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THE SYSTEM Na_2CO_3–K_2CO_3–$CaCO_3$ AT 1 KILOBAR AND ITS SIGNIFICANCE IN CARBONATITE PETROGENESIS

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ABSTRACT. Except for a small region near the $CaCO_3$ apex, the system Na_2CO_3–K_2CO_3–$CaCO_3$ at 1 kb is ternary and has a liquidus surface characterized as follows: the join Na_2CO_3–$CaCO_3$ has a compound $Na_2(CO_3)_2$ (nyerereite) which melts congruently at 817° and eutectics at NC 47 CC 53 and 813°C and at NC 78.5 CC 21.5 and 725°C. The system K_2CO_3–$CaCO_3$ has a compound $K_2Ca(CO_3)_2$ (fairchildite) which melts congruently at 809°C and a compound $K_2Ca_2(CO_3)_3$ (phase A) which melts incongruently at 810°C with a reaction point at KC 42 CC 58. There are eutectics at KC 54 CC 46 and 790°C and at KC 76.5 CC 23.5 and 735°C. Maximum solid solution of CC in NC is 16 wt percent and in KC is about 11 wt percent. Nyerereite has a lower stability limit of 400°C; shortite has an upper stability limit of 335°C with excess NC and of 400°C without excess NC. Fairchildite is stable from its melting point (809°C) down to 547°C, where it inverts to buetschliite. Phase A is stable between 810° and 512°C. NC-KC appears to be a solid solution series. The ternary system has as liquidus phases: $(NC\text{-}KC\text{-}CC)_{ss}$ $(NY\text{-}FC)_{ss}$, phase A, and calcite. The cotectic between $(NC\text{-}KC\text{-}CC)_{ss}$ and $(NY\text{-}FC)_{ss}$ has a minimum at 665°C. The cotectic between $(NY\text{-}FC)_{ss}$ and CC and between $(NY\text{-}FC)_{ss}$ and phase A has a reaction point at NC 7 KC 42.5 CC 50.5 and 795°C and a minimum at NC 4 KC 47 CC 49 and 785°C.

The crystallization of natrocarbonatite lavas (lengaite) from the volcano Oldoinyo Lengai in Tanzania is interpreted in terms of the ternary system, and good accord is found between the phase equilibria and field observations. The proposal that the lavas are the result of melting troniferous lacustrine sediments is rejected in the light of isotopic data, and it is concluded that the lava has probably separated immiscibly from a nephelinite magma. It is suggested that alkalic carbonatite magmas are relatively common but that they persist only when the silica activity is too low to permit the formation of silicates, when the CO_2 activity is high enough to form alkali carbonates and the magma is dry. In most alkalic carbonatite magmas the silica activity is high enough to bind part of the alkali content as silicates (biotite, amphibole, pyroxene), and a fluid phase is sufficiently rich in water to remove excess alkalies and become a fenitizing fluid. This removal leaves an alkali-depleted magma which crystallizes as the commoner calcitic, dolomitic, and/or ankeritic carbonatite. Fenitizing fluids may derive both from carbonatitic magmas and silicate magmas.

INTRODUCTION

The existence of carbonatite magmas was for many years the subject of controversy (see Tuttle and Gittins, 1966; Heinrich, 1966, for summaries). However, with a wealth of field and experimental data now available, the magmatic origin of carbonate rocks as members of alkaline and alkaline-ultrabasic complexes is widely recognized.. Experimental studies have demonstrated the general compatibility of crystallization temperatures with those predicted from field observations. The question still arises, however, as to the exact composition of the primary carbonatite magma. In the majority of alkalic-carbonatite rock complexes sövites are greatly dominant, with subordinate yet important dolomitic, ankeritic, and sideritic differentiates. In marked contrast, during 1960-1961 the volcano Oldoinyo Lengai in Tanzania erupted carbonatite lavas whose mineralogy was dominated by Na–K–Ca carbonates. This im-

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mediately raised the problem as to whether primary carbonatite magmas initially contain alkalis (compare Von Eckermann, 1948), which are subsequently lost to the country rock in the form of fenitizing fluids during intrusion.

In this paper we present phase relationships in the system Na_2CO_3–K_2CO_3–$CaCO_3$ at 1 kb, trace the course of crystallization of potential alkali-rich carbonatites, and review the status and possible mode of evolution of such rocks.

The lavas from Oldoinyo Lengai have been referred to in the literature as "natrocarbonatite". The term is used in this paper, but in publications on the rocks by McKie and Dawson the term "lengaite" has been introduced.

PREVIOUS WORK

Most of the early work on the Na_2CO_3–K_2CO_3–$CaCO_3$ system has been at low pressure. Le Chatelier (1894) and Niggli (1916) discovered the compound $Na_2Ca(CO_3)_2$. The system was studied by Gittins and Tuttle in 1960 (unpub.), and the stabilities of both $Na_2Ca(CO_3)_2$ and $Na_2Ca_2(CO_3)_2$ (shortite) established at 1 kb. Recent confirmatory evidence of this earlier work and of that reported here has been given by Frankis and McKie (1973) in a note on the subsolidus region in Na_2CO_3–$CaCO_3$–H_2O at 0.5 to 1.5 kb.

K_2CO_3–$CaCO_3$: The system was partially investigated by Niggli (1916) and more comprehensively by Kroger, Illner, and Graeser (1943), both studies being at 1 atm pressure. Balascio and White (1972) investigated H_2O-rich sections of both Na_2CO_3–$CaCO_3$–H_2O and K_2CO_3–$CaCO_3$–H_2O systems up to pressures of 2 kb in attempts to grow coarse crystals of optical quality calcite.

Na_2CO_3–K_2CO_3: Liquidus relationships have been determined in a number of studies concerning behavior in ternary reciprocal salt mixtures (Kurnakov and Zhemchuznyi, 1907; Makarov and Shul'gina, 1940a, b; Volkov and Bergmann, 1942; Sementsova, Erdokimova, and Bergmann, 1959). The system was also investigated by Niggli (1919), again at 1 atm pressure.

Na_2CO_3–K_2CO_3–$CaCO_3$: The quadilateral Na_2CO_3–K_2CO_3–$Na_2Ca(CO_3)_2$–$K_2Ca(CO_3)_2$ within the ternary system has been investigated by Niggli (1919).

EXPERIMENTAL METHOD

Starting materials were prepared from analytical grade Na_2CO_3, K_2CO_3, and $CaCO_3$ with careful precautions to ensure the dryness of the mixes during preparation and subsequent storage. All determinations were made in standard cold seal pressure vessels (Tuttle, 1949). Pressure was monitored on a 100,000 psi Bourdon tube Heise gauge (Astrogauge). Temperature was controlled by Thermo-Electric Co. proportional controllers (model 32106) and monitored continuously on a Kaye multichannel automatic recorder. Experiments above the solidus were all of 30 min duration, and subsolidus experiments of 7 days duration. Quench-

ing was with air blast or by immersion in cold water with pressure maintained during the quench. Temperatures on 30 min experiments are controlled to ±2° and on 7 day experiments to ±5°C.

All capsules were weighed after the run to test for leakage, and the physical characteristics of the capsule and charge were noted. Identification of the phases was by optical and X-ray methods. All refractive index measurements were in monochromatic (Na_D) light using calibrated index liquids and an Abbé refractometer and are believed to have an accuracy of ±0.001.

The extent of Ca substitution in Na_2CO_3 solid solutions and the compositions of $Na_2Ca(CO_3)_2$–$K_2Ca(CO_3)_2$ solid solutions coexisting with known liquid compositions in the ternary system were determined by electron microprobe analysis.

Compositions of phases and abbreviations used in the text are summarized below:

Na_2CO_3	NC
K_2CO_3	KC
$CaCO_3$	CC
$(Na_2, Ca)CO_3$	NCss — sodium carbonate solid solution in NC-CC binary system
$(K_2, Ca)CO_3$	KCss — potassium carbonate solid solution in KC-CC binary system
$(Na_2, K_2, Ca)CO_3$	(NC-KC-CC)ss — sodium-potassium-calcium-carbonate solid solution in NC-KC-CC ternary system
$Na_2Ca(CO_3)_2$	NY — nyerereite
$K_2Ca(CO_3)_2$	FC — fairchildite
$K_2Ca(CO_3)_2$	BU — buetschliite
$(Na_2K_2)Ca(CO_3)_2$	(NY-FC)ss — nyerereite-fairchildite solid solution in NC-KC-CC ternary system
$Na_2Ca_2(CO_3)_3$	SH — shortite
$K_2Ca_2(CO_3)_3$	A — unnamed potassic analogue of shortite

RESULTS

The system Na_2CO_3–$CaCO_3$

Phase relationships at 1 kb are illustrated in figure 1, and selected results necessary to define the field boundaries are listed in table 1. The configuration above 1000°C is taken from Wyllie and Tuttle (1960), and the melting point of Na_2CO_3 from Koster van Groos and Wyllie (1966) who determined it by high pressure differential thermal analysis as 872°C at 1 kb.

The system has two intermediate compounds: shortite — $Na_2Ca_2(CO_3)_3$ and nyerereite — $Na_2Ca(CO_3)_2$, the nomenclature of which is discussed in a later section. Shortite has an upper stability limit of 400°C, where it undergoes subsolidus breakdown to calcite and nyerereite according to the reaction:

$$Na_2Ca_2(CO_3)_3 \rightleftarrows CaCO_3 + Na_2Ca(CO_3)_2 \qquad (1)$$

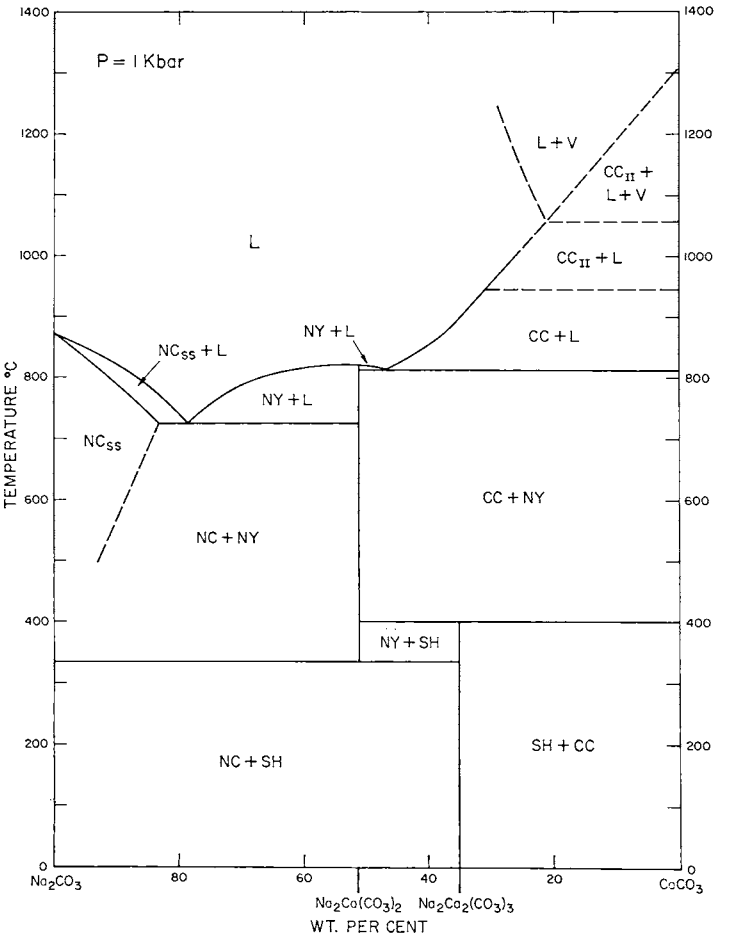


Fig. 1. Isobaric equilibrium diagram for the system Na_2CO_3–$CaCO_3$ at 1 kb. NC = Na_2CO_3, NC_{ss} = sodium carbonate solid solutions, NY = $Na_2Ca(CO_3)_2$ (nyerereite), SH = $Na_2Ca_2(CO_3)_3$ (shortite), CC = $CaCO_3$, L = liquid, V = vapor. Calcite II may be stable above 945°C. The join is binary except for a small region near the melting point of calcite. Data above 900°C are from Wyllie and Tuttle (1960).

In the presence of sodium carbonate shortite reacts to form nyerereite at 335°C:

$$Na_2Ca_2(CO_3)_3 + Na_2CO_3 \rightleftarrows 2Na_2Ca(CO_3)_2 \qquad (2)$$

Nyerereite thus has a lower limit to its stability field, and shortite is not a liquidus phase. Subsolidus relationships are almost identical to those presented by Frankis and McKie (1973) for the hydrous system, except that their field boundary at 315°C is 20°C lower than our determination.

In order to ascertain whether this discrepancy could be explained by the reaction kinetics of a dry versus a wet system, the same composition (NC40) was run both dry and with 10 percent water at 325°C for 23 days. In both cases the products were shortite plus sodium carbonate, and the discrepancy remains.

Nyerereite melts congruently at 817°C at 1 kb. The liquidus in the system is characterized by a very gentle slope on the NC side of the NY composition before dropping steeply to a eutectic at NC 78.5 at 725°C. On the CC side of the NY composition the liquidus drops very gently to a eutectic at NC 47 at 813°C. It then rises very steeply to the melting point of calcite at about 1300°C.

Liquidus temperatures have an accuracy of ±5°C except on the NC side of the eutectic composition NC 78.5, where it is extremely difficult to detect melting owing to the similar appearance of NCss in equilibrium with quenched liquid and quenched liquid alone.

The question arises whether $Na_2Ca(CO_3)_2$ merits a name. Kapustin (1971) has given the name natro-fairchildite to a mineral with composi-

TABLE 1

Selected data necessary to define field boundaries in the system Na_2CO_3–$CaCO_3$ at 1 kb

Mix composition (wt%)	Temp °C	Products	Mix composition (wt%)	Temp °C	Products
NC 27	990	L	NC 55	820	L
NC 27.5	970	CC + L		810	NY + L
NC 28	980	L	NC 60	820	L
NC 31.2	940	CC + L		810	NY + L
	950	L	NC 63.5	810	L
	405	NY + CC		800	NY + L
	395	SH + CC(+NY)	NC 67.9	800	L(+NY)
NC 35	900	L	NC 70	795	L
	890	CC + L		785	NY + L
	405	NY + CC		720	NY + NC
	395	SH	NC 73	770	L(+NY)
NC 40	855	L	NC 76	750	L
	845	CC + L		740	NY + L
NC 45	820	L		720	NY + NC
	810	NY + CC	NC 78	735	L
	405	NY + CC		720	NY + L
	395	NY + SH	NC 81	750	L
	330	SH + NC		740	NC + L
NC 49.4	820	L		735	NC_{84} + L
	815	NY + L		720	NC + NY
	810	NY + CC	NC 88	810	L(+NC)
	340	NY + SH		750	NC_{88}
NC 51.4	820	L		700	NCss
	810	NY	NC 90	835	NC + L
	405	NY		810	NCss
	395	NY (+SH)			
	340	NY (+SH)			
	330	SH + NC			

Abbreviations are the same as for figure 1. Brackets indicate that only a trace of the phase is present.

tion $(Na_{1.99}K_{0.66})(Ca_{0.96}Ba_{0.01}Sr_{0.02})(CO_3)_2$ that occurs in late-stage calcite-burbankite veins in the Vuorijarvi alkalic rock-carbonate complex. As shown later there is complete solid solution between $Na_2Ca(CO_3)_2$ and $K_2Ca(CO_3)_2$ (fairchildite). A member of this series has been known for some years as an essential constituent of the natrocarbonatite lavas of the volcano Oldoinyo Lengai in Tanzania (Dawson, 1962a; 1966). The name nyerereite was approved by the Commission on New Mineral Names for this mineral, and it has been referred to as such by Milton (1968), but the mineral data were never published. In a recent note on subsolidus relations in the system Na_2CO_3–$CaCO_3$–H_2O, Frankis and McKie (1973) refer to the natural mineral as nyerereite and to $Na_2Ca(CO_3)_2$ as synthetic nyerereite.

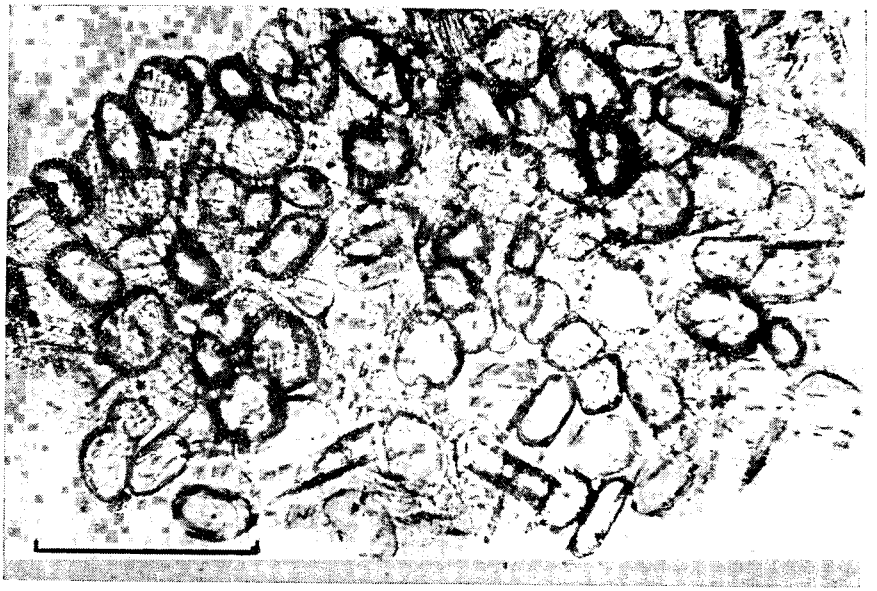
It would seem most logical to apply the name nyerereite to the composition $Na_2Ca(CO_3)_2$ on the understanding that natural occurrences will be solid solutions of nyerereite and $K_2Ca(CO_3)_2$ (fairchildite). This is the practice we have adopted in this paper, and the Oldoinyo Lengai mineral is expressed as $NY_{80.4}FC_{19.6}$. At the same time, it should be remembered that there are several polytypes of $Na_2Ca(CO_3)_2$, and there are likely to be further reviews of the nomenclature in the future. The nomenclature proposed here is at least a workable interim measure.

Primary phases.—$CaCO_3$: Calcite generally forms rounded to ellipsoidal grains (average grain size 0.056 mm), although rarely a stubby prismatic habit is observed (pl. 1-A).

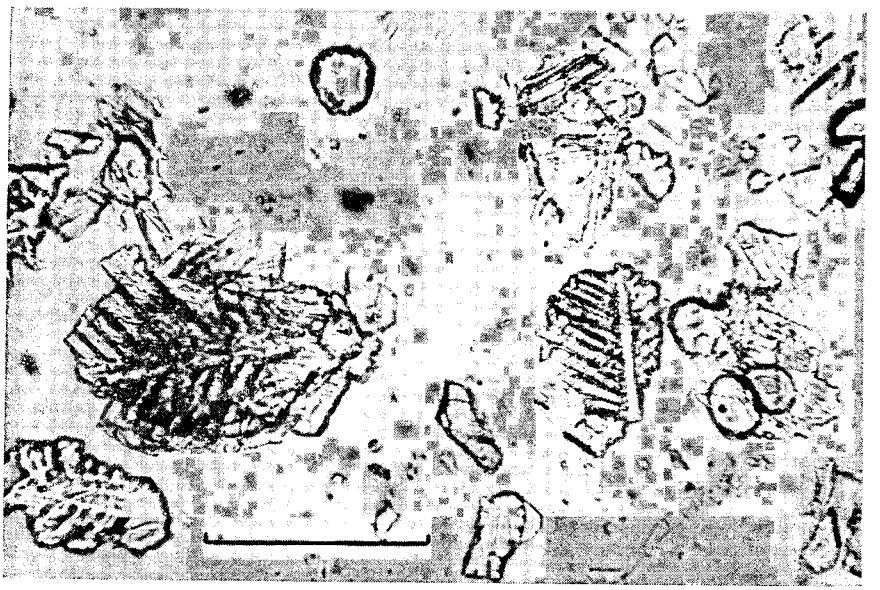
$Na_2Ca(CO_3)_2$: Nyerereite forms clear, stubby prismatic, bubble-included grains, with an average grain size of 0.19 × 0.06 mm. Rounded basal sections exhibiting minimum birefringence are typically cross-hatch twinned. It is possible to eliminate this twinning, however, by very rapid quenching, and twinning is not observed in nyerereite crystals grown on quench. Crystallographic studies with heating cameras have shown the existence of a high-low inversion in natural nyerereite from Oldoinyo Lengai (McKie, personal commun.), and it appears that the twinning forms during inversion from the high temperature form. In another study Evans and Milton (1973) report three transitions α-N, β-N, γ-N during heating experiments on the dehydration of gaylussite ($Na_2Ca(CO_3)_2 \cdot 5H_2O$) and pirssonite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$).

Our determination of the optical properties of synthetic nyerereite give ω1.546 ± 0.001, ε1.500 ± 0.001, uniaxial negative with occasional biaxial crystals ($2V < 15°$). These are essentially the values given by Eitel and Skaliks (1929): ω1.547 ± 0.002, ε1.504 ± 0.004. However, McKie reports (personal commun.) that natural nyerereite has α1.5112, β1.5333, γ1.5345, $2V_\alpha = 29°$. He also reports that synthetic $Na_2Ca(CO_3)_2$ is orthorhombic, and Evans and Milton (1973) also report orthorhombic symmetry for α-N and β-N, which would suggest that our twinned product also is orthorhombic. However, our refractive index measurements have an accuracy of ±0.001 and would not distinguish the difference of 0.0012 between the β and γ indices quoted by McKie. It is clear that the crystallography of nyerereite-fairchildite solid solutions is

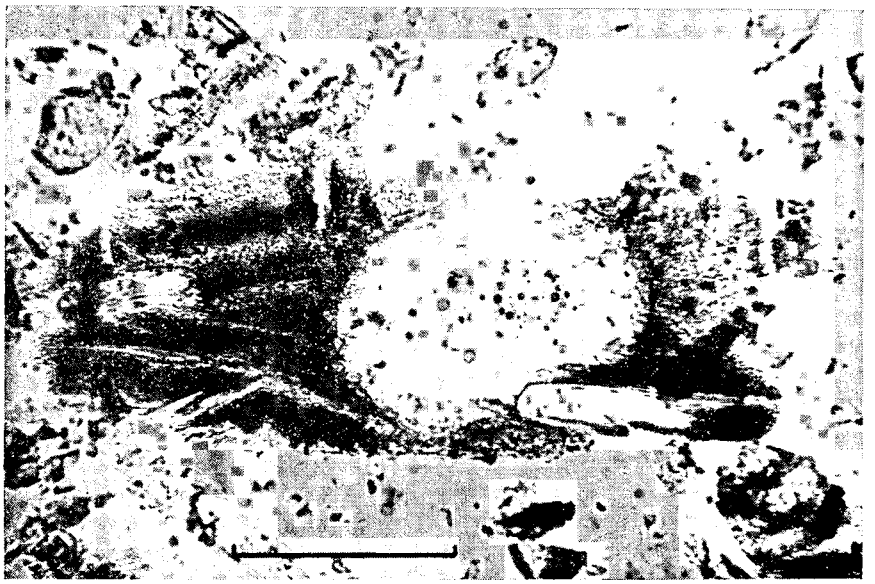
PLATE 1



A. Spherical, ellipsoidal, and stubby prismatic primary grains of calcite enclosed within fibrous nyerereite-rich quench. Composition of starting material $KC_{10}NC_{20}CC_{70}$; 890°C. Scale bar 200μ.



B. Primary spherical grains of calcite with dendritic calcite and fibrous nyerereite quench. Composition of starting material $NC_{35}CC_{65}$; 880°C. Scale bar 200μ.



C. Clear, basal, and prismatic sections of primary nyerereite crystals enclosed within quenched liquid. The former liquid is composed of a microcrystalline NC-rich aggregate cross cut by elongate quench nyerereite needles, some of which have nucleated on primary host grains, parallel c-axis. Composition of starting material $NC_{50}KC_{10}CC_{40}$; 800°C. Scale bar 200μ.

very complicated, but that for practical purposes the synthetic (NY-FC)ss generally appears uniaxial in the run products.

Na_2CO_3: Sodium carbonate forms rounded, highly birefringent primary grains (avg grain size 0.18 mm), almost indistinguishable from coarse NC-rich quench in compositions between NC 80 and NC 100.

Electron microprobe analysis of products from mix compositions NC 81 and NC 88 run at 735°C indicate phases of composition NC 84 and NC 88 respectively, the former coexisting with liquid.

This suggests that the primary phase on the NC-rich side of the eutectic is an Na_2CO_3 solid solution which coexists with liquid only within a narrow field extending from the melting point of Na_2CO_3 to the solidus between the eutectic composition NC 78.5 and NC 83.5. The composition NC 83.5 represents the maximum solubility limit of Ca in sodium carbonate, with solubility presumably decreasing with fall of temperature within the subsolidus region, as indicated diagrammatically in figure 1.

$Na_2Ca_2(CO_3)_3$: Shortite forms microcrystalline equigranular aggregates (max grain size 0.03 mm) in subsolidus assemblages, coexisting with rounded calcite or faintly brown sodium carbonate.

Liquid: As is typical of most carbonate systems, liquids do not quench to glass but to micro-crystalline aggregates. The character of

the quenched liquid is strongly dependent on original composition. In the field of CC +L the liquid quenches to an aggregate of fibrous nyerereite needles and dendritic calcite (pl. 1-B). In the field of NY + L, the presence of a liquid prior to quench is more readily ascertained than elsewhere in the system. Rounded and prismatic grains of primary nyerereite are enclosed within a brown, vermicular, microcrystalline aggregate rich in NC. This in turn is cross cut by elongate needles of clear nyerereite that have grown during the quench. Occasionally these quench needles nuculeate on a primary crystal forming a tail, with individual fibers paralleling the c-axis of the host (pl. 1-C). In the field of NCss + L, compositions close to the eutectic yield an easily discernible liquid phase composed of fibrous crystalline aggregates surrounding or growing interstitial to coarse rounded primary NC grains. In more NC-rich compositions the quenched liquid phase becomes progressively more coarsely crystalline, and textural interpretation more difficult.

Vapor: Minimal (1-2 percent) dissociation of carbonates takes place within the temperature range 0° to 1000°C at 1 kb. Rare, rounded vacuoles presumably originally occupied by CO_2 are present in charges run at near liquidus temperatures from compositions close to that of NY. A marked increase, with up to 5 percent vapor was noticed in CC-rich compositions above 950°C, where capsules after the run are commonly slightly puffed. However, phases that might have resulted from decarbonation reactions (for example, CaO) have not been recognized in products examined in crushed grain mounts.

A peculiar characteristic of many near liquidus charges, particularly those resulting from NC-rich mixes is the presence of carbon. In compositions close to NY this occurs as a faintly disseminated phase, while in NC-rich mixes the charge is commonly completely blackened. On opening such capsules a faint smell of SO_2 was detected. Identical observations were made by Koster van Groos (1966) who suggested two explanations: (A) that hydrogen diffused through the walls of the capsule and reduced CO_2 to C or (B) that sulphur impurities in the gold reacted with CO_2 producing SO_2 and C. In either situation this would necessitate minor dissociation of the sodium carbonate.

The system K_2CO_3–$CaCO_3$

Liquidus relationships in the system potassium carbonate-calcium carbonate have been investigated in part by Niggli (1916) and more fully by Kroger, Illner, and Graeser (1943). More recently, in an attempt to grow calcite from alkali-calcic carbonate aqueous solutions, Balascio and White (1972) investigated H_2O-rich sections of the system K_2CO_3–$CaCO_3$–H_2O, and Pabst (1974) has reported on the synthesis, properties, and structure of buetschliite.

Phase relationships at 1 kb are illustrated in figure 2, and selected results necessary to define these relationships are listed in table 2. It is

not possible to distinguish primary KC from quenched liquid in the range KC 100 to 90, and so a direct determination of the melting point of KC was not possible. Instead it has been assumed that the effect of pressure on the melting of KC is similar to that of NC, namely 16 ± 1°C/kb as determined by high pressure differential thermal analysis (Koster van Groos and Wyllie, 1966) and the 1 atm melting point extrapolated to 912°C at 1 kb.

There are three intermediate compounds: fairchildite–$K_2Ca(CO_3)_2$, the low-temperature polymorph of fairchildite–buetschliite $K_2Ca(CO_3)_2$,

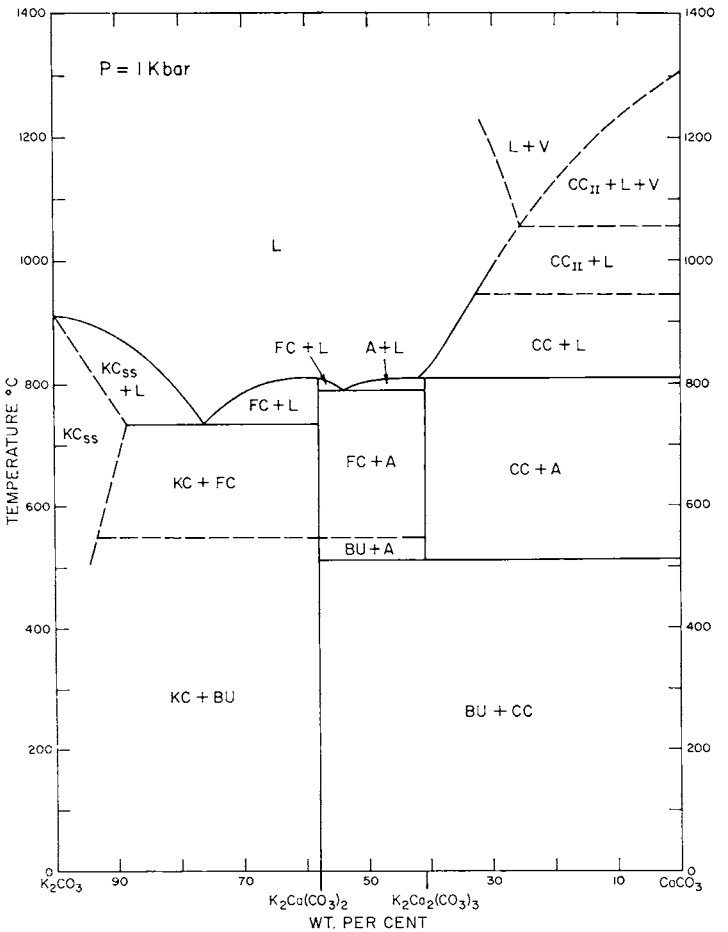


Fig. 2. Isobaric equilibrium diagram for the system K_2CO_3–$CaCO_3$ at 1 kb. KC = K_2CO_3, KC_{ss} = potassium carbonate solid solution, FC = $K_2Ca(CO_3)_2$ (fairchildite), BU = $K_2Ca(CO_3)_2$ (buetschliite), A = $K_2Ca_2(CO_3)_3$, CC = $CaCO_3$, L = liquid, V = vapor. Calcite II may be stable above 945°C. The join is binary except for a small region near the melting point of calcite. Data above 900°C are from Wyllie and Tuttle (1960).

and the unnamed $K_2Ca_2(CO_3)_3$ called in this study phase A. Phase A is not known in nature. Both fairchildite and A appear on the liquidus. Fairchildite melts congruently at 809°C. It seems unlikely that there is solid solution between $Na_2Ca_2(CO_3)_3$ (shortite) and $K_2Ca_2(CO_3)_3$ (A). Published analyses of shortite (Fahey, 1939; Watkinson and Chao, 1973) show no substitution of K for Na, and electron microprobe analysis of phase A synthesized in the ternary NC-KC-CC system shows negligible substitution of Na for K (maximum Na_2O 1.00 percent).

Phase A previously synthesized by Kroger, Illner, and Graeser (1943) begins to melt incongruently at 810°C to calcite and a liquid that quenches largely to fairchildite. There is a marked inflexion in the liquidus at the reaction point (KC 42, 810°C), from a steep gradient on the CC-rich side to almost isothermal bounding the primary field of A + L. Fairchildite and A co-precipitate from liquid at a shallow eutectic at 790°C (KC 54).

TABLE 2

Selected data necessary to define field boundaries in the system K_2CO_3–$CaCO_3$ at 1 kb

Mix composition (wt%)	Temp °C	Product	Mix composition (wt%)	Temp °C	Product
KC 30	875	L	KC 58	543	BU(+FC)
	540	A + CC		515	BU
KC 35	925	L	KC 65	810	L
	900	CC + L		805	FC + L
	800	CC + A	KC 70	795	L
	500	BU + CC		787	FC + L
KC 40.8	825	L		730	FC + KC
	815	CC + L	KC 72	770	FC + L
	805	A(+CC)	KC 75	750	L
	515	A		740	FC + L
	508	BU + CC		730	FC + KC
KC 45	815	L	KC 77.5	750	KC + L
	805	A + L		735	KC + FC
	790	A(+L)	KC 80	795	L
	785	A + FC		785	KC + L
KC 50	810	L	KC 84.6	845	L
	800	A + L		837	KC + L
	795	A + L			
	785	A + FC			
	543	A + BU			
	508	BU + CC(+A)			
KC 55	800	L			
	795	FC + L			
	785	FC + A			
KC 57	795	FC + L			
	790	FC + L			
KC 58	815	L			
	805	FC			
	550	FC(+BU)			

Abbreviations are as in figure 2. Brackets indicate that only a trace of that phase is present.

Phase A has a minimum stability limit of 512°C, where it undergoes subsolidus breakdown to calcite and buetschliite according to the reaction:

$$K_2Ca_2(CO_3)_3 \rightleftarrows CaCO_3 + K_2Ca(CO_3)_2$$

Buetschliite was originally described by Milton and Axelrod (1947) as having the composition $K_6Ca_2(CO_3)_5 \cdot 6H_2O$. This was corrected by Mrose, Rose, and Marinenko (1966) who determined that buetschliite and fairchildite are polymorphs. The polymorphism has been confirmed in the present study, and the inversion established at 547°C at 1 kb by repeated inversions in both directions. This temperature is apparently at variance with the results of Mrose, Rose, and Marinenko (1966) who synthesized fairchildite in the range 704° to 970°C and buetschliite in the range 593° to 704°C at 1 atm pressure. The explanation is probably to be found in the kinetics of the inversion which occurs so easily that fairchildite synthesized between 593° and 704° would during the relatively slow cooling of a crucible invert to buetschliite, whereas in the conditions of rapid cooling employed in the 1 kb work fairchildite is quenched. It is interesting to note in this regard that several museum specimens of fairchildite formed in forest fires and collected shortly after the fires were extinguished were found to have inverted to buetschliite during room temperature storage.

Balascio and White (1972) using mol percent compositions of 3.2 $CaCO_3$–8.0K_2CO_3–88.8H_2O and 10.0$CaCO_3$–7.4K_2CO_3–82.6H_2O synthesized BU + KC+ H_2O and BU + CC + H_2O respectively in the range 450° to 650°C at pressures less than 1 kb. Between 1 and 2.25 kb the assemblages are CC + KC + H_2O. This work would tend to suggest that the buetschliite-fairchildite inversion takes place at temperatures greater than 650°C at pressures less than 1 kb, and that buetschliite is not stable above 1 kb. To test this possibility we conducted a series of experiments in the range 0.75 to 2.0 kb using the composition KC 58 CC 42 with various percentages of water between 450° and 800°C. Results are listed in table 3.

From these results it is apparent that the failure to synthesize fairchildite or A by Balascio and White in any of the high pressure runs (1 kb) is due simply to the H_2O rich starting compositions. At high

TABLE 3

Run no.	Starting composition (wt%)	Pressure	Temperature	Products
1	KC 58	2 kb	800°C	FC (Liquid)
2	KC 58	2 kb	780°C	FC (Subsolidus)
3	KC 58	2 kb	600°C	FC (Subsolidus)
4	FC + 10.79 wt% H_2O	2 kb	600°C	A + tr FC + H_2O
5	KC 58 + 13.61 wt% H_2O	2 kb	600°C	A + tr FC + H_2O
6	KC 58 + 31.19 wt% H_2O	2 kb	600°C	CC + H_2O
7	KC 58 + 5.60 wt% H_2O	0.75 kb	600°C	FC + A + H_2O
8	KC 58 + 7.24 wt% H_2O	1.5 kb	450°C	BU + tr CC + H_2O
9	KC 58 + 6.75 wt% H_2O	0.75 kb	450°C	BU + tr CC + H_2O

concentrations of H_2O all the K_2CO_3 goes into solution, and the $CaCO_3$ merely recrystallizes during the run. This is illustrated in the sequence of runs 3 to 6 in table 3. At 2 kb pressure and 600°C with an initial solid composition KC 58, it is found that an increase of water causes the crystalline products to become progressively more calcic ($K_2Ca(CO_3)_2$ → $K_2Ca_2(CO_3)_3$ → $CaCO_3$) and the solution with which they coexist correspondingly more potassic. Ultimately the water added is capable of dissolving all K_2CO_3 from the original mix, independent of whether this is in the form of K_2CO_3 mixed mechanically with $CaCO_3$ or chemically tied in fairchildite (run 4).

Whereas the data of Balascio and White appear to suggest that in the presence of water there is a drastic shift in the buetschliite-fairchildite inversion temperature and breakdown of both phases above 1 kb, the results of our runs 4, 7, 8, and 9 are compatible with inversion temperature of 547°C determined in the anhydrous system K_2CO_3–$CaCO_3$ (fig. 2) and confirm that both fairchildite and buetschliite are stable at pressures above 1 kb.

The only remaining difficulty is the synthesis by Balascio and White of buetschliite above 547°C. The only plausible explanation is that it formed during quench.

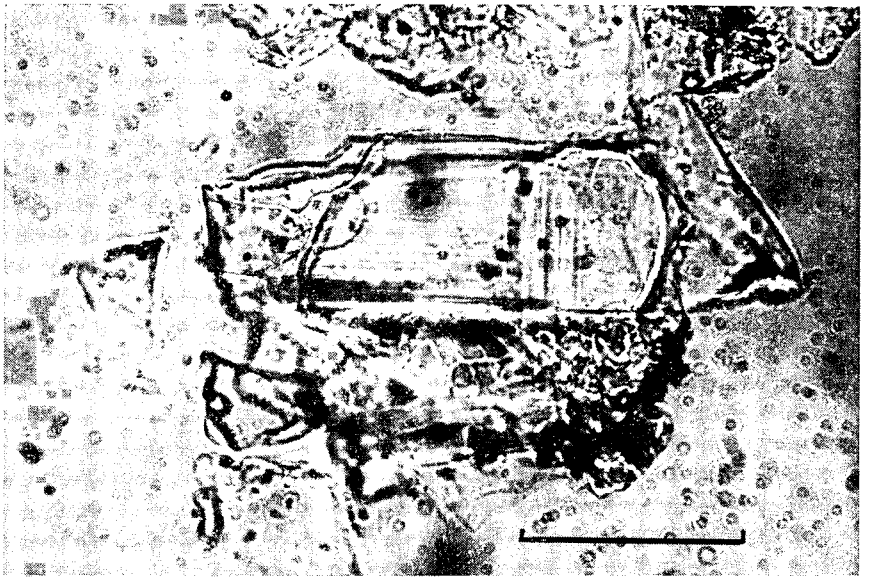
Primary phases.—$CaCO_3$: As in the Na_2CO_3–$CaCO_3$ binary system, calcite forms rounded, ellipsoidal or stubby prismatic crystals with an average grain size of 0.06 mm.

$K_2Ca_2(CO_3)_3$: Phase A forms hexagonal to rounded pale yellow-green granules, with an average grain size of 0.07 to 0.10 mm. In the ternary system NC-KC-CC an elongate prismatic form is occasionally developed (max grain size 0.60 × 0.05 mm). The grains are always traversed by twin lamellae, generally with two individual sets clearly discernible, parallel and perpendicular to the c axis of prismatic sections (pl. 1-C). Phase A is uniaxial positive with $\omega = 1.560 \pm 0.001$, $\varepsilon = 1.576 \pm 0.001$. The same phase, synthesized in the ternary system, has identical refractive indices.

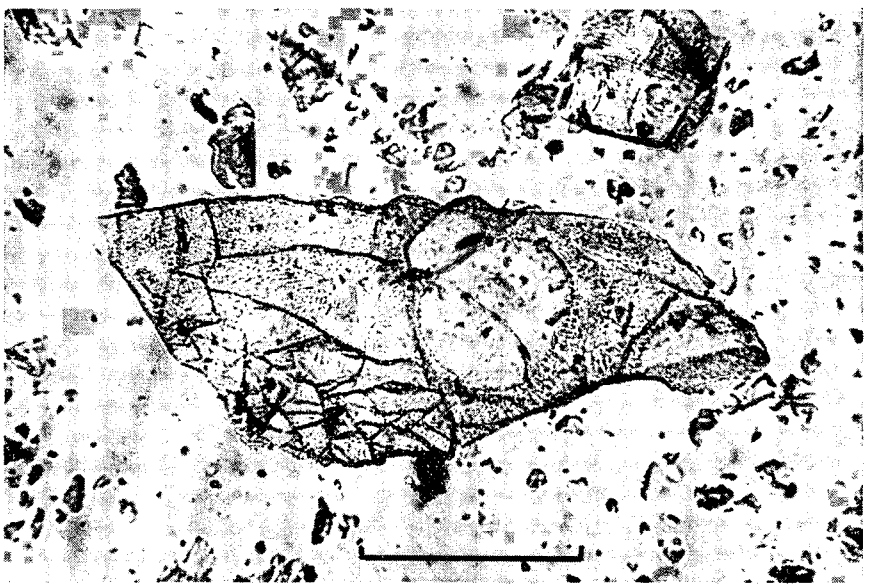
$K_2Ca(CO_3)_2$: Fairchildite, like nyerereite, forms stubby, clear bubble-included prisms (avg grain size 0.19 mm × 0.07 mm) which commonly show development of pyramidal terminating faces. Apart from the absence of polysynthetic twinning in basal sections, the form and textures of fairchildite are identical to those described for nyerereite. Fairchildite is uniaxial with $\omega = 1.536$, $\varepsilon = 1.496 \pm 0.001$ [compare values of $\omega = 1.530$, $\varepsilon = 1.480$ cited by Milton and Axelrod, 1947, for natural fairchildite].

K_2CO_3: Potassium carbonate crystallizing from mixes between the eutectic composition KC 76.5 and KC 90 occurs as readily identifiable rounded grains surrounded by finer grained dendritic or fibrous quench (pl. 2-A). For compositions more potassic than KC 90, charges from liquid, crystal + liquid, and subsolidus fields appear identical.

PLATE 2



A. Prismatic grains of $K_2Ca_2(CO_3)_3$ (phase A) exhibiting polysynthetic twin lamellae parallel and perpendicular to the c-axis. Phase A coexists here with calcite, a member of the $(NY\text{-}FC)_{ss}$ series and quenched liquid. Composition of starting material $NC_5KC_{10}CC_{55}$; 795°C. Scale bar 80μ.



B. A rounded primary grain of KC_{ss} enclosed within microcrystalline dendritic quenched liquid. Composition of starting material $KC_{84.7}CC_{15.3}$; 787°C. Scale bar 200μ.

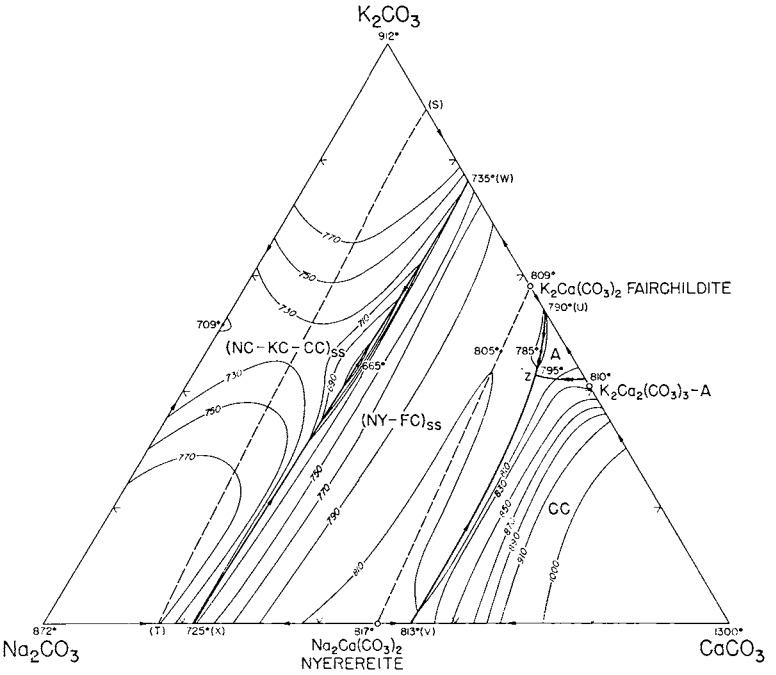


Fig. 3. Isobaric equilibrium diagram for the system Na_2CO_3–K_2CO_3–$CaCO_3$ at 1 kb. (NC-KC-CC)ss = ternary solid solutions, (NY-FC)ss = nyerereite–fairchildite solid solutions, A = $K_2Ca_2(CO_3)_3$, CC = $CaCO_3$.

The system Na_2CO_3–K_2CO_3

Because of the difficulty of recognizing quenched liquid in the NC- and KC-rich parts of the NC-CC and KC-CC systems, we have not attempted to determine phase relationships in the system NC-KC at 1 kb.

The system has previously been investigated experimentally at 1 atm pressure by a number of workers, all of whom demonstrate a solid solution series with a minimum melting temperature. Kurnakov and Zhemchuzhnyi (1907) reported in Nyankovskaya (1953) determined a minimum temperature of 712°C at 36 mol percent K_2CO_3, Niggli (1919) 712°C at 46 mol percent K_2CO_3, Makarov and Shul'gina (1940a, b) 706° at 40 mol percent K_2CO_3, Volkov and Bergmann (1942) 718° at 43 mol percent K_2CO_3, and Sementsova, Erdokimova, and Bergmann (1959) 696° at 45 mol percent K_2CO_3.

The intermediate compound $Na_2CO_3 \cdot K_2CO_3$ was reported by Makarov and Shul'gina (1940a, b), but no evidence for the existence of such a phase as a liquidus or near-liquidus phase has been found in our work.

TABLE 4

Selected data necessary to define field boundaries in the system Na_2CO_3–K_2CO_3–$CaCO_3$ at 1 kb

Composition—wt% CC	KC	NC	Phase(s) coexisting with liquid	Temperature of crystallization (°C)
70	20	10	CC	>915
70	10	20	CC	>915
60	30	10	CC	890
60	20	20	CC	880
			CC + (NY-FC)ss	807
60	10	30	CC	865
			CC + (NY-FC)ss	812
55	40	5	CC	830
			CC + (NY-FC)ss + A	795
50.5	42	7.5	CC + (NY-FC)ss	803
53.5	43	3.5	A	808
52	45	3	A	807
50	10	40	(NY-FC)ss	810
50	30	30	"	807
50	30	20	"	803
50	40	10	"	798
47.5	46	65	"	800
43	50	7	"	807
43.5	45	11.5	"	807
44	40	16	"	812
40	50	10	"	805
40	40	20	"	804
40	30	30	"	804
40	20	40	"	806
40	10	50	"	808
30	60	10	"	780
30	50	20	"	775
30	40	30	"	770
30	30	40	(NY-FC)ss	770
30	20	50	"	777
30	10	60	"	777
25	40	35	"	740
20	70	10	(NC-KC-CC)ss	755
20	60	20	"	735
20	50	30	"	710
			(NC-KC-CC)ss +(NY-FC)ss	695
20	40	40	(NC-KC-CC)ss	720
			(NC-KC-CC)ss +(NY-FC)ss	680
20	30	50	(NC-KC-CC)ss	760?
			(NC-KC-CC)ss +(NY-FC)ss	720
20	20	60	(NC-KC-CC)ss	770
20	10	70	"	765
10	60	30	"	760
10	50	40	"	approx. 730
10	40	50	"	<740
10	30	60	"	>750; <780
10	20	70	"	775

Abbreviations are as in figure 3.

The system Na_2CO_3–K_2CO_3–$CaCO_3$

Phase relationships in the ternary system are illustrated in figure 3, and selected results that define the field boundaries are listed in table 4. There are four primary phase fields characterized by the initial crystallization of (NC-KC-CC)ss, (NY-FC)ss, CC, and phase A.

The nyerereite-fairchildite join is a thermal barrier to trends of liquid fractionation such that Ca-rich compositions trend toward the cotectic UV and Na-K rich compositions trend toward the cotectic WX. The join is a solid solution series with a minimum at 805° and $FC_{79}NY_{21}$, confirming the original description by Niggli (1919), at 1 atm pressure.

On the Ca-rich side of the NY-FC join, the primary fields of CC and phase A are separated by a reaction curve extending from the reaction point in the KC-CC binary to the cotectic curve UV at Z. The ternary reaction point where calcite, $K_2Ca_2(CO_3)_3$ (phase A), and a member of the NY-FC series can coexist with liquid is at $NC_{7.0}KC_{42.7}CC_{50.3}$ and 795°.

Compositions of liquids within the primary field of calcite, to the Na-poor side of a line joining the ternary reaction point Z and the $CaCO_3$ apex, will initially crystallize calcite, causing the liquid composition to migrate to the reaction curve. Here phase A begins to crystallize, commonly in the form of stubby polysynthetically twinned prisms, with concomitant reaction of early formed calcites with the liquid. At the ternary reaction point Z, calcite and phase A are joined by a (NY-FC)ss, and the temperature remains constant until calcite is used up by reaction. If liquid remains after the elimination of calcite, its compositional trend would be toward a minimum in the cotectic curve at $NC_4CC_{49.2}KC_{46.8}$ and 785°C.

Compositions within the CC field to the Na-rich side of the line joining the $CaCO_3$ apex with the ternary reaction point Z will initially crystallize calcite with the liquid composition trending toward the cotectic UV. Calcite is joined here by a member of the (NY-FC)ss series. Tie lines connecting liquid and crystal compositions are indicated in figure 4. With the crystallization of a member of the (NY-FC)ss series, the liquid composition becomes more potassic along the cotectic. (NY-FC)ss, by reaction with the liquid, becomes progressively richer in the FC component.

Initial compositions on the Na-K rich side of the broad thermal divide, but more Ca-rich than the cotectic WX will crystallize (NY-FC)ss. Tie lines connecting initial liquid and initial crystal compositions are indicated in figure 4. Liquid compositions follow a probable curved path toward the cotectic WX, where (NY-FC)ss is joined by a member of the (NC-KC-CC)ss series. Compositions of (NC-KC-CC)ss lie along the dashed line ST which is based on the maximum solubility of $CaCO_3$ in NCss determined in the binary system.

The minimum liquidus temperature along the cotectic WX and in the ternary system as a whole is 665°C and $CC_{23.5}KC_{44.5}NC_{32.0}$. However, due to the solid solution nature of both crystalline phases coexisting with

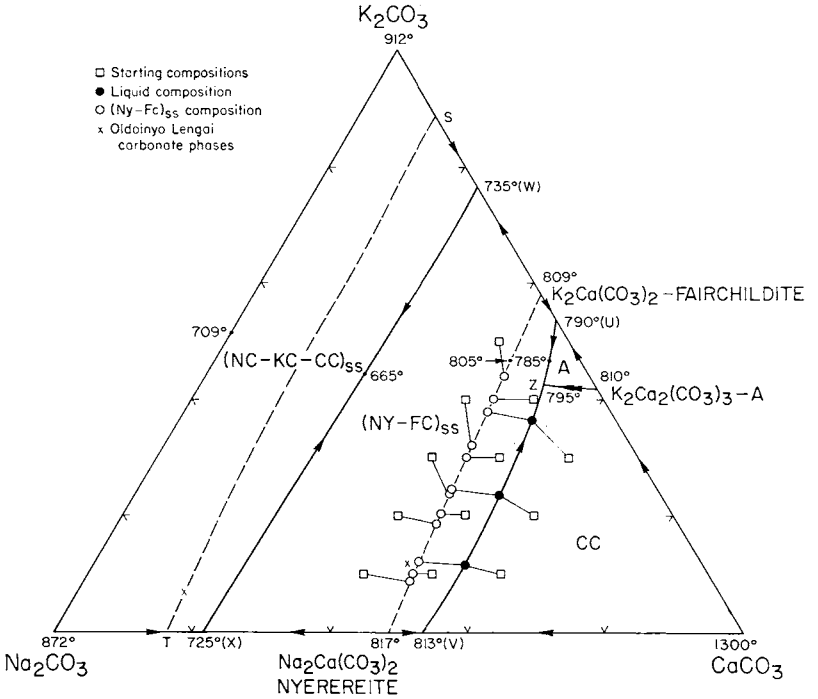


Fig. 4. Compositions of nyerereite–fairchildite solid solutions coexisting with liquids on the cotectic UV. Compositions were determined by electron microprobe analyses of the nyerereite–fairchildite solid solution that coexists with liquid and the first appearance of calcite during melting of the starting composition shown by an open square. Also shown are the compositions of nyerereite–fairchildite solid solutions that coexist with the first liquid to form during the melting of initial compositions that lie in the primary field of (NY-FC)ss. The compositions of the (NY-FC)ss and the (NC-KC-CC)ss from the Oldoinyo Lengai lava are shown by crosses.

liquid, this minimum temperature will be reached by liquids from only a small range of compositions.

(NC-KC-CC)ss clearly exist in the synthetic system, and our microprobe analyses of the two principal phases in the natural lava suggest that one of these is essentially a (NC-KC-CC)ss (fig. 5). It has, however, been pointed out by McKie (personal commun.) that the natural mineral gives only diffuse X-ray reflections that are related to those of (NY-FC)ss and that it may contain some of the anions F, CL, PO_4, and SO_4. The possibility exists, therefore, that the natural mineral is rather more complicated.

Applications to carbonatite magmas and the volcano Oldoinyo Lengai

The volcano Oldoinyo Lengai is part of the Neogene volcanic province of Northern Tanzania and is still active. The cone rises about 2000 m above the plains and is primarily composed of ijolitic pyroclastics with lesser amounts of melanephelinite, nephelinite, and phono-

lite flows. In 1960 and 1961 the active summit crater erupted sodium-rich carbonatite lava that has subsequently come to be known as natrocarbonatite, and in 1966, and probably on several earlier occasions, it erupted carbonatite ash in sufficient volume to bury completely the carbonatite lavas.

These natrocarbonatite lavas have considerable interest both as an unusual rock type and for their bearing on the broader problem of carbonatite magmas. The rocks are composed of microphenocrysts of (NY-FC)ss and (NC-KC)ss enclosed within a microcrystalline quenched groundmass composed of (NY-FC)ss, (NC-KC-CC)ss, minor fluorite, nahcolite, and pyrrhotite. The texture of the rocks bears a striking resemblance to the experimental textures observed in run products of the system NC-KC-CC and is illustrated in plate 2-B. A particular point of similarity is the manner in which elongate crystals of nyerereite grown on quench cut across areas of microcrystalline quenched liquid.

It is clear that the crystallization history of these unusual lavas can be explained by reference to the system NC-KC-CC. Although it may be reasonably assumed that the bulk composition of the lava is that of the magma from which it crystallized, with the possible exception of some loss of volatile constituents, it cannot be plotted in the system with certainty. If all Na_2O, K_2O, and CaO were calculated as carbonates the analysis would plot in the field of (NY-FC)ss, on the Na-K rich side of the nyerereite-fairchildite join. However, the analysis (table 5) does not contain enough CO_2 to accommodate all the Na_2O, K_2O, CaO, SrO, and BaO as carbonates, and it is not known in what

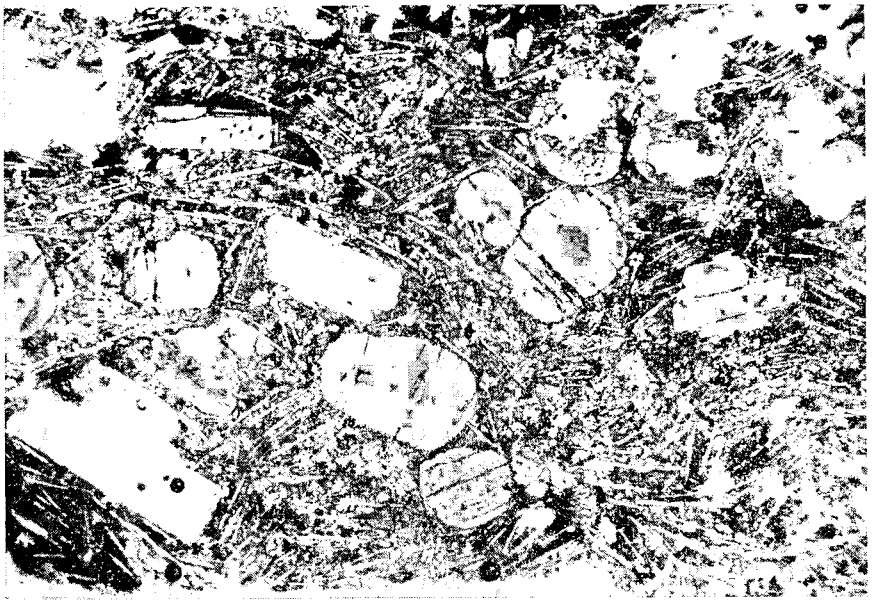
TABLE 5

Chemical composition of natrocarbonatite (lengaite) lavas

SiO_2	tr	tr	1.18	1.12
TiO_2	0.10	0.08		
Al_2O_3	0.08	0.09	1.64	1.70
Fe_2O_3(total)	0.26	0.32		
MnO	0.04	0.24	—	—
CaO	12.74	12.82	19.09	17.52
BaO	0.95	1.05	1.05	1.02
SrO	1.24	1.20	0.89	0.85
MgO	0.49	0.41	1.43	2.35
Na_2O	29.53	29.70	29.00	30.00
K_2O	7.58	6.58	6.90	7.50
P_2O_5	0.83	1.06	—	—
H_2O(total)	8.59	8.27	1.81	1.91
CO_2	31.75	32.40	31.98	30.73
F	2.69	1.84	—	—
CL	3.86	2.64	2.07	3.03
SO_3	2.00	2.18	2.79	2.88
S	—	—	0.08	0.13
	102.73	100.88	99.91	100.74
Less O for F, CL, and S	2.00	1.36	0.57	0.75
	100.73	99.52	99.34	99.99

Analyses from Dawson (1966)

PLATE 3



Photomicrograph of natrocarbonatite lava from Oldoinyo Lengai volcano, Tanzania. Rounded phenocrysts of $(NC\text{-}KC\text{-}CC)_{ss}$ and tabular prismatic phenocrysts of $(NY\text{-}FC)_{ss}$ are enclosed within a microcrystalline groundmass in which needles of quench nyerereite solid solution define a pronounced trachytic texture. Width of field view is 3.25 mm. Specimen P7-857, Univ. Toronto Petrology Collection.

proportion these elements are combined with F, Cl, PO_4, and SO_4 or indeed to what extent these anions are present in the principal mineral phases or in accessory fluorite, apatite, et cetera. The evidence of the crystallization experiments on the natural lava in which NY is the liquidus phase suggests that the bulk composition must plot in the (NY-FC)ss field probably close to the cotectic WX.

The anhydrous liquidus of the natural lava was determined as 655°C at 1 kb with nyerereite as the liquidus phase. Nyerereite is joined by (NC-KC-CC)ss at 620°C, but the solidus was not determined. The natural anhydrous liquidus is lower than the lowest temperature in the synthetic system, but two factors combine to bring them into closer accord. Temperatures in the anhydrous system at 1 kb are 16° to 20° higher than at 1 atm which was the pressure on the lava during its crystallization, and one might expect that the effect of F(2.69 percent), Cl(3.86 percent), and SO_3(2.00 percent) would be to lower the liquidus still further. This would accord with Dawson's observation that moving lavas were not incandescent at night.

Although the magmatic character of lavas observed to come from a volcanic vent can hardly be questioned, the suggestion has been made (Milton, 1968) that the natrocarbonatite does not belong to the alkalic magma stem but represents troniferous sediments melted by nephelinitic

magma. Troniferous sediments are common in Lake Natron and Lake Magadi in the vicinity of Oldoinyo Lengai. Most people would prefer the converse view that the sediments are in fact due to the evaporation of solutions derived from leaching of natrocarbonatite lavas and ashes by rain. If the lavas were derived from the melting of lacustrine sediments, their volume should be little more than that corresponding to the cross-sectional area of the volcanic conduit, and they ought to have been erupted long before the volcano had reached a height of 2000 m.

The case for a truly magmatic origin is greatly strengthened by the isotopic data. Bell, Dawson, and Farquhar (1973) report $^{87}Sr/^{86}Sr$ ratios of 0.7059 and 0.7061, similar to those of the silicate lavas of Oldoinyo Lengai, whereas the troniferous sediments of Lake Natron and Lake Magadi have $^{87}Sr/^{86}Sr$ ratios of 0.7048 to 0.7114. The sediments therefore overlap the range of the lavas, and the data can be interpreted in either way. However, Bell, Dawson, and Farquhar (1973) have pointed out that an origin of the lavas from the sediments would require a 60 fold concentration of potassium which is a most unlikely event.

Oxygen isotope studies have been reported by Vinogradov and others (1971). Whereas natrocarbonatites have δO^{18} of 8.7 ± 0.1 per mil the upper crust on saturated brine from Lake Magadi has δO^{18} of 36.7 ± 0.3 per mil and the lower crust 29.0 ± 0.2 per mil. Although Vinogradov and others do not report δO^{18} values for the nephelinites of Oldoinyo Lengai, values reported elsewhere for nepheline-bearing igneous rocks (Taylor, 1968; Dontsova and Gerasimovskiy, 1969) are all in the range 6.4 to 10.5 per mil. Again a sedimentary origin is ruled out by the necessity of changing O^{18} from 29-36 to 8.7 per mil. This is highly unlikely to happen given the available exchange medium.

Carbon isotope data are reported in Denaeyer (1970), Vinogradov, Kropotova, and Gerasimovskiy (1970), and O'Neill (1971, personal commun., *in* Deines and Gold, 1973). δC^{13} varies from −4.5 per mil to −7.1 per mil with an average value of −5.8 per mil. This value is identical to the average sovite δC^{13} value for nearby Kerimasi quoted by Vinogradov, Kropotova, and Gerasimovskiy.

Taylor, Frechen, and Degens (1967) postulated a δO^{18} to δC^{13} field for primary carbonatites based on the small isotopic compositional spread of carbonates from the Laacher See Valcano. They argued that the Laacher See rocks are most likely to represent unaltered carbonatite by virtue of their recent eruption (Late Pleistocene to Recent) and of their rapid transportation to the surface from depth. In this way they have probably escaped isotopic alteration processes to which older more deeply dissected plutonic carbonatites seem prone. Within experimental error the δO^{18} and δC^{13} values for the Oldoinyo Lengai natrocarbonatites plot in this primary field.

The isotopic data offer a convincing refutation of the sedimentary origin hypothesis. The fundamental problem remains, however, of how such a natrocarbonatite magma derives from a silicate magma parent. The question of liquid immiscibility between carbonatite and silicate

liquids must be examined in this regard, and the work of Koster van Groos and Wyllie on the system Na_2O–CaO–Al_2O_3–SiO_2–CO_2–H_2O is particularly relevant. In the join plagioclase-sodium carbonate (with 10 percent water) (Koster van Groos and Wyllie, 1973) there is a wide composition range at 1 kb above 750°C, where a carbonate-poor peralkaline silicate liquid coexists with a silicate-poor carbonate liquid. The carbonate liquid is strongly enriched in CaO relative to the silicate liquid — a composition $Pl_{65}NC_{35}$ within the join $Ab_{50}An_{50}$–NC has a carbonate liquid with a composition $CaCO_3$ 46 percent, Na_2CO_3 54 percent. The liquid quenches to a mixture of Na_2CO_3 and $Na_2Ca(CO_3)_2$, analogous both to the behavior predicted in the NC-CC binary system (fig. 1) and to the mineral assemblage in the natural Oldoinyo Lengai natrocarbonatite. Similar immiscible liquids are present in the anhydrous system (Koster van Gross and Wyllie, 1966, fig. 5, p. 245; Koster van Groos, ms).

It seems very probable that the natrocarbonatite liquid at Oldoinyo Lengai has separated immiscibly from the nephelinitic parent magma. Yet the nephelinites are not chemically anomalous, and so why should alkalic carbonatite magmas not be far more common than they appear to be. The problem may well be that petrogenetic thought is conditioned by the *apparent* uniqueness of the Oldoinyo Lengai rocks, carbonatites in general being calcitic, dolomitic, or ankeritic, and rarely sideritic but not markedly alkalic. Perhaps alkalic carbonatite magmas form very commonly but change their character before crystallizing.

It was von Eckermann (1948) who, in his classic Alnö memoir, first advanced the suggestion that the carbonatite magma is the active agent in a carbonatite-alkalic rock complex, that it is initially potassic, and that through a series of metasomatic processes it transforms the country rocks into progressively desilicated alkalic rocks and in so doing itself becomes depleted in alkalies. This point of view was taken up again by Dawson (1964) who, drawing on the eruptions of Oldoinyo Lengai, argued that sodic as well as potassic carbonatite magmas are possible and play a critical role in fenitization. The acceptance of carbonatite magmas has been a very slow process (Tuttle and Gittins, 1966), and it is probably fair to say that this acceptance still does not usually embrace alkalic carbonatite magma. The Oldoinyo Lengai lava is considered by most petrologists to be an extreme case without significance to carbonatite petrogenesis in general, and the views of von Eckermann and Dawson do not seem to have found ready acceptance. The debate becomes further confused by the fact that von Eckermann argued that all the alkalic silicate rocks of the Alno complex were ultimately the result of fenitization.

Few petrologists today would argue this far; there is general acceptance that carbonatite complexes involve both a silicate magma and a carbonatite magma. What is generally at issue is from which magma the fenitization derives. Some arguments have supported ijolitic magma as the source of fenitizing fluids usually pointing out that carbonatite tends

to be intruded late in the history of most complexes, whereas other arguments use the presence of fenites in complexes devoid of ijolites to contend that carbonatitic magma is the source of the fluids.

It appears that most controversies in geology must evolve through a stage where two propositions become polarized, but the time has surely come to state the obvious, namely that fenitization is associated both with some types of silicate magmas and some types of carbonatite magmas. It simply is not an either/or situation.

Reasonable arguments can be advanced that alkalic carbonatite magmas develop commonly but do not in general retain their alkalies. Compilations of average carbonatite compositions suffer from a paucity of good analyses but suggest that the total alkali content rarely exceeds 2 percent with K>Na (Pecora, 1956; Gold, 1963; Heinrich, 1966). This is of course in sharp contrast to the Oldoinyo Lengai lavas in which total alkalies are 35.9 to 37.5 percent and Na_2O/K_2O is 3.9 to 4.5.

Where alkalies are present in carbonatites they are bound as silicates — K in biotite or phlogopite and Na and K in amphiboles and/or pyroxenes. Water clearly has been a constituent of most carbonatite magmas, as the presence of micas and amphiboles readily attests. It is probable that alkalies are retained in a carbonatite magma in which water is present only to the extent that silica is available to fix them as micas and amphiboles. Only very small amounts of Al_2O_3 are necessary for this, because carbonatite amphiboles generally have very low Al_2O_3 contents, and micas often are depleted or lacking in Al_2O_3, its place having been taken by Fe_2O_3. Assuming that the geometry of the aqueous system remains essentially the same as the anhydrous system, a composition in the primary field of calcite might be expected to crystallize calcite, and as the water content of the remaining liquid increases in consequence, the alkali carbonates are likely to dissolve and be lost to the country rocks as fenitizing fluids.

Some solubility data on NC and KC exist, but they are of limited applicability to petrology. Waldeck, Lynn, and Hill (1932) showed that the solubility of NC in water increases from 6.5 percent at 0°C to 33.6 percent at 30°C and then decreases to 2.0 percent at 348°C. Morey and Chen (1956) determined a solubility of less than 0.2 percent at the critical temperature of water. However, there is nothing to indicate that P_{CO_2} was controlled during these experiments, and the solubility is clearly a function both of P_{CO_2} and of the Ph of the solution. It is also possible that this negative slope to the solubility curve with increasing temperature will not hold for the solubility of NC in brine. Such is the case with anhydrite, and it has been argued that fenitizing fluids are brines (Currie and Ferguson, 1971). Even apart from these considerations it is the solubility of NC in supercritical water that is of greater interest in the present context, and of this little is known. Koster van Groos and Wyllie (1968, fig. 3B) suggest that this solubility might be as much as 10 percent at 800°C and 1 kb. The solubility of KC in water is decidedly higher than NC, and further support is provided

by the experiments in the system CC–KC–H_2O summarized earlier as table 3. A mix of fairchildite composition (a potential potassic carbonatite) with excess water at 2 kb and 600°C yields the assemblage calcite + aqueous solution. The same mix under anhydrous conditions yields fairchildite. Fairchildite, although it melts congruently, dissolves in water incongruently to yield calcite + aqueous solution. The solubility of KC in supercritical water is readily demonstrated by these experiments.

It would seem then that a silica-deficient anhydrous carbonatite would preserve its alkalies in the form of alkali carbonates assuming high P_{CO_2} in the system. We suggest that alkalies are normally lost from a hydrous carbonatite magma and that alkali carbonatites crystallize from dry magmas.

We therefore strongly support the view that alkali carbonatite magmas both sodic and potassic develop relatively commonly during the evolution of carbonatite-alkalic rock complexes but that the alkalies are normally lost in aqueous solution as fenitizing fluids. We believe that the common calcitic, dolomitic,and ankeritic carbonatites are often the depleted residue of alkali carbonatite magma. Support for this view is to be found in the very common presence of fenites adjacent to calcitic and dolomitic carbonatite dikes. The source of the alkalies for such fenites has always presented a quandary. Considerable variation in the Na/K ratio is probably possible in these alkalic carbonatite magmas which is undoubtedly the reason why some dikes are bounded by aegirine and/or riebeckite fenites whereas others are bordered by biotitic or phlogopitic zones. The biotite pyroxenites of the Powderhorn (Iron Hill) complex in Colorado have been described as a general alteration of pyroxenite due to the effects of the carbonatite magma (Temple and Grogen, 1965). Biotite is developed abundantly in pyroxenite adjacent to carbonatite dikes. Allen (ms) has described phlogopite/biotite zones 1 to 10 cm wide as occurring commonly along carbonatite dikes cutting pyroxenites of the Cargill complex in Ontario. Examples of calcitic and dolomitic carbonatite dikes bounded by riebeckite zones are widespread.

It is well known that NC is miscible with virtually all silicates and most oxides at 1 atm. This is the basis of classical wet chemical analysis wherein the rock to be analyzed is fused in NC. Koster van Groos and Wyllie (1966) confirmed the miscibility of NC and albite at 1 atm and established the presence of immiscibility at 33 bars. The immiscibility is thus pressure dependent. No pressure data are given for the appearance of immiscibility in the plagioclase-NC system, but it is presumably not very different.

This places further constraints on the persistence of natrocarbonatite lavas. If nephelinite magma is immiscible with natrocarbonatite liquid at pressures above 33 bars, it is clear that a column of magma only 140 m deep is sufficient to maintain immiscibility. Conversely, however, as the magma rises in the volcanic conduit, it will no longer be immiscible with the silicate rocks when it is less than 140 m below

the summit crater, and reaction with wall rocks will commence if the rate of rise is sufficiently slow. The eruption of natrocarbonatite lava at Oldoinyo Lengai presumably indicates that it was expelled from the conduit fairly rapidly. It therefore seems likely that in some circumstances the volcano should erupt lavas that are a solution of nephelinite in natrocarbonatite. Again by analogy to classical wet chemical analysis, such a rock would dissolve in water only slightly more slowly than the natrocarbonatite itself, and it is not surprising that they have not been found. Indeed it is well to remember how fortuitous was the discovery of the natrocarbonatites. Any lavas erupted prior to 1960 were dissolved by rain, and in 1966 the 1960 lavas were buried from sight by ash eruptions.

In conclusion we support the view that alkali carbonatite magmas are relatively common in the evolution of carbonatite-alkalic rock complexes, but that in most cases they are a transitory phenomenon whose existence can be deduced only indirectly. They will persist only if the magma is dry, and unless they are ejected from the volcano relatively rapidly they will become miscible with silicate melts at low pressure and so will react with their silicate wall rocks to form a silico-carbonatate liquid. We believe that the loss of alkalies from a hydrous alkali carbonatite magma results in fenitizing fluids, but this is not to say that all fenitization derives from the carbonatite magma. There is strong field evidence to suggest that fenitization can also be associated with ijolitic and nephelinitic magma.

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