temp. (°C)	Time (hours)	Products[1]
57070 Foyaite, Ilímaussaq, Greenland		
A. *With NNO Buffer Assemblage*		
860	48	Gl.
845	72	Gl. + Cpx.
835	72	Gl. + Cpx. + Fp.
820	72	Gl. + Cpx. + Fp. + Ne.
760	90	Gl. + Cpx. + Fp. + Ne. + Am.
B. *With HM Buffer Assemblage*		
880	18	Gl.
850	24	Gl. + Cpx.
825	72	Gl. + Cpx. + Fp.
800	80	Gl. + Cpx. + Fp. + Ne.
775	100	Gl. + Cpx. + Fp. + Ne. + Am.
57033 Lujavrite, Ilímaussaq, Greenland		
A. *With NNO Buffer Assemblage*		
865	48	Gl.
855	48	Gl. + Cpx.
835	72	Gl. + Cpx. + Fp.
800	80	Gl. + Cpx. + Fp. + Eud. + Ne.
755	90	Gl. + Cpx. + Fp. + Eud. + Ne. + Am.
B. *With HM Buffer Assemblage*		
870	28	Gl.
860	28	Gl. + Cpx.
820	72	Gl. + Cpx. + Fp.
805	72	Gl. + Cpx. + Fp. + Ne.?
795	78	Gl. + Cpx. + Fp. + Ne. + Eud.
770	96	Gl. + Cpx. + Fp. + Ne. + Eud. + Am.

[1] Abbreviations are the same as in the footnote of Table III.

  Magnetite is an ubiquitous in all runs.

crystalline phases in unbuffered (P_{H_2O}) and in experiments at atmospheric pressure. Although the temperatures of appearance of various phases differed slightly under the conditions of the two buffers used no change was observed in the sequence of crystallization.

Unfortunately solidus temperatures could not be determined for these rocks because at lower temperatures the effectiveness of the buffer is considerably diminished preventing accurate control of P_{O_2} (EUGSTER and WONES, 1962).

DISCUSSION OF RESULTS

a) Introduction

As mentioned earlier, the present study has been undertaken as a continuation of the previous investigation (PIOTROWSKI and EDGAR, 1970) in an attempt to explain the differences in melting behaviour of the volatile-rich agpaitic rocks from the Ilímaussaq Intrusion compared to miaskitic alkaline undersaturated rocks. The results reported in this paper confirm that the long melting intervals at atmospheric pressure, found in the previous study, persist under the more geologically feasible conditions used in the present experiments. However, when interpreting the results of both studies the limitations of the methods used must be kept in mind.

These limitations are as follows:–

a) Differences in reaction kinetics between the laboratory studies and the reactions in nature. Kinetics may be particularly slow in the runs at one atmosphere where there is no fluxing effect of water, and the liquidus temperatures must be considered as maximum temperatures.

b) The natural starting materials represent the final products of a process or processes which may have been accomplished in a number of different ways, whereas in the laboratory our results are based on a single procedure i.e. heating and *quenching*. In nature, for example, many of the rocks have been slowly cooled and may have undergone post-consolidation changes. By reversing the process, as has been done in these experiments, we may be overlooking some of the natural factors involved in the genesis of the rock.

c) Inherent difficulties in the experimental techniques, principally: loss of Fe due to alloying with Pt, which is not believed to be a serious error (see PIOTROWSKI and EDGAR, 1970, p. 18–19); problems of establishing equilibrium criteria for the liquidus curves (see PIOTROWSKI and EDGAR, 1970, p. 17–18). In the present study, selected runs were reversed i.e. approached from both a low temperature solid assemblage and a high temperature liquid assemblage, and are noted on the Tables of run data. In anhydrous experiments, temperatures are believed to be within $\pm 10°$ C, in P_{H_2O} and P_{O_2} runs temperatures are within $\pm 5°$ C of the stated values.

Despite these limitations, there is, in many cases, a close correspondence between the observed crystallization sequences and those deduced from textural and field relations. In the few cases where field and petrographic evidence provides an indication of liquidus and solidus temperatures, there is also a close agreement with the experimentally determined results. These results attest to the usefulness of the technique.

The discussion of the present results will be concerned with four major topics:–

(1) comparison of melting relations,

(2) the relationship between agpaicity and volatile contents,

(3) the effects of P_{H_2O} and P_{O_2} on the crystallization of undersaturated alkaline rocks,

(4) and a comparison of field and laboratory evidence of their genesis.

b) Comparison of Liquidus Temperatures under Atmospheric, Water Vapour and Partial Oxygen Pressure Conditions

Liquidus temperatures and primary phases at the liquidus for experiments under atmospheric pressure, under P_{H_2O} and under P_{O_2} conditions are summarized in Table VII.

The principal effect of water vapour pressure is in lowering liquidus temperatures by amounts ranging from 235° C (U 880) to 325° C (58281)

Table VII. *Liquidus Temperatures in °C and Primary Phases*[1])
Under Different Experimental Conditions

Rock No.	Liq. 1 Atm./ Primary Phase	Liq. Argon/ Primary Phase	Liq. 1030 Bars P_{H_2O}/ Primary Phase	T = Liq 1 Atm. Liq. 1030 Bars P_{H_2O}	Norm. Alk. Fp. + Ne. + Lc. + Ns.	Liq. 1030 Bars P_{H_2O} with NNO Buffer	Liq. 1030 Bars P_{H_2O} with HM Buffer
57041	1195/Sod.[2])	1195/Sod.[2])	910/Sod.	285	72.50	—	—
57070	1125/Fp.[2])	—	885/Fp.	240	68.57	855/Cpx.	860/Cpx.
57033	1125/Fp.[2])	—	880/Fp.	245	66.06	860/Cpx.	870/Cpx.
58281	1185/Cpx.	—	875/Cpx.	310	75.03	—	—
27113	1155/Ne.[2])	1125/Ne.[2])	885/Cpx.	270	70.60	—	—
K 16	1175/Cpx.	1165/Cpx.	885/Cpx.	290	75.11	—	—
K 24	1120/Cpx.	1095/Cpx.	875/Cpx.	235	62.71	—	—
U 880	1123/Ne.[2])	1110/Cpx.[2])	885/Cpx.	238	67.49	—	—

[1]) Abbreviations are the same as those in the footnote of Table III.
[2]) From PIOTROWSKI and EDGAR (1970).

for the first kilobar increment of pressure. Considering the diversity of compositions used this lowering is fairly consistent and represents the minimum liquidus temperature as in all runs the capsules exuded water on quenching indicating that the liquid was water-saturated. Variations in lowering depend on the relative abundances of felsic (principally nepheline and alkali feldspars) to mafic (principally clinopyroxene) minerals in the system. This is more fully discussed in a later section.

Increase in pressure favours the concentration of water in the silicate melts. Due to the low molecular weight of water in comparison to silicates, small changes in the concentration of dissolved water produce large changes in both liquidus and solidus temperatures. However, as the vapour pressure increases, the relative solubility of water decreases and the liquidus temperatures decrease only slightly.

Under P_{H_2O} conditions there is also a change in the primary phase at the liquidus for some samples in comparison to the primary phase at one atmosphere pressure. In the foyaite (27113) and phonolite (U880), clinopyroxene is the primary phase at 1030 and 2070 bars P_{H_2O} in contrast to nepheline at one atmosphere. This phase change is possibly related to the large depression of fusion temperatures of nepheline and feldspars compared with clinopyroxenes under P_{H_2O} conditions as has been demonstrated in synthetic systems involving these mineral components (YODER, 1958). The effect of the larger lowering of melting temperatures of nephelines and feldspars compared to clinopyroxenes is clearly shown in Fig. 13, where the lowering of liquidus temperatures between one atmosphere and 1030 bars P_{H_2O} has been plotted against normative percentages of felsic minerals (alkali feldspars, nepheline, leucite, NS). The linear relationship indicates that this is probably the main factor in the differential lowering of liquidus temperatures.

With the exception of the agpaitic rocks, which will be discussed later, the temperature intervals in which the principal crystalline phases appear, particularly under hydrothermal conditions, is very short (30–40° C). This implies that in nature the liquids from which these rocks have crystallized have compositions lying close to what would be the cotectic boundary curves in the corresponding complex synthetic systems. The close correspondence between some of the rock compositions and certain synthetic systems has previously been noted by PIOTROWSKI and EDGAR (1970, figs. 12–15).

The effect of controlling P_{O_2} at a total pressure of 1030 bars P_{H_2O} is to further lower the melting temperatures of the two samples investigated, as noted previously, and to change the primary phase to clinopyroxene from feldspar, the primary phase in the runs without P_{O_2} control. Otherwise, the sequence of crystallization for both rocks is unchanged under P_{O_2} conditions. This change in primary phase may have important
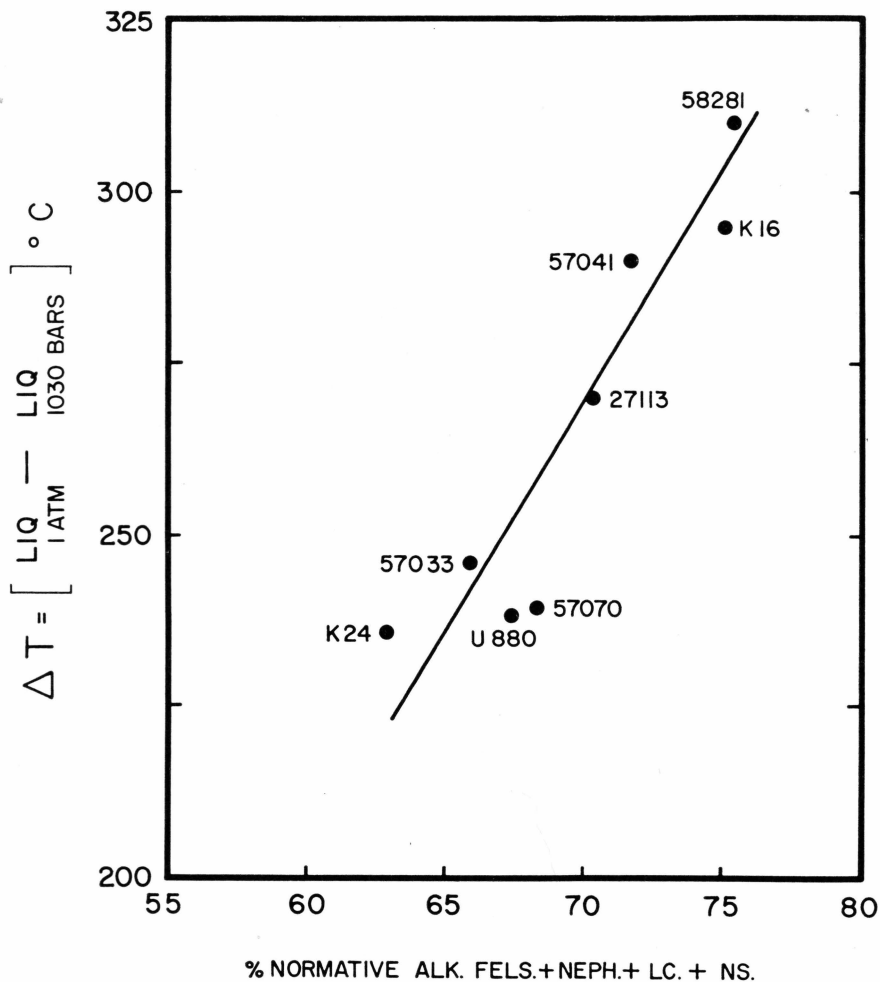
Fig. 13. Relationship between ΔT (Liq. Atm. – Liq. 1030 bars) °C and the norma-
tive contents of feldspathic minerals. (For sample numbers, see Table I.).

implications in determining whether an alkaline rock will follow an agpai-
tic or miaskitic trend, as discussed in a later section.

c) Relationship between Agpaitic Indices, Melting Intervals and Volatile Contents

In the previous study of melting of rocks from the Ilímaussaq Intru-
sion, PIOTROWSKI and EDGAR (1970, p. 40–41) noted a strong correlation
between the melting intervals, agpaitic indices and volatile contents of
the rocks. Rocks with a high agpaitic index and rich in volatile-bearing
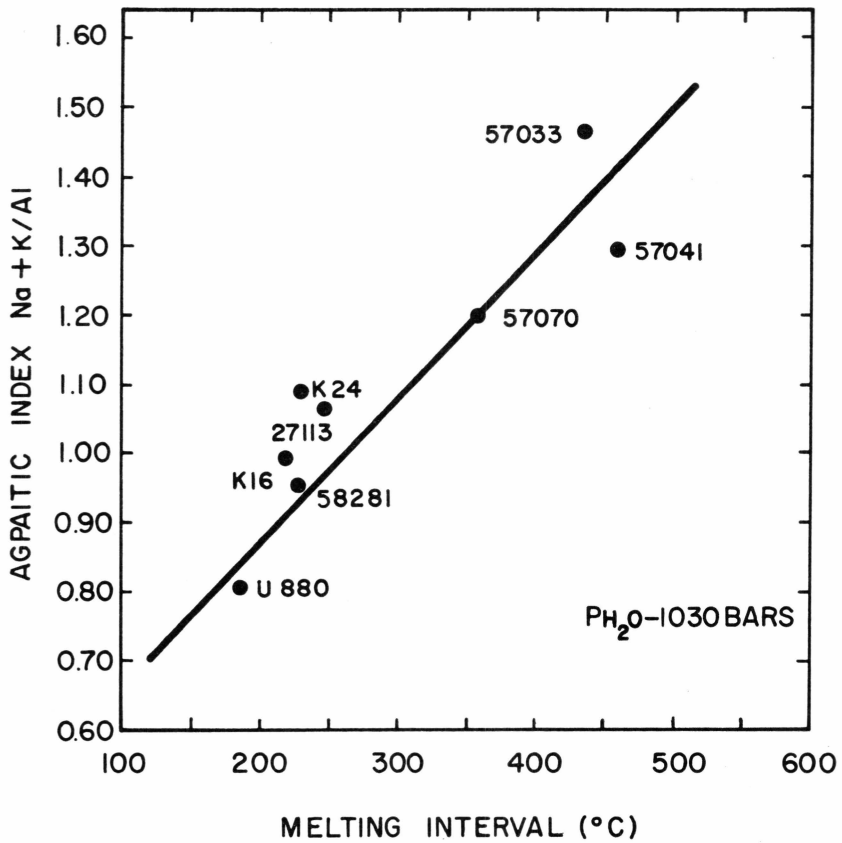minerals had a much longer melting interval than miaskitic rocks with

Fig. 14. Relationship between melting intervals and agpaitic indices at 1030 bars P_{H_2O}. (For sample numbers, see Table I.).

Table VIII. *Modal Content of Volatile Bearing Minerals,*
Agpaitic Indices and Melting Intervals

Rock	Modal Volatile Bearing Minerals[1]	Agpaitic Index	Melting Interval (at 1030 Bars P_{H_2O} °C)
57041...................	49.0[2]	1.29	460
57033...................	19.0[2]	1.47	450
57070...................	10.2	1.18	365
27113...................	8.1	1.05	260
58281...................	7.1	0.95	240
K24....................	6.1	1.08	240
U880...................	5.0	0.80	185
K16....................	4.0	0.99	220

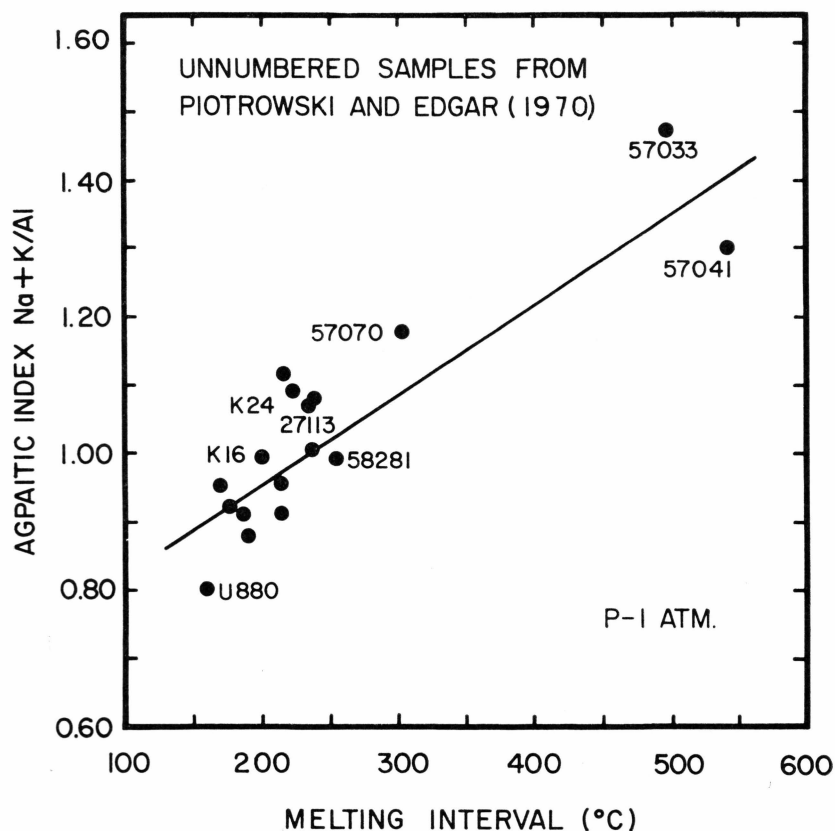[1]) Exclusive of very fine grained material.

[2]) From Ferguson (1964).

Fig. 15. Relationship between melting intervals and agpaitic indices at one atmosphere in air. (For sample numbers, seee Table I.).

lower volatile contents. To a first approximation the relationship between the agpaitic index and the melting interval at atmospheric pressure was shown to be linear (PIOTROWSKI and EDGAR, 1970, Fig. 16) but no explanation of this phenomenon was offered.

In the present study this relationship is shown to persist in experiments at 1030 bars P_{H_2O}. Data for the melting intervals, agpaitic indices and volatile-bearing minerals are given in Table VIII and plotted in Fig. 14. In Fig. 15 rocks of the present study and those of PIOTROWSKI and EDGAR melted at one atmosphere pressure have been plotted. Although there is considerable scatter in both of these diagrams the general trend of high agpaicity corresponding to long melting intervals is undoubtedly true.

The probable explanation of these long melting intervals in agpaitic rocks is related to their higher alkalis and higher contents of certain volatiles in comparison to miaskitic undersaturated alkaline

3*

rocks. and to the "fixation" and concentration of these volatiles in the solid and liquid phases respectively rather than in the gaseous phase during cooling.

Agpaitic rocks are richer in the volatiles Cl, F, P and S than miaskitic rocks or any other igneous rock (Gerassimovsky, 1965. 1966). During crystallization these volatiles, particularly Cl and F, tend to be "fixed" in the sodium-rich minerals, sodalite, eudialyte, arfvedsonite and probably villiaumite. Kogarko and Gulyayeva (1965) have shown that halogens lower the crystallization temperatures and viscosity, and change the fields of crystallization and the degree of polymerization of anions in a silicate melt. On the basis of calculations on the constants of exchange reactions between silicates, fluorides and chlorides, and from data on silicate-halide systems Kogarko and Rhyabchikov (1961) conclude that separation of volatile components into the gaseous phase becomes less likely as the alkalinity of the melt increases. Also the activity coefficients of Cl and F are much lower in alkaline liquids. Thus in the highly alkaline melts forming agpaitic rocks, the volatile components are likely to be present in the liquid and solid phases rather than in the gaseous phase. In addition, separation of the gas phase will depend on the critical point of water under the P-T conditions of formation of the rock, the solubility of volatiles in the melt and the amount of volatiles available after crystallization of the solid phases.

The longer melting interval in agpaitic rocks in comparison to miaskitic rocks basically depends on two factors, the presence of three or more important volatiles (especially H_2O, Cl, F etc.) instead of one (H_2O) in the miaskitic rocks, and the initial excess of alkalies, principally Na, in comparison to Al in these melts. This idea may be expounded with reference to the melting results of the present study. Sample 57041 contains sodalite, eudialyte and amphibole as the principal volatile-bearing minerals, crystallizing in the sequence sodalite-eudialyte-amphibole. In these minerals the principal volatile in sodalite is Cl, in eudialyte F, Cl and OH, and in amphibole OH and F. At one atmosphere pressure in 57041 sodalite appears at 1190° C (liquidus), eudialyte at 1095° C and amphibole at 932° C (Fig. 2). At 1030 bars P_{H_2O} the sequence is the same but the temperature ranges are narrower (Fig. 9, Table V).

On the assumption that the original melt contained Cl⁻, F⁻ and OH⁻ and an excess of alkalies (principally Na) with respect to Al, the excess Na combined with the Cl forming potential NaCl molecules which unite with the nepheline forming sodalite crystallizing at the liquidus. On further cooling the amount of sodalite increases and the concentration of Cl in the residual melt decreases. (Increase in sodalite was noted both optically and in the X-ray diffraction patterns). The decrease in the concentration of Cl will supress the crystallization of sodalite as a principal

phase but sodalite may persist as a minor phase throughout the crystallization history of the melt or cease to crystallize at a stage where residual Cl is used up. Such a condition would result in the enrichment of OH and/or possibly F to initiate the crystallization of eudialyte. This crystallization would progress to a stage where F and OH are sufficiently enriched to cause the precipitation of amphibole (F-rich type). Amphibole will now increase and continue to crystallize until the solidus is reached, or until a volatile-rich gas phase develops (below the critical temperature) and any remaining volatiles are lost as this phase is dissipated. Although this is a very simple explanation of what is undoubtedly a complex process in nature, it explains why agpaitic rocks containing at least three volatiles rather than a single volatile as in most rocks, each acting more or less independently and dominating one period of the cooling sequence, produce long melting intervals.

This hypothesis may also be considered in the light of field evidence on the differentiation at Ilímaussaq. The veining in naujaite may possibly be the result of the above mechanism and especially the sodalite rich veins, termed sodalitites by Ussing (1912), may represent differentiates formed during the primary "chlorine" (or "sodalite") stage of the magmatic crystallization. The absence or presence of sodalite in the later members would depend on the original concentration of Cl in the melt and the extent of fractionation of the melt. The presence of sodalite as a minor phase in lujavrites has been noted by Sørensen (1958) and Ferguson (1964) but no sodalite was present in the sample studied.

In a normal agpaitic sequence of crystallization, the later members, such as lujavrites, are enriched in F primarily due to its failure to be incorporated in earlier minerals e.g. nepheline, feldspar and aegirine. Thus it is mainly contained in eudialyte and arfvedsonite. Any excess of F and Na not used in these phases will form villiaumite (NaF) as a magmatic phase or as replacement product of earlier minerals. Villiaumite in naujaites and lujavrite has been reported by Bondam and Ferguson (1962) but was not present in the samples studied.

Comparison of data in Figs. 9–11 and in Table II shows that field of crystallization of amphibole is related to the fluorine content of the rock. Thus the F content of the residual melt modifies the appearance of amphibole- and aegirine-rich lujavrites and the presence of these rocks at Ilímaussaq indicates that the role of F in the melt became important towards the end stages of the crystallization history of the Intrusion.

Comparison of the temperatures of appearance of sodalite, eudialyte and amphibole in sample 57041 at 1 atmosphere and at 1030 bars P_{H_2O} (Fig. 9) indicates that there is a much shorter temperature interval between crystallization of the sodalite and eudialyte at 1030 bars P_{H_2O} than at one atmosphere pressure. In the hydrothermal runs the liquid is saturated

with water. Thus the higher concentration of (OH), relative to the one atmosphere runs, may explain the earlier eudialyte crystallization.

In samples 57033 (lujavrite) and 57070 (foyaite), there are only two important volatiles, H_2O and F. In both samples the H_2O content is much higher than in 57041 (Table II) and amphibole crystallizes earlier than in 57041 due to the higher OH^- concentration.

Lack of data does not permit any comment on the role played by other volatiles in this hypothesis with the exception of CO_2. Sample K 24 contains the highest CO_2 content of the rocks studied (Table II) but has a short melting interval. This agrees with GERASSIMOVSKY (1966) who has suggested that CO_2 is probably relatively unimportant in the genesis of agpaitic rocks where it is usually low, although it is a common constituent of miaskitic rocks.[1]

d) Importance of P_{O_2} in the Crystallization of Undersaturated Alkaline Rocks

The importance of varying P_{O_2} in the crystallization of basalts has been recognized for many years (*cf.* KENNEDY, 1948; OSBORN, 1959, 1963; YODER and TILLEY, 1962; FUDALI, 1965 *etc.*), and its importance has been stressed for undersaturated alkaline rocks (EDGAR and NOLAN, 1967). P_{O_2} may play an important role in determining whether a magma follows a miaskitic (subalkaline) or agpaitic (peralkaline) trend during crystallization. Preliminary results on the two agpaitic samples from the Ilímaussaq Intrusion suggest a possible mechanism whereby fluctuating P_{O_2} conditions during crystallization might provide a mechanism by which a miaskitic or agpaitic crystallization trend might take place.

Buffered runs done under controlled P_{O_2} conditions at a constant total water vapour pressure have a considerably lower P_{O_2} than experiments at P_{H_2O} of 1030 bars but unbuffered (EUGSTER, 1959). The data in Table VI and Fig. 12 show that the lower P_{O_2} conditions decrease liquidus temperatures and also change the primary phase at the liquidus from a feldspathic mineral to clinopyroxene. Therefore under low P_{O_2} the early crystallization of aegirine (or an acmitic pyroxene) would be expected and may be important in determining whether a magma follows a miaskitic or agpaitic trend. Under conditions of low P_{O_2} (buffered runs) the early crystallization of clinopyroxene, rather than feldspar or nepheline, will enrich the residual liquids in Al_2O_3 and possibly Na_2O, depending on the composition of the clinopyroxene. If the magma was originally undersaturated, and differentiation could take place between the crystallization of clinopyroxene and the feldspathic phases or the residual liquid

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[1] CO_2 trapped as gas-liquid inclusions in nephelines (ROEDDER, 1965) would not participate in the reactions described.

could be removed crystallization might follow a miaskitic trend. In contrast early crystallization of nepheline, feldspar or sodalite under high P_{O_2} conditions (unbuffered runs) would deplete the residual liquid in alumina and might produce an agpaitic trend.

The magnitude of this effect will depend to some extent on the composition of the clinopyroxene crystallizing at the liquidus. If the early clinopyroxene is a diopsidic augite, as is the case from textural evidence in many alkaline complexes, then the residual liquid will be depleted in Ca and Al and the subsequent crystallization trend might be agpaitic. However, in the case of the early crystallizing pyroxene being acmitic (or hedenbergitic) the residual magma will be depleted in Na and Fe and the subsequent trend might be expected to be miaskitic.

In comparison to most alkaline rocks those of Ilímaussaq are very low in CaO and MgO (Table II) and consequently the clinopyroxenes are acmitic. Semiquantitative electronmicroprobe analysis of the clinopyroxenes formed at 5° C below the liquidus in 57070 and 57033 show that CaO and MgO are negligible, thus the conditions of our experiments and the natural processes do not differ too greatly.

GERASSIMOVSKY (1966) in a review of the geochemical differences between agpaitic and miaskitic nepheline syenites concludes (p. 115) that crystallization of intrusive rocks is governed not only by the chemical properties of the melt but also by the temperature, pressure and sequence and rate of crystallization. He also states (p. 116) that magmatic differentiation of an alkaline melt initially leads to the formation of nepheline syenites of the miaskite series, and subsequently produces agpaitic nepheline syenites with a higher content of rare and dispersed elements. The results of our melting experiments under different P_{O_2} conditions suggest a process whereby these two different types of nepheline syenites might be produced. In the early stages of crystallization under low P_{O_2} conditions (corresponding to the buffered experimental runs) the rocks will be miaskitic while on further crystallization with increasing P_{O_2} they would become agpaitic. In this connection FERSMAN (1937) suggested that increase in the oxygen content (which may be approximately correlated with increased P_{O_2}) of a high alkaline melt would produce complex anions such as $(TiO_4)^{-4}$, $(ZrO_4)^{-4}$ and $(FeO_4)^{-5}$. GERASSIMOVSKY (1966, p. 117) states that "residual melts which gave rise to agpaitic nepheline syenites probably owed their origin to more complex processes" (than crystallization differentiation, diffusion, assimilation etc.). The present results suggest that one such process is increased P_{O_2} due to early crystallization (and removal) of an Al-poor mineral such as clinopyroxene. The studies of BAILEY and SCHAIRER (1966) in the system Na_2O-Al_2O_3-Fe_2O_3-SiO_2 indicate that an initially undersaturated melt is not a necessary prerequisite to an undersaturated peralkaline trend provided Fe^{+3}

may substitute for Al^{+3} in feldspars and nephelines, a tendency which would be enhanced under high P_{O_2} conditions.

Under natural conditions it is unlikely that P_{O_2} would remain constant but might be expected to increase, decrease or even fluctuate due to reactions between the solid and liquid phases. The thin feldspar-rich and pyroxene-rich bands in the lujavrites of Ilímaussaq reported by Ferguson (1964) may have been produced by fluctuations in the P_{O_2} during crystallization; the feldspar bands forming during high P_{O_2} conditions, the pyroxene-bands during low P_{O_2} conditions.

e) Correlation of Experimental Results with Field and Petrographic Data

The applicability of melting experiments to the genesis of alkaline rocks may be evaluated by comparing the liquidus and solidus temperatures and crystallization sequences with those deduced from field and petrographic evidence. Data on liquidus and final consolidation temperatures for most igneous rocks are either not known or within such a wide range that they are of little use when attempting a comparison with laboratory data. For the agpaitic rocks from the Ilímaussaq Intrusion, Sørensen (1958) and Ferguson (1964) have shown that naujaite formed in the early stages of magmatic differentiation whereas the lujavrite crystallized from a rest magma. In the melting experiments naujaite (57041) has a liquidus temperature of 910° C at 1030 bars P_{H_2O} and lujavrite has a liquidus of 880° C at this pressure; this sequence being in agreement with the sequence of crystallization obtained from field relations. For the lujavrite Sørensen (1960) concluded that consolidation took place around 400° C, a value in very close agreement to the experimentally determined beginning of melting temperature (430° C at 1030 bars P_{H_2O}) for this rock. Similar data for other rocks studied are not available.

Phenocrysts and idiomorphic crystals in an igneous rock are believed to represent the first phases to crystallize from a magma, and therefore these phases should appear at, or close to, the liquidus in the melting experiments. Sodalite occurs as idiomorphic crystals in naujaite (57041) and is also the primary phase at its liquidus at 1030 bars P_{H_2O}. In foyaites 57070 and K 16, feldspar and nepheline form idiomorphs; in the former feldspar appears as the primary crystallizing phase whereas in the latter clinopyroxene is the primary crystallizing phase but is closely followed by feldspar and nepheline. Similarly in nepheline syenite (K 24) nepheline occurs as idiomorphs but the primary crystallizing phase is clinopyroxene again closely followed by nepheline and feldspar. In phonolite (U 880) nepheline and clinopyroxene form phenocrysts and both occur as primary phases at the liquids in the melting experiments. Thus there is generally

Table IX. *Experimentally Determined and*
Petrographically Deduced Sequences of Crystallization of the Rocks Studied
at 1030 Bars P_{H_2O}

Ilímaussaq Suite, Greenland

Rock name	Experimentally determined	Petrographically deduced
Naujaite (57041)	Sodalite-eudialyte-nepheline-feldspar-clinopyroxene-amphibole	Sodalite-nepheline-feldspar-pyroxene-amphibole (SØRENSEN, 1958, p. 12)
Foyaite (57070)	Feldspar-nepheline-pyroxene-amphibole	Feldspar-nepheline-sodalite?-pyroxene-amphibole (present study)
Lujavrite (57033)	Feldspar-pyroxene-nepheline-eudialyte, amphibole	First nepheline and sodalite were deposited then feldspar and some eudialyte crystals and finally the interstitially trapped magma crystallized into arfvedsonite (SØRENSEN, 1962, p. 148). No sodalite is present in the rock studied and mafics are afrvedsonite and aegirine.

Grønnedal-Íka Suite, Greenland

Foyaite (27113)	Clinopyroxene-feldspar-nepheline-amphibole	Feldspar-nepheline-pyroxene-biotite or amphibole (EMELEUS, 1964)
Nepheline syenite	Clinopyroxene-$\left(\begin{smallmatrix}\text{nepheline-}\\\text{feldspar?}\end{smallmatrix}\right)$ feldspar-amphibole	Feldspar-nepheline-pyroxene-amphibole (EMELEUS, 1964)

Sample from Tanzania

Phonolite (U 880)	Pyroxene-feldspar nepheline-amphibole	Pyroxene-feldspar-nepheline-sphene?-amphibole (present study)

Rocks from Kenya

Foyaite (K 16)	Pyroxene-feldspar-nepheline-amphibole	Feldspar-pyroxene-nepheline-amphibole (present study)
Nepheline Syenite (K 24)	Pyroxene-feldspar-nepheline-amphibole	Nepheline-pyroxene-feldspar-amphibole-calcite

a good correlation between the petrographically deduced early crystallizing minerals and those determined in the melting experiments. DAWSON (1962) reported various proportions of feldspars, nepheline and pyroxenes in very rapidly cooled phonolitic lavas which would suggest any of those minerals can become the primary phase followed by other

minerals over short temperature intervals. The short temperature range over which these phases appear in our experiments support such an observation.

In Table IX the sequences of crystallization determined petrographically are compared with the experimentally determined sequences at 1030 bars P_{H_2O}. Generally there is good correlation, particularly for the Ilímaussaq samples. The main discrepancy is in the iron-bearing phases, clinopyroxene and amphiboles, and is probably caused by differences in P_{O_2} between the natural and laboratory conditions or attributable to the long and complicated crystallization histories of the plutonic rocks.

CONCLUSIONS

From the results of melting and crystallization of eight analysed alkaline rocks under water vapour and controlled oxygen pressures the following relationships have been established:

a) liquidus temperatures decrease by 240–300° C with the first 1030 bar increment of P_{H_2O} and by lesser amounts for subsequent increments,

b) sequences of crystallization are slightly altered under hydrothermal compared with dry (atmospheric) conditions,

c) for agpaitic rocks there is a very long melting interval at both atmospheric and water vapour pressure conditions compared with miaskitic rocks,

d) decreasing the P_{O_2} slightly lowers liquidus temperatures and changes the primary crystallizing phase from a feldspathic mineral (feldspar, nepheline or sodalite) to clinopyroxene compared with runs at higher P_{O_2}.

The long melting intervals of agpaitic rocks are believed to be due to their enrichment of certain volatiles and initial high alkali to alumina ratio in their parent liquids compared with miaskitic rocks. During crystallization these volatiles are concentrated in the liquid and solid rather than the vapour phase and become concentrated, more or less independently of one another, in the sodium-rich minerals (sodalite, eudialyte, arfvedsonite and villiaumite). Thus the variety and independent role played by these volatiles during crystallization prolongs the melting intervals of agpaitic rocks. In contrast, miaskitic rocks commonly have only one principal volatile (H_2O) and low initial alkali to alumina ratio, resulting in a shorter melting interval. It is indicative from the present study that Cl, F and H_2O are more important volatiles in modifying the crystallization history of alkaline-peralkaline melts than CO_2. The linearity of the relationship between agpaitic index and melting interval (Figs. 13 and 14) would be more emphatically established by choosing compositions of intermediate agpaicity.

Because of the early crystallization of clinopyroxene, rocks formed under low P_{O_2} conditions may follow a miaskitic trend of differentiation; whereas rocks formed under high P_{O_2} conditions crystallizing early feldspathic minerals may follow an agpaitic trend of differentiation.

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