[AMERICAN JOURNAL OF SCIENCE, VOL. 275, FEBRUARY, 1975, P. 163-185]

THE EFFECT OF HIGH CO_2 PRESSURES ON ALKALIC ROCKS AND ITS BEARING ON THE FORMATION OF ALKALIC ULTRABASIC ROCKS AND THE ASSOCIATED CARBONATITES

A. F. KOSTER VAN GROOS

University of Illinois, Chicago, Illinois 60680

ABSTRACT. The phase relations between solid + liquid silicate assemblages and solid + liquid carbonate assemblages were studied at pressures up to 10 kb. The distribution of FeO, MgO, CaO, Na_2O, and K_2O was determined in order to elucidate the relations between carbonatites and the associated alkalic ultrabasic rocks. At 10 kb an immiscibility field between silicate liquids and carbonate liquids is intersected between granitic liquids and $CaCO_3$-rich carbonate liquids and between quartz syenite liquids and $CaCO_3$-rich liquids. Experiments using melteigite and ijolite compositions, plus excess CO_2, in the presence of 10 wt percent H_2O at 10 kb and between 650° and 725° result in the formation of a carbonate liquid + solid assemblage, enriched with CaO and Na_2O, and a crystalline basaltic silicate assemblage, which is enriched with FeO, MgO, and K_2O. The results are consistent with a hypothesis that carbonatitic magmas, rich in CaO, MgO, FeO, and alkalies, are primary and are formed in the mantle by concentration of carbonate droplets. When this magma reaches higher levels in the mantle it reacts with the silicate assemblage of the mantle resulting in the rocks present in carbonatite complexes.

INTRODUCTION

The origin of carbonatites and the associated alkalic rocks has not been satisfactorily explained. Many hypotheses have been proposed (Heinrich, 1966), but definitive experimental data do not exist.

The existence of a miscibility gap between carbonate and silicate liquids in the join $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3–H_2O (Koster van Groos and Wyllie, 1966, 1968a, 1973) suggests that liquid immiscibility may provide a mechanism explaining the origin of the various rocks in carbonatite complexes. While the results of the study of this join are very interesting, the miscibility gap was found to separate an alkalic carbonate liquid, which was strongly enriched with CaO, from an undersaturated silicate liquid (Koster van Groos and Wyllie, 1973), the absence of major components such as Fe_2O_3, FeO, MgO, and K_2O in the join studied makes extrapolation to natural rocks speculative.

In this study I investigate the compositional ranges of carbonate liquid + solid phase assemblages coexisting with geologically reasonable silicate phase assemblages and the distribution of elements between these assemblages. By applying this information to rocks of the carbonatite alkalic-complexes, it is possible to restrict the number of hypotheses explaining the formation of these rocks. Unfortunately, the temperature necessary to melt ultrabasic silicate assemblages could not be attained in the apparatus used. Therefore, the experimental approach was to vary in steps the starting compositions from mixtures with lower melting temperatures to the ultrabasic rocks associated with these complexes. In this way the information obtained in one series of experiments could be used in the following series.

An important distinction between the procedure used in the join $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3–H_2O and this series of experiments is

that in this join the reaction between a silicate and Na_2CO_3 was studied, whereas in the current investigation the effect of CO_2 on a silicate assemblage is determined. To simplify this approach only artificial starting compositions were used. All compositions are in weight percent.

EXPERIMENTAL TECHNIQUE

Starting materials

The major oxides present in carbonatites and the associated rocks are SiO_2, CO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, P_2O_5, and H_2O, and in addition F_2. This represents a 13-component system which would be very difficult to study. The number of components was reduced by deleting TiO_2, FeO, P_2O_5, and, for most compositions, F_2. The presence of both iron oxides could have caused a problem, because it would have been necessary to maintain the oxygen fugacity of the runs at some unknown value in order to maintain the desired FeO/Fe_2O_3 ratio. The presence of Fe_2O_3 is essential in the starting compositions because the rocks under consideration contain modal aegirine (acmite) or aegirine-augite, and, therefore, it influences the distribution of Na_2O between the silicate phases and coexisting carbonate phases. This is especially relevant because acmite is stable at the P, T, and f_{O_2} conditions of the runs, which were made at the Ni-NiO buffer (Bailey, 1969). FeO was deleted because possible reactions with O_2 and Na_2O would result in the formation of additional acmite. TiO_2 was not added. It occurs in the rocks of carbonatite complexes combined mainly with FeO in ilmenite and in a titaniferous magnetite (Heinrich, 1966). Its absence further reduces the need for FeO to be present. It is not expected that the results of this study would change significantly if these oxides were added.

The starting compositions selected in this study are artificial, simplified rock compositions based on a pantellerite, a nepheline syenite, a melteigite, and an ijolite. The latter two represent rocks from the urtite–ijolite–melteigite series, which are typical of carbonatite complexes (Heinrich, 1966). The compositions, listed in tables 1 to 7, decrease in SiO_2 and increase in CaO, MgO, and Fe_2O_3 toward the ijolite composition.

A convenient method of adding CO_2 to the bulk composition is to add components as carbonates. The separate addition of H_2O to the starting mixture controls the H_2O/CO_2 ratio in the sample.

The simplified rock compositions were obtained by mixing a dehydrated gel of the desired SiO_2–Al_2O_3 ratio, which was prepared following the procedure of Luth and Ingamells (1965), with the appropriate amounts of Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, NaF, NaCl, and Fe_2O_3. All starting materials were ground to pass 200 mesh, dried to constant weight, mixed in a mechanical shaker for 15 minutes, and stored in a dessicator.

Apparatus and method

All runs were made in conventional and high-pressure cold-seal pressure vessels (Tuttle, 1949; Luth and Tuttle, 1963), using standard techniques (Wyllie and Tuttle, 1960; Koster van Groos and Wyllie, 1968a).

Bulk compositions were obtained by pipetting a known amount of distilled water in a gold capsule and adding the desired weight of the starting mixture. The total amount of the sample was usually between 30 and 40 mg. Temperature measurements are believed accurate to ± 5°C. Pressures up to 4 kb were measured with commercial bourdon-type gauges, which are accurate to within 5 percent; higher pressures, measured with a manganin cell circuit, are accurate to ± 150 bars.

Most runs were kept at the desired temperature and pressure for 36 to 48 hrs. Some runs were of a much longer duration (up to 240 hrs) in order to determine whether equilibrium conditions had been reached. The results were completely compatible with the shorter runs, and it is assumed that all runs approached equilibrium. The vessel was quenched by directing an air blast against the hottest part of the vessel; during this quench pressure in the high-pressure vessel decreased about 30 percent.

The amount of CO_2 in the gas phase of the quenched run was determined by the weight difference of the capsule before and after it was punctured to allow CO_2 to escape. Then, the capsule was dried at 110°C and again weighed to determine the loss of H_2O. The error of these weighings may be ± 10 percent, due to the small amount of material present. Therefore, the values of the CO_2/H_2O ratio of the vapor phase, which are included with the results, are accurate to ± 25 percent. This ratio is not directly representative for the vapor phase during the run because the carbonate liquid will release H_2O during the quench reducing the CO_2/H_2O ratio.

Subsequently, the sample was removed from the capsule and crushed under acetone. A small amount of the sample was examined optically. Next, the sample was analyzed by X-ray diffraction. Then it was treated with 2 ml of acetic acid (0.1 molar); the residue was washed 5 times using 2 ml distilled water each time, and the combined solution of the carbonates was prepared for analysis by atomic absorption using standard methods. The insoluble residue was again analyzed by X-ray diffraction and prepared for analysis by atomic absorption following the method of Bernas (1967) for determination of the composition of the silicates.

The vapor phase probably formed deposits during the quench; they may have dissolved in acetic acid together with carbonates (Koster van Groos and Wyllie, 1973), affecting the results of the analyses of the carbonate phases. These vapor deposits are likely to be alkali-rich, possibly producing higher values for the alkali content of the carbonate phase. The accuracy of the analyses for the major constituents is better than 5 percent. The analyses of the fraction soluble in acetic acid are calculated to form carbonates. All analyses are calculated to total 100 percent.

Identification of phases

The phases were identified using the appearance of the capsule, the physical characteristics of the sample after it was removed from the capsule, petrographic study of the crushed sample, and X-ray powder diffrac-

tion patterns. Refractive indices were measured in sodium light. They are assumed to be accurate to ± 0.001.

The phases encountered are described below.

Feldspar was present as a very fine grained sub-solidus phase and as small platy to lath-shaped crystals when a silicate liquid was present. No effort was made to determine its composition.

Nepheline was identified by X-ray methods in several subsolidus runs. Its grain size was too small for optical identification.

Quartz was identified by X-ray methods only.

Pyroxene formed small colorless stubby crystals, about 0.05 mm long, in the presence of a silicate liquid. In sub-solidus runs the crystals were too small for optical identification.

Acmite formed light-green stubby crystals, 0.1 mm long.

Hematite was found in some runs where it covered the inside of the gold capsule with a fine small amount of reddish powder. It may have been formed during the quench.

Calcite was difficult to recognize optically in the fine-grained carbonate phase. When coexisting with a silicate liquid, roundish grains of calcite, typical of primary calcite crystals (Wyllie and Tuttle, 1960), were found as inclusions in the silicate liquid. These grains were up to 0.15 mm in diameter.

Silicate liquid quenches to a clear glass. In many runs fine-grained spherical carbonate inclusions of up to 0.10 mm diameter were present.

Carbonate liquid does not quench to a glass but to a fine grained carbonate assemblage. The spherical inclusions in the silicate glass mentioned above, which are quite distinct from the roundish inclusions of calcite, are considered evidence of the liquid nature of the inclusion at the conditions of the run (Koster van Groos and Wyllie, 1968a, 1973). In the absence of a silicate liquid, it was necessary to infer from the composition of the carbonates whether a carbonate liquid was present during the run.

Vapor was present in all runs as was indicated by the presence of CO_2 and H_2O in the puffed capsules. No silica-rich deposits typical for a vapor phase in silicate–H_2O systems were found.

RESULTS AND DISCUSSION

Experiments with artificial pantellerites

Pantellerites are peralkaline rhyolites very low in MgO and CaO. The CO_2 content is always very small. Compositions modeled after this rock type were used because of their low melting temperature.

Initially a natural occurring pantellerite plus oxalic acid dihydrate was used as a starting material. The results were discouraging, probably because of the uncertainty in its composition, and the use of natural materials was abandoned in favor of artificial mixtures.

The starting compositions of the first series of experiments were modeled after a pantellerite glass D 100126 (table 1) of the Gold Flat Member of the Thirsty Canyon tuff (Noble, 1965). The purpose of this

series of reconnaissance experiments was to determine whether in rocks containing normative Na_2SiO_3 carbonates would form at moderate CO_2 pressures.

Four starting mixtures were used, P_1 to P_4, see table 1. P_1 contains neither Fe_2O_3 nor NaCl + NaF, P_2 contains Fe_2O_3, P_3 contains NaCl + NaF, and P_4 contains both Fe_2O_3 and NaCl + NaF. P_4 approaches the pantelleritic composition D 100126 closely, except that no FeO is present. Thus, assuming that acmite is the stable Fe-silicate phase in the runs, no additional acmite could form by oxidation of FeO to Fe_2O_3. The presence of NaCl + NaF changed the amount of normative Na_2SiO_3 without changing the amount of sodium in the starting mixture.

Runs were made at 800° and 850°C at 1, 2, and 3 kb pressure; 5 percent H_2O was added to all runs. In the runs with the composition P_1, P_2, and P_3 respectively 4 percent, 2 percent, and less than 1 percent carbonate inclusions were found in silicate glass (N_{glass} = 1.516-1.518). These

TABLE 1

Pantelleritic starting compositions

	D100126	P_1	P_2	P_3	P_4
SiO_2	69.25	69.25	69.25	69.25	69.25
Al_2O_3	9.10	9.10	9.10	9.10	9.10
Fe_2O_3*	3.70	—	3.70	—	3.70
FeO	2.61	—	—	—	—
MgO	0.011	—	—	—	—
CaO	0.06	—	—	—	—
Na_2O	7.00	7.00	7.00	7.00	7.00
K_2O	4.29	4.29	4.29	4.29	4.29
rare alkali	0.16	—	—	—	—
H_2O^+	0.14	—	—	—	—
H_2O^-	0.01	—	—	—	—
TiO_2	0.25	—	—	—	—
ZrO_2	0.78	—	—	—	—
P_2O_5	0.01	—	—	—	—
MnO	0.19	—	—	—	—
CO_2**	0.00	6.98	6.98	4.99	4.99
SO_3	0.08	—	—	—	—
Cl	0.78	—	—	0.78	0.78
F	1.30	—	—	1.30	1.30
Other	0.62	—	—	—	—
Less O	0.72	—	—	0.72	0.72
Total	99.63	96.62	100.32	95.99	99.69
C.I.P.W. norm (excluding CO_2)					
q	32.2	32.9	31.5	35.6	34.2
or	25.4	25.4	25.4	25.4	25.4
ab	22.9	22.9	22.9	22.9	22.9
en	0.02	—	—	—	—
fs	4.7	—	—	—	—
wo	0.1	—	—	—	—
ac	10.7	—	10.7	—	10.7
ns	0.14	8.45	5.62	2.97	0.14
NaCl	1.29	—	—	1.29	1.29
NaF	2.87	—	—	2.87	2.87
ilm	0.47	—	—	—	—
ap	0.02	—	—	—	—

*, ** See table 2.

inclusions are spherical and appeared to contain a fine grained carbonate aggregate, similar in appearance to ones encountered in earlier studies (Koster van Groos and Wyllie, 1968a, 1973). They are considered to be evidence for the presence of a carbonate liquid coexisting with a silicate liquid. No attempt was made to determine the composition of the carbonate phase, the amount present being too small. The amount of carbonate was not measurably affected by the variation in temperature and pressure. In runs with P_4 no carbonate phases were found. A small amount of acmite, less than 2 percent, was present in runs with P_2 and P_4.

The amount of CO_2 present in the vapor phase as determined by weight-loss on puncturing the capsule increased from about 4 percent to about 5 percent of the sample from runs with P_1 to runs with P_4. The amount of H_2O in the vapor phase as determined by drying the sample at 110°C increased from about 2.5 percent to 3.5 percent. Thus, the molar ratio CO_2/H_2O of the vapor phase in these runs is about 0.6. Comparison of the amount of CO_2 present in the starting mixture with the amount of CO_2 in the vapor phase combined with the CO_2 content of the carbonate phase confirms that the solubility of CO_2 in silicate liquids at these pressures is very low (Wyllie and Tuttle, 1959; Eggler, 1973).

It is concluded from these results that carbonate liquids may coexist with silicate liquids, even when the silicate liquids are SiO_2-rich. The amount of carbonate formed appears to be proportional to the amount of normative Na_2SiO_3 in the starting material. Furthermore, acmite is stable in the presence of a CO_2-rich vapor phase at the conditions of these runs.

Experiments with an artificial pantellerite with additional CaO and MgO

In the next phase of this investigation 10 percent CaO and 5 percent MgO were added to P_4 to form mixture P_5 (table 2).

Runs were made at 10 kb pressure between 650° and 725°C, the maximum temperature obtainable at this pressure with externally heated pressure vessels. The H_2O content of the runs is listed in table 2. These conditions were selected so the runs would be within the stability field of either the magnesite + quartz or the magnesite + enstatite assemblage (Johannes, 1969) as well as within the stability field of siderite (Weidner, 1972), thus increasing the probability that the MgO and the FeO content of the carbonate phase would be significant. The presence of NaCl and especially NaF is desirable because these salts lower the melting temperature of silicates (Koster van Groos and Wyllie, 1968b, 1969) and favor the formation of a silicate liquid at temperatures that can be attained by the apparatus.

The analytical results are presented in table 2, other run data are listed in table 3. The composition of P_5 is recalculated to 100 percent excluding CO_2 to facilitate comparison with the composition of the silicate assemblages. The runs at 650° and 675°C were fine crystalline mixtures of quartz, feldspar, diopside, acmite, and carbonate. No silicate glass, representing a quenched silicate liquid, was observed. In the run

TABLE 2

Analytical results of runs with the composition P_5 at 10 kb

	Starting Mixture P_5	Recal-culated to 100%	T=650°C +8% H_2O Sil.	Carb.	T=675°C +8% H_2O Sil.	Carb.	T=675°C +16% H_2O Sil.	Carb.	T=675°C +25% H_2O Sil.	Carb.	T=700°C +8% H_2O Sil.	Carb.	T=725°C +8% H_2O Sil.	Carb.	T=725°C +16% H_2O Sil.	Carb.
SiO_2	69.25	62.7	67.6	—	68.7	—	68.9	—	69.5	—	68.5	—	69.0	—	68.3	—
Al_2O_3	9.10	8.2	9.5	—	9.2	—	9.1	—	8.8	—	9.2	—	9.3	—	9.3	—
Fe_2O_3*	3.70	3.4	4.1	—	4.0	—	3.6	—	3.3	—	3.7	—	3.8	—	3.8	—
FeO	—	—	—	0.5	—	0.3	—	0.3	—	0.3	—	0.3	—	0.1	—	0.2
MgO	5.00	4.5	4.8	1.1	4.8	0.5	4.7	0.4	4.3	0.3	5.7	0.4	5.0	0.2	4.4	0.2
CaO	10.00	9.1	5.3	46.1	4.3	46.8	4.1	46.5	6.1	42.9	4.3	44.3	3.2	45.6	5.8	42.9
Na_2O	7.00	6.3	4.9	6.6	5.1	6.1	5.6	6.3	3.5	12.6	4.7	8.3	4.7	8.7	4.8	12.5
K_2O	4.29	3.9	4.0	2.7	3.9	3.1	3.9	3.6	4.5	0.9	3.5	3.5	4.9	2.1	3.6	0.9
Cl†	0.78	0.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—
F†	1.30	1.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CO_2**	18.35	16.6	—	43.0	—	43.3	—	43.1	—	43.4	—	43.1	—	43.3	—	43.3
less 0	0.72	0.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Total†	128.05	115.9	100.2	100.0	100.0	100.1	99.9	100.2	100.0	100.4	99.6	99.9	99.9	100.0	100.0	100.0
mol.CO_2/H_2O	—	—	0.14	—	0.22	—	0.10	—	0.06	—	0.22	—	0.18	—	0.09	—
C.I.P.W. norm																
q		14.4	17.9	—	20.9	—	21.4	—	23.3	—	20.1	—	21.6	—	19.8	—
or		22.8	23.6	—	23.0	—	23.0	—	26.6	—	20.7	—	28.9	—	21.3	—
ab		20.6	26.6	—	25.6	—	25.1	—	20.2	—	27.8	—	20.6	—	27.8	—
en		11.3	12.0	—	12.0	—	11.7	—	10.7	—	14.2	—	12.5	—	11.0	—
wo		18.7	11.0	—	8.9	—	8.5	—	8.9	—	8.9	—	6.6	—	12.1	—
ac		9.7	11.8	—	11.6	—	10.4	—	8.3	—	10.5	—	11.0	—	11.0	—
ns		0.1	0.3	—	1.0	—	2.4	—	—	—	—	—	—	—	0.1	—
NaCl		1.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
NaF		2.9	—	—	—	—	—	—	—	—	—	—	—	—	—	—
hem		—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
cc		—	—	82.1	—	83.6	—	83.0	—	76.6	—	79.5	—	81.4	—	76.5
mc		—	—	2.3	—	1.1	—	0.8	—	0.6	—	0.8	—	0.4	—	0.4
fc		—	—	0.8	—	0.5	—	0.5	—	0.5	—	0.5	—	0.2	—	0.3
nc		—	—	11.3	—	10.4	—	10.7	—	21.5	—	14.2	—	14.9	—	21.4
kc		—	—	4.0	—	4.5	—	5.3	—	1.3	—	5.1	—	3.1	—	1.3

* Fe_2O_3 is present in the starting mixture. In the results iron is calculated as Fe_2O_3 in the silicate fraction and as FeO in the carbonate fraction.

** CO_2 is ignored in the norm calculation of P_5. In the analyses it is calculated to form 100 percent carbonates.

† Cl and F are ignored in the analyses.

Sil., Carb. = analysis of the silicate/carbonate assemblage respectively.

at 700°C, with 8 percent H_2O, about 10 percent glass (N = 1.508) was present, increasing to about 80 percent (N = 1.520) in a run at 725°C, with 16 percent H_2O. Small spherical carbonate inclusions containing either primary calcite or fine-grained crystalline aggregates were observed in the silicate glass, proving the coexistence of a silicate liquid and a carbonate liquid. It is difficult to establish whether a carbonate liquid was present at lower temperatures. However, a carbonate assemblage with a composition as shown in table 2 and containing a small amount of NaF and NaCl would begin to melt at about 560°C at 1 atm pressure (Levin, Robbins, and McMurdie, 1964). Considering that H_2O lowers the melting point of carbonates at elevated pressures (Wyllie and Tuttle, 1960; Koster van Groos and Wyllie, 1968a; Wyllie and Boettcher, 1969), it is concluded that a significant proportion of the carbonates formed a carbonate liquid in these runs.

The chemical analyses of the runs (table 2) show that the carbonate assemblage contains about 80 percent $CaCO_3$, with Na_2CO_3 constituting about 15 percent, K_2CO_3 about 3 percent, and $MgCO_3$ and $FeCO_3$ about 1 percent. Thus, the carbonate phase assemblage is strongly enriched with CaO and, to a lesser degree, with Na_2O. It is, however, slightly depleted in K_2O. MgO and FeO are strongly enriched in the silicate assemblage. The low FeO content of the carbonates may indicate that iron occurs mainly as Fe_2O_3 as is shown by the presence of acmite (table 3). Considering, however, the lower thermal stability of $FeCO_3$ as compared with $MgCO_3$, the low FeO content of the carbonate assemblage is not surprising.

The normative composition of the carbonates illustrates the effect of increasing temperature and H_2O content. The amount of Na_2CO_3 (nc) almost doubles, from about 11 percent at 650°C and an H_2O content of 8 percent to 21 percent at 725°C and an H_2O content of 25 percent; the K_2CO_3 (kc) content, however, diminishes sharply from about 4 to 1.3 percent. Increase of temperature results in the reduction of the amount of $MgCO_3$ and $FeCO_3$ in the carbonates. These effects probably will be reversed with increasing pressure, for they result from the lowering of the partial pressure of CO_2 with the higher H_2O contents and the

TABLE 3

Run data for the composition P_5 at 10 kb

Temperature	650°C	675°C	675°C	675°C	700°C	725°C	725°C
H_2O content	8%	8%	16%	25%	8%	8%	16%
Silicate phases*	q,f, cpx,ac	q,f, cpx,ac	q,f, cpx,ac	q,f, cpx,ac	f,L_{s11}, cpx,ac	L_{s11}, cpx,ac	L_{s11}, cpx
Silicate glass	—	—	—	—	10%	70%	80%
N glass	—	—	—	—	1.508	1.520	1.520
Carbonate phases	15%	15%	15%	15%	15%	15%	15%
Spherical inclusions	—	—	—	—	yes	yes	yes

* Abbreviations: q = quartz, f = feldspar, cpx = diopside, ac = acmite.

decrease in the stability of the carbonates, especially of $MgCO_3$ and $FeCO_3$, with increased temperature.

The presence of excess Na_2O in the silicate assemblage, as indicated by normative Na_2SiO_3, may be the result of some NaF and possibly NaCl dissolved in the silicate liquid. The presence of acmite in the runs shows that this phase is stable in a CO_2-rich vapor phase at high pressures. The compositions of the silicate and carbonate assemblages do not appear to to be affected significantly by the presence or absence of a silicate liquid. The silicate composition is essentially a granite with normative diopside and acmite. The coexisting carbonate phase assemblage is composed mainly of $CaCO_3$ and Na_2CO_3.

In conclusion, the P_5 series of runs shows that at 10 kb a carbonate crystal + liquid assemblage, containing about 80 percent $CaCO_3$, coexists with a granitic assemblage up to 725°. The presence or absence of a silicate liquid does not appear to affect the composition of either the silicate or the carbonate assemblage. At the conditions of this series of experiments MgO and FeO fractionate strongly toward the silicate phase assemblage.

Nepheline syenite composition

The next series of experiments was made with a composition similar to a nepheline syenite but low in Al_2O_3, high in $CaCO_3$, and with excess Na_2O (table 4). Neither NaF or NaCl were added. Runs, containing 10 percent H_2O, were made between 650° and 725°C at 10 kb. The analytical results are presented in table 4; other run data are listed in table 5. The runs at 650° and 675°C contained a microcrystalline aggregate of quartz, feldspar, diopside, acmite, and carbonate; no silicate glass was present. A run at 700°C contained 30 percent glass (N = 1.508), and a run at 725°C contained 60 percent glass (N = 1.518). Both glasses had a large number of carbonate inclusions consisting of roundish, primary calcite crystals and micro-crystalline spherical aggregates establishing the presence of two immiscible liquid phases. The amount of carbonates, about 20 percent, does not vary significantly between the runs.

The analyses of the silicate phase assemblages (table 4) show that these are slightly oversaturated with SiO_2 as compared with the undersaturated starting mixture. The composition of the silicate assemblage is similar to an alkalic quartz syenite. In the runs at 700° and 725°C, normative hematite is present in addition to acmite. This indicates that the alkali content of the silicate fraction is lower than in the previous series of experiments. No hematite was found in the samples. The composition of the carbonate assemblages is very similar to those in the runs with P_5. $CaCO_3$ is the dominant carbonate, constituting about 80 percent of the assemblage, and Na_2CO_3 the most important alkali carbonate with about 15 percent present. Again, the amount of CaO and K_2O, together with MgO and FeO, decreases with increasing temperature while the amount of Na_2O increases.

In conclusion, these runs establish that for compositions undersaturated with SiO_2, a CO_2-rich vapor phase at high pressure will stabilize

TABLE 4

Analytical results of runs with a syenite composition and 10% H_2O present at 10 kb

Starting Composition		T=650°C		T=675°C		T=700°C		T=725°C	
		Sil.	Carb.	Sil.	Carb.	Sil.	Carb.	Sil.	Carb.
SiO_2	55.0	64.3	—	65.3	—	64.6	—	62.8	—
Al_2O_3	10.0	13.0	—	12.4	—	11.8	—	11.7	—
Fe_2O_3*	3.0	3.8	—	3.5	—	2.9	—	3.6	—
FeO	—	—	0.2	—	0.1	—	0.1	—	0.1
MgO	5.0	4.4	1.6	5.9	0.6	5.4	1.0	6.0	0.4
CaO	15.0	4.1	48.8	3.1	47.3	7.3	47.4	7.8	44.2
Na_2O	7.0	7.4	4.0	7.2	6.3	6.0	5.6	5.0	10.9
K_2O	3.0	3.0	1.8	2.6	2.5	2.2	2.4	3.2	1.0
CO_2**	23.6	—	43.9	—	43.5	—	43.5	—	43.4
Total	121.6	100.0	100.3	100.0	100.3	100.2	100.0	100.1	99.9
mol. CO_2/H_2O	—	0.16	—	0.22	—	0.28	—	0.37	—
C.I.P.W. norm									
q	—	4.5	—	6.7	—	6.5	—	4.7	—
or	17.7	17.7	—	15.4	—	13.2	—	18.9	—
ab	17.7	50.2	—	49.3	—	48.3	—	41.3	—
ne	9.2	—	—	—	—	—	—	—	—
en	12.5	11.1	—	14.7	—	13.5	—	14.9	—
wo	31.7	8.5	—	6.4	—	15.1	—	16.1	—
ac	8.7	11.0	—	10.1	—	1.8	—	0.9	—
ns	3.4	—	—	0.1	—	—	—	—	—
hem	—	—	—	—	—	2.3	—	3.3	—
cc	—	—	87.1	—	84.5	—	84.6	—	78.9
mc	—	—	3.4	—	1.3	—	2.1	—	0.8
fc	—	—	0.3	—	0.2	—	0.2	—	0.2
nc	—	—	6.8	—	10.8	—	9.6	—	18.7
kc	—	—	3.6	—	3.7	—	3.5	—	1.5

*,** See table 2.

Sil., Carb. = analysis of the silicate/carbonate assemblage respectively.

a $CaCO_3$-rich carbonate crystal + liquid assemblage which may coexist with a quartz syenite silicate assemblage. It is shown again that the composition of the carbonates is not affected by the formation of a silicate liquid. Notable is the low MgO and FeO content of the carbonates in these runs.

Ultrabasic rock compositions

The final series of experiments was made with two mixtures (tables 6 and 7) which were modeled after rocks from the urtite–ijolite–melteigite series. This series is characteristic of carbonatite complexes (Heinrich, 1966). The actual compositions were made after analyses from a garnet-biotite melteigite (MC-113) and an ijolite (MC-217) of the alkalic igneous complex at Magnet Cove, Ark. (Erickson and Blade, 1963, table 13, 21). Both are very low in SiO_2 and high in CaO. The melteigite is peraluminous, as is indicated by normative anorthite; the ijolite is slightly peralkaline. The starting mixtures were recalculated to total 100 percent, excluding CO_2.

Runs with 10 percent H_2O present were made between 650° and 725°C at 10 kb. The analytical results are shown in tables 6 and 7. All runs contained a micro-crystalline aggregate of feldspar, diopside, forsterite, nepheline, hematite, and carbonate. No silicate glass was detected in any run.

The chemical composition of the silicate fraction of each mixture is fairly constant within the temperature range. The SiO_2 content is significantly higher than in the starting mixtures, but the composition remained undersaturated with SiO_2 as is shown by normative forsterite and nepheline.

The CaO content of the silicate fraction is too low to form normative wollastonite in excess of the required amount needed to form diopside. All silicate fractions are peraluminous as is illustrated by the presence of normative anorthite. The chemistry of these assemblages is somewhat similar to a nepheline basalt with excess of alkalies.

The carbonate fraction, about 30 percent of the sample, is very rich in $CaCO_3$, the melteigite containing about 90 percent $CaCO_3$, and the ijolite about 85 percent $CaCO_3$. Similar to the other experimental data, the next most abundant carbonate is Na_2CO_3, while MgO and FeO contents are low. The effect of increasing temperature is, again, an increase in Na_2O and a decrease in MgO and FeO, and perhaps in K_2O. The CaO

TABLE 5

Run data for the nepheline syenite composition with 10% H_2O at 10 kb

Temperature	650°C	675°C	700°C	725°C
Silicate phases*	q,f,cpx,ac	q,f,cpx,ac	f,L_{sil}, cpx,ac	L_{sil}, cpx,ac
Silicate glass	—	—	30%	60%
N glass	—	—	1.506	1.516
Carbonate phases	20%	20%	20%	20%
Spherical inclusions	—	—	yes	yes

* For abbreviations, see table 3.

TABLE 6

Analytic results of runs with a melteigite composition with 10% H_2O present at 10 kb

MC113†		Starting Mixture	Recalculated to 100%	T=650°C Sil.	T=650°C Carb.	T=675°C Sil.	T=675°C Carb.	T=700°C Sil.	T=700°C Carb.	T=725°C Sil.	T=725°C Carb.
SiO_2	40.08	40.0	45.2	54.5	—	56.3	—	54.0	—	54.5	—
Al_2O_3	11.74	11.5	13.0	15.2	—	16.0	—	14.9	—	14.7	—
Fe_2O_3*	7.19	7.0	7.9	9.4	—	7.8	—	7.0	—	7.1	—
FeO	4.75	—	—	—	0.5	—	0.3	—	0.5	—	0.5
MgO	6.72	6.7	7.6	8.6	1.2	8.7	0.8	8.1	0.8	8.5	0.7
CaO	15.69	15.7	17.7	3.0	53.2	2.9	52.6	6.4	50.8	6.2	51.5
Na_2O	3.89	4.0	4.5	5.2	0.6	5.2	1.4	5.3	2.6	5.1	2.5
K_2O	3.47	3.5	4.0	4.1	0.5	3.1	1.0	4.2	1.5	4.0	1.0
CO_2**	0.18	24.2	27.3	—	44.0	—	43.9	—	43.8	—	43.6
TiO_2	3.44	—	—	—	—	—	—	—	—	—	—
Other	3.06	—	—	—	—	—	—	—	—	—	—
Total	100.04	112.7	127.3	100.0	100.0	100.0	100.0	99.9	100.0	100.1	99.8
mol CO_2/H_2O	—	—	—	0.29	—	0.44	—	0.39	—	0.44	—
C.I.P.W. norm											
or	—		—	24.2	—	18.3	—	24.8	—	23.6	—
ab	—		—	36.8	—	44.0	—	23.7	—	27.1	—
an	4.32		3.5	6.0	—	11.2	—	4.5	—	5.4	—
ne	17.83		20.7	3.9	—	—	—	11.5	—	8.7	—
lc	16.08		18.3	—	—	—	—	—	—	—	—
en	9.93		11.0	3.2	—	7.3	—	9.9	—	9.2	—
wo	22.81		26.2	3.7	—	1.4	—	11.4	—	10.6	—
fo	4.77		5.5	12.8	—	10.1	—	7.2	—	8.4	—
cs	5.81		6.8	—	—	—	—	—	—	—	—
hem	3.49		7.9	9.4	—	7.8	—	7.0	—	7.1	—
mgt	5.37		—	—	—	—	—	—	—	—	—
ilm	6.53		—	—	—	—	—	—	—	—	—
cc	0.41		—	—	95.2	—	94.0	—	90.8	—	92.0
mc	—		—	—	2.3	—	1.7	—	1.7	—	1.5
fc	—		—	—	0.8	—	0.5	—	0.8	—	0.8
nc	—		—	—	1.0	—	2.4	—	4.4	—	4.3
kc	—		—	—	0.7	—	1.5	—	2.2	—	1.5

*,** See table 2.

† Analysis of a garnet-biotite melteigite (Erickson and Blade, 1963)

Sil., Carb. = analysis of the silicate/carbonate assemblage respectively.

TABLE 7

Analytic results of runs with an ijolite composition with 10% H_2O present at 10 kb

	MC217†	Starting Mixture	Recalculation to 100%	T=650°C Sil.	T=650°C Carb.	T=675°C Sil.	T=675°C Carb.	T=700°C Sil.	T=700°C Carb.	T=725°C Sil.	T=725°C Carb.
SiO_2	36.89	37.0	42.6	51.4	—	50.3	—	52.7	—	53.0	—
Al_2O_3	13.28	13.0	15.0	17.8	—	17.7	—	17.4	—	16.9	—
Fe_2O_3*	7.58	7.5	8.6	10.7	—	10.7	—	10.6	—	10.8	—
FeO	3.71	—	—	—	1.1	—	1.2	—	2.5	—	0.5
MgO	4.22	4.5	5.2	6.3	1.1	6.4	1.3	5.9	2.2	5.3	0.2
CaO	14.80	15.0	17.3	1.6	49.1	3.7	44.4	1.9	40.5	1.7	49.1
Na_2O	5.29	5.3	6.1	5.7	3.1	4.9	6.5	4.9	7.4	6.3	6.2
K_2O	4.62	4.6	5.3	6.5	1.9	6.7	3.1	6.6	4.4	6.0	0.5
CO_2**	1.54	22.7	26.1	—	43.6	—	43.1	—	43.1	—	43.7
TiO_2	3.32	—	—	—	—	—	—	—	—	—	—
Other	4.81	—	—	—	—	—	—	—	—	—	—
Total	100.06	109.6	126.1	100.0	99.9	100.4	99.6	100.0	100.1	100.00	100.2
mol CO_2/H_2O	—	—	—	0.28	—	0.21	—	0.32	—	0.22	—
C.I.P.W. norm											
or	—		—	38.4	—	39.6	—	39.0	—	35.5	—
ab	—		—	17.0	—	8.2	—	21.5	—	24.3	—
an	—		—	3.8	—	6.5	—	6.0	—	0.1	—
ne	23.07		25.7	16.9	—	18.0	—	10.9	—	15.7	—
lc	21.41		24.5	—	—	—	—	—	—	—	—
en	1.82		—	1.5	—	4.3	—	1.2	—	3.0	—
wo	16.54		16.0	1.7	—	4.9	—	1.4	—	3.5	—
fo	6.09		9.1	10.0	—	8.2	—	9.4	—	7.2	—
cs	7.45		14.6	—	—	—	—	—	—	—	—
ac	1.92		3.7	—	—	—	—	—	—	—	—
hem	5.31		7.4	10.7	—	10.7	—	10.6	—	10.8	—
mgt	2.34		—	—	—	—	—	—	—	—	—
ilm	6.31		—	—	—	—	—	—	—	—	—
cc	3.50		—	—	87.7	—	79.3	—	72.3	—	87.7
mc	—		—	—	2.3	—	2.7	—	4.6	—	0.4
fc	—		—	—	1.8	—	1.9	—	4.0	—	0.8
nc	—		—	—	5.3	—	11.1	—	12.7	—	10.6
kc	—		—	—	2.8	—	4.6	—	6.5	—	0.7

*,** See table 2.

† Analysis of a fine-grained ijolite (Erickson and Blade, 1963).

Sil., Carb. = analysis of the silicate/carbonate assemblage respectively.

content appears to decrease, but this effect is less pronounced than in previous runs. Because the composition of the carbonate assemblage is similar to those in the previous experiments, it is concluded that in these runs a carbonate liquid was present also.

An alkali-basalt, which is somewhat similar in composition to the silicate fractions of these runs, begins to melt in the presence of H_2O at 610°C and 10 kb (Yoder and Tilley, 1962). With a vapor phase with an initial molar ratio $CO_2/H_2O = 1$ a tholeiitic basalt begins to melt at about 725°C and 10 kb (Hill and Boettcher, 1970). Therefore, it was expected that the silicate fractions at 725°C would melt in the presence of a vapor phase with a CO_2/H_2O ratio of about 0.2 to 0.4. However, the absence of a silicate liquid in these runs indicates that the CO_2/H_2O ratio may have been substantially higher during the run. This may be explained by the high solubility of H_2O in a carbonate liquid under pressure (Koster van Groos and Wyllie, 1968a; Wyllie and Boettcher, 1969), which will release H_2O during the quench, thus reducing the CO_2/H_2O ratio. It is likely, though, that the silicate assemblage will begin to melt at only a slightly higher temperature.

The results of these series of experiments clearly show that mixtures representing rocks highly undersaturated with SiO_2 and rich in CaO will react with a CO_2-rich vapor phase at 10 kb and temperatures up to 725°C to form a $CaCO_3$-rich carbonate crystal + liquid assemblage coexisting with a silicate assemblage that has a composition of a nepheline basalt with excess alkalies. Depending on the temperature a carbonate liquid may form. While no silicate liquid was formed at these conditions in the presence of a CO_2-rich vapor phase, at some higher temperature the silicate fraction will begin to melt. It is reasonable to expect that at this temperature a CaO-rich carbonate liquid, which is poor in MgO and FeO but which contains an appreciable amount of alkalies, will coexist with a basaltic silicate liquid.

Conclusions

Compositions ranging from peralkaline pantellerites to the ultrabasic melteigite and ijolite were studied at 10 kb and between 650° and 725°C. The results establish that the miscibility gap between silicate and carbonate liquids present in the join $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3–H_2O at elevated pressures (Koster van Groos and Wyllie, 1973) extends into systems containing in addition MgO, K_2O, and Fe_2O_3.

Chemical analyses show that the carbonate solid + liquid assemblages coexisting with the silicate phases are rich in $CaCO_3$, with Na_2CO_3 being the second most abundant constituent. K_2CO_3, $MgCO_3$, and $FeCO_3$ are present in minor amounts. The presence or absence of a silicate liquid in the runs does not affect the carbonate composition. Increase in temperature causes an increase in the $NaCO_3$ content of the carbonate assemblage while reducing the $CaCO_3$, $MgCO_3$, and $FeCO_3$ contents (tables 2, 4, 6, and 7).

I conclude that at 10 kb and between 650° and 725°C a CO_2-rich vapor will react with a peralkaline silicate assemblage following a reaction,

$$Na_2SiO_3 + CO_2 \rightleftharpoons Na_2CO_3 + SiO_2 \quad (1)$$

and that, if CaO is present, a similar reaction,

$$CaSiO_3 + CO_2 \rightleftharpoons CaCO_3 + SiO_2 \quad (2)$$

takes place also. With compositions highly undersaturated in SiO_2 reaction (2) seems to be more dominant (tables 6 and 7) than in quartz-normative compositions (table 2).

MgO and FeO in the starting compositions remain almost entirely in the silicate assemblages, as only 2.5 percent $MgCO_3$ is found in the carbonate assemblages at 650°C, and this decreases sharply with increasing temperature. Because the solubility of $MgCO_3$ in calcite at 10 kb and 650°C is about 10 percent (Goldsmith and Newton, 1969), it appears that calcite present in the carbonate assemblage is undersaturated with $MgCO_3$. Dolomite, therefore, does not occur in these runs.

The ultrabasic melteigite and ijolite starting mixtures react with CO_2 at 10 kb and up to 725°C to form a CaO-poor nepheline basalt composition with excess alkalies. In this reaction a carbonate solid + liquid assemblage rich in $CaCO_3$ and containing a significant amount of Na_2CO_3 is produced (tables 6, 7).

PETROLOGICAL APPLICATIONS

The limestone assimilation hypothesis

Runs with a CaO-enriched pantelleritic composition (table 2) show that a granitic melt may coexist with a carbonate liquid at moderate to high CO_2 pressures. This result is relevant with respect to limestone assimilation (Daly, 1910; Shand, 1945). Watkinson and Wyllie (1969) showed in the join $NaAlSi_3O_8$–$CaCO_3$–H_2O that addition of up to 15 percent $CaCO_3$ to a silicate melt, which is saturated with H_2O, results in the formation of a plagioclase–wollastonite–liquid assemblage. With further addition of $CaCO_3$ nepheline forms at the expense of plagioclase, but the melt crystallizes because of an increase of the solidus temperature. The decrease in the fugacity of H_2O, caused by the release of CO_2 in the vapor phase, also enhances crystallization. They concluded that the assimilation of limestone by a granitic melt is severely limited by these factors in most natural situations.

The results of the present study show that an increase of the CO_2 pressure in the vapor phase may stabilize the carbonates, thus halting further reaction. If only very little CO_2 escapes from the contact zone between a granitic magma and limestone, reaction will stop quickly. This process, therefore, also limits assimilation of limestone.

The experiments indicate that a carbonate liquid would be formed if the carbonates become enriched with alkalies, especially in the presence of H_2O. Because its solidus is below the solidus temperature of the in-

truding silicate magma, it would persist even after crystallization of this silicate magma. The excess alkalies would, most likely, dissolve in the vapor phase (Koster van Groos and Wyllie, 1968a), and possibly cause a slight alkali metasomatism of the country rock.

This process may be illustrated on a small scale at a syenite-marble contact near Karaçyir, Turkey, where the marble "changed to a coarse carbonatite pegmatite" protruding into the syenite (Schuiling, 1961).

The origin of carbonatites

The various hypotheses which have been proposed to explain the origin of carbonatites, disregarding a non-magmatic origin, may be divided into two groups:

1. Carbonatite magmas are primary and juvenile. Reactions of these magmas with silicate assemblages in the upper mantle or crust generate the alkalic rocks associated with carbonatites (Dawson, 1964; von Eckermann, 1948; Holmes, 1952).
2. Carbonatite magmas are secondary and are formed from parent melts such as carbonated alkali peridotite or ijolite magmas either by the formation of an immiscible liquid fraction (von Eckermann, 1961; King, 1965; Dimroth, 1970) or by processes of continuous crystallization differentiation in which the carbonate melt represents the residual liquid (Tomkeieff, 1961; King and Sutherland, 1960; Heinrich, 1966; Watkinson and Wyllie, 1971). The CO_2 is usually considered to be juvenile.

A. *Physical and chemical restrictions.*—The two groups of hypotheses for the origin of carbonatites were described by Heinrich (1966) as having a Hen-versus-Egg conflict. Both require the presence of either a carbonatite magma or a CO_2-containing silicate magma in the upper mantle. Therefore, it is important to know the state of CO_2 in the upper mantle (Irving and Wyllie, 1973). Is it present in a vapor phase, in complex silicate carbonate minerals, in crystalline or liquid carbonate, or dissolved in silicate melts?

The presence of CO_2 as a vapor phase in the mantle was verified by Roedder (1965), who described nearly pure CO_2 inclusions in minerals taken from olivine-bearing nodules found in basalts. The inclusions have a degree of filling corresponding to a P_{CO_2} of 3 to 5 kb at the temperature range of basaltic liquids. These relatively low pressures explain the absence of carbonate, as $MgCO_3$ is not stable at these conditions in the presence of pyroxene, which was shown by Johannes (1969). Extrapolation of his data to 15 kb shows that forsterite and CO_2 will react to form enstatite and magnesite when the temperature is below approximately 800°C. Because current estimates of the temperature in the mantle at 15 kb are about 550°C under continental shields and 800°C under the ocean floor (Clark and Ringwood, 1964), I conclude that the presence of a CO_2-rich vapor is unlikely in the upper mantle under continental shields. A CO_2 vapor phase, however, may be present under ocean areas. The pres-

sence of H_2O in the vapor phase does not alter this conclusion, for Johannes (1969) showed that a decrease in the $CO_2/(H_2O + CO_2)$ ratio from 1 to about 0.25 does not affect the magnesite stability significantly. Because $CaCO_3$ is considerably more stable than $MgCO_3$, it appears that CO_2 and CaO-rich silicates from the mantle will react to form aragonite to even higher temperatures. This means that under oceanic regions $CaCO_3$ is probably stable to the expense of a CO_2 vapor phase.

Inclusions of carbonates in mantle-derived pyropes (McGetchin and Besancon, 1973) further suggest that CO_2 in the upper mantle may be present in carbonates rather than in a vapor phase. CO_2 may occur also in complex silicate minerals such as spurrite and scapolite. However, no firm evidence has been found to support the latter.

A $MgCO_3$–$CaCO_3$ assemblage melts partially to a liquid with a composition somewhere between $CaCO_3$ and $MgCO_3$ at about 1200°C and 20 kb, which is below the peridotite solidus (Irving and Wyllie, 1973). The formation of such a liquid at normal mantle conditions seems unlikely if current temperature estimates for these depths are accepted (Clark and Ringwood, 1964). However, a carbonate liquid could be present at these conditions if it is enriched with alkalies, as is indicated by the present study, or at a slightly higher temperature.

Aragonite melts in the presence of H_2O at approximately 500°C at 20 kb to a liquid depleted in CO_2 (Wyllie and Boettcher, 1969). The experimental evidence supports, therefore, the possibility that carbonate melts may be present in the mantle. It could occur either as interstitial liquid or in small pockets.

CO_2 may dissolve in a silicate melt, depending on the temperature, pressure, and composition of this melt. The solubility of CO_2 in a granitic melt is considered to be negligible at pressures up to 2 kb (Wyllie and Tuttle, 1959); a $NaAlSi_3O_8$ melt coexisting with a H_2O-CO_2 vapor containing about 87 percent CO_2 is estimated to dissolve only about 0.9 percent CO_2 at 20 kb (Eggler, 1973). Basic melts may contain more CO_2, for example a $CaMgSi_2O_6$ melt at 20 kb can dissolve up to 4 percent CO_2 (Eggler, 1973); alkalic melts may contain even more CO_2. No definite data are available on the solubility of CO_2 in natural intermediate and basic melts. It appears to be low at pressures but to increase substantially above 10 to 15 kb (Hill and Boettcher, 1970). The solubility of CO_2 in these melts is probably about the same as was determined by Eggler (1973) for the $CaMgSi_2O_6$ melt, about 1 to 2 percent at 10 kb and about 4 percent at 20 kb.

Any additional CO_2 must form either a carbonate or a vapor phase. At the relative high temperature of a silicate magma, a part or all of the carbonates will form a liquid. No definite data are available at the higher pressures to suggest whether such a liquid is immiscible with the silicate melt or will dissolve in the silicate melt, further increasing its CO_2 content. The current study supports the formation of a pair of immiscible liquids, at least when the silicate melt is basaltic. If a free CO_2-rich vapor phase is formed, it will not enrich further the silicate melt with

CO_2, for it will ascend because of its lower density and be removed from the magmatic assemblage.

Thus, CO_2 in the upper mantle under continental shields will be present mainly in crystalline carbonate. Depending on the alkali or H_2O content of the carbonates, a carbonate liquid could form at slightly higher temperatures. In the presence of a silicate liquid, CO_2 will dissolve in this liquid. Additional CO_2 may be present in a carbonate solid + liquid assemblage. It appears unlikely that a CO_2-rich vapor phase can persist. In the upper mantle under oceanic regions, however, a CO_2 vapor phase may be stable.

B. *The formation of a carbonatite magma.*—The formation of a carbonatite magma requires the concentration of CO_2 and, eventually, of carbonates. The simplest mechanism is the concentration of a carbonate melt which may be present in the upper mantle as interstitial liquid or in small pockets, as was discussed above. The conditions at which such a dispersed carbonate melt occurs is determined by the stability of the carbonate + silicate assemblage. After the carbonate liquid is concentrated to form a magma, silicates may not be present in this magma. The conditions at which this magma can occur are, therefore, determined only by the stability of the carbonate melt with respect to dissociation reactions, except at the contact zone with the silicates. Such a carbonatite magma, therefore, can intrude higher levels in the mantle without significant loss of carbonates through reaction with silicates, whereas in a rock containing interstitial carbonates complete reaction would have digested all carbonates. The volume of the ascending carbonatite magma may be fairly small.

The formation of a carbonatite magma by a process of fractional crystallization of a CO_2-rich silicate melt is more complex (Watkinson and Wyllie, 1971), even aside from the problem of the formation of such a melt. If this melt becomes saturated with CO_2, both crystallization and decrease in pressure caused by an ascending melt will result in either a gradual release of CO_2 in a vapor phase or continuous formation of a carbonate phase assemblage. If CO_2 is released into a vapor phase, the magma will become depleted in CO_2, and no carbonatite magma would form. If a carbonate assemblage is formed, it will, most likely, be composed of a liquid + crystal assemblage. In this process the carbonatite melt coexists with a silicate magma and cannot be considered a residual melt. Crucial is the solubility of CO_2 in the silicate melt. For example, fractional crystallization of a magma at low H_2O activity can result in the formation of an undersaturated alkalic melt (Mysen, 1973), which may have a high CO_2 solubility (Morey and Fleischer, 1940). Watkinson and Wyllie (1971) found continuous miscibility between a $CaCO_3$ liquid and a $NaAlSiO_4$ liquid. This indicates that an undersaturated alkalic melt may dissolve substantial quantities of carbonate.

The process of fractional crystallization of a CO_2-rich silicate magma is more complex than a simple concentration of a carbonate liquid, for which reason I prefer the latter. Nevertheless, both processes, or perhaps

a combination of these, could result in the formation of a carbonatite magma.

The pressure and temperature at which concentration of carbonates may occur is not known. A possible approach is to use the composition of the carbonatite melts to place limits on the conditions at which they were formed. The carbonatites vary from alkali-rich, MgO- and FeO-poor natrocarbonatites (Dawson, 1962) to almost pure $CaCO_3$ sövites (von Eckermann, 1948) to MgO and FeO-rich beforsterites and sideritic sövites (von Eckermann, 1948; Garson, 1962). This does not mean that the composition of the original melt is known. A carbonatite melt may have changed considerably in composition by reacting with sub-crustal and crustal rocks. Especially the presence of alkali-rich fenitizing fluids during and after the bulk of the carbonatite magma crystallized, which is characteristic for carbonatites (Heinrich, 1966), shows that this magma contains an appreciable amount of alkalies.

The experimental evidence presented in this study places a lower pressure limit of 10 kb at 650°C for the presence of significant amounts of MgO and FeO in the carbonate phases when in equilibrium with silicates. The carbonates may contain MgO and FeO at higher temperatures in the absence of silicates (Harker and Tuttle, 1955). In this case the amount of MgO and FeO depends on the stability of the $MgCO_3$ and $FeCO_3$ components in the carbonates, determined by the dissociation reactions of dolomite, ankerite, magnesite, and siderite. Dissociation of the carbonates will occur at lower temperatures in the presence of an H_2O-CO_2 vapor phase, depending on the composition of the vapor, but for a CO_2-rich vapor this effect is small (Walter, Wyllie and Tuttle, 1962).

McGetchin and Besancon (1973) found some carbonate inclusions in mantle derived pyropes which were extremely rich in MgO and FeO. Using clinopyroxene inclusions in the same pyropes they determined tentatively that the pyrope and the clinopyroxene equilibrated at about 850°C and 16 kb. These values may represent conditions at which a MgO-rich carbonate could form, but extrapolation of the upper limit of 650°C at 10 kb, derived from the present investigation for the presence of MgO in the carbonate phase, to 850°C suggests a higher equilibrium pressure, and it seems likely that the carbonates were included at a higher pressure and survived because they were mantled by pyrope.

Based on the previous considerations, I conclude that carbonatite magmas are primary and originate in the upper mantle provided these magmas contain MgO and FeO. The MgO and FeO-poor natrocarbonatites of Oldonyo Lengai (Dawson, 1962) and the $CaCO_3$ pure sövites may be formed at considerably lower pressures. Furthermore, as was discussed above, carbonates and especially Mg-rich carbonates are more stable in the upper mantle under continental shield than under oceanic regions. This may explain why carbonatite magmas are apparently almost exclusively formed below continental shields (Heinrich, 1966).

C. *The formation of alkalic ultrabasic rocks and carbonatites.*—The experimental data of this study show that at high CO_2 pressures the ultra-

basic melteigite and ijolite rocks, commonly associated with carbonatites, react to form a basaltic type composition together with a carbonatitic assemblage. Thus, in reverse, a mixture of basalt and an immiscible alkali-rich carbonate liquid must react at low CO_2 pressures to form these ultrabasic rocks.

Considerations on the state of CO_2 in the mantle show, as was discussed above, that in the absence of a silicate melt CO_2 most likely will be present in crystalline carbonates; at slightly higher temperatures the carbonates will form a solid + liquid assemblage, composed of $CaCO_3$, $MgCO_3$, $FeCO_3$, $NaCO_3$, et cetera.

Therefore, I propose that in the mantle, especially under continental shields, carbonates occur that are partially or completely liquid; this liquid may be present as interstitial liquid, liquid inclusions, or in small pockets. The composition of the liquid must be complex, containing in addition to CaO, MgO, FeO, and alkalies, other constituents such as elements of the R. E. group and others that may be incompatible with the silicate minerals in the mantle (Green and Ringwood, 1967). A significant amount of H_2O may be dissolved in the carbonate also. This liquid will begin to concentrate under certain conditions, probably over long periods of time.

When a certain amount of the carbonate liquid is accumulated, it must begin to move upward because it is gravitationally unstable. Because of the low viscosity of the carbonate liquid the move upward may well be adiabatic. Because the density of the carbonatite liquid is considerably lower than that of the surrounding silicate material the carbonate magma may begin its upward move before a large amount is concentrated. The volume of the magma is, thus, likely to be small.

At a higher level in the mantle the hot carbonate melt may cause partial melting of the silicates and generate the formation of a basaltic melt (Green, 1973). The carbonate melt may not be in equilibrium with the silicate solid-liquid phase assemblage and react, releasing CO_2 into a vapor phase. This could initiate the explosive volcanic activity associated with carbonatite complexes (von Eckermann, 1948; Garson, 1962). Following the reaction a silicate solid-liquid assemblage would form, enriched with MgO, FeO, CaO, and alkalies, and reach compositions of the urtite–ijolite–melteigite series, typical of carbonatite complexes. The vapor phase would be enriched with alkalies, forming fenetizing solutions at low temperatures.

Increase of the CO_2 pressure, combined with a continuous supply of the primitive carbonatite liquid may stabilize the alkali carbonates first and later $CaCO_3$. $MgCO_3$ and $FeCO_3$, being the most reactive in the presence of silicates, would be depleted in the carbonate liquid. This is illustrated by the coexistence of a $CaCO_3$-rich liquid with MgO-rich silicates, which has been reported in mantle derived kimberlite-carbonatite associations (Dawson and Hawthorne, 1973; McGetchin and Nikhanj, 1973). A continuing supply of the carbonatite liquid would reduce the contamination and reaction with the rocks of the upper mantle and

crust, so MgO and FeO-rich carbonate liquids could reach high levels in the Earth's crust. MgO and FeO-rich carbonatite would, therefore, be intruded at a late stage of the intrusive sequence of a carbonatite complex, as was concluded by von Eckermann (1948) in his study of the Alnö carbonatite.

This model is similar to the one Dawson (1962) proposed as an explanation for the decreasing amount of silicate in the extrusive rock sequence of Oldonyo Lengai. He suggested a reaction of a natrocarbonatite with crustal material which would deplete the environment of silicates with continuing supply of the highly reactive carbonate melt, until the natrocarbonatite melt could reach the Earth's surface unaltered.

The model presented here may not be valid for all carbonatite occurrences. The most important condition for the formation of a carbonatite liquid is the presence of a CO_2-rich environment at pressures high enough to stabilize carbonates. The development of Na_2CO_3- or $CaCO_3$-rich liquids may not require pressures exceeding those present in the Earth's crust. However, high MgO contents of the carbonate liquid do require pressures exceeding those present in the crust if this liquid coexists with or is a descendent of a silicate liquid.

ACKNOWLEDGMENTS

I thank W. C. Luth for enabling me to use the high-pressure equipment at Stanford University. Furthermore, I am grateful for the financial support of the National Academy of Sciences which allowed me to carry out the analyses at Goddard Space Flight Center. Discussions with A. J. Piwinskii and L. S. Walter were very helpful. Furthermore, I thank W. C. Forbes for reviewing the manuscript.

REFERENCES

Bailey, D. K., 1969, The stability of acmite in the presence of H_2O: Am. Jour. Sci., v. 269-A, Schairer v., p. 1-16.

Bernas, B., 1967, A new method for decomposition and comprehensive analysis of silicates by atomic absorption spectrometry: Anal. Chemistry, v. 39, p. 1682-1686.

Clark, S. P., and Ringwood, A. E., 1964, Density distribution and constitution of the mantle: Rev. Geophysics., v. 2, p. 35-88.

Daly, R. A., 1910, Origin of alkaline rocks: Geol. Soc. America Bull., v. 21, p. 87-118.

Dawson, J. B., 1962, The geology of Oldoinyo Lengai: Bull. volcanol., v. 24, p. 349-387.

———— 1964, Reactivity of the cations in carbonate magma: Geol. Assoc. Canada Proc., v. 15, p. 103-113.

Dawson, J. B., and Hawthorne, J. B., 1973, Magmatic sedimentation and carbonatitic differentiation in kimberlite sills at Benfontein, South Africa: Geol. Soc. London Jour., v. 129, p. 61-85.

Dimroth, Erich, 1970, Meimechites and carbonates of the Castignon Lake complex, New Quebec: Neues Jahrb. Mineralogie Abh., v. 112, p. 239-278.

Eckerman, H. von, 1948, The alkaline district of Alnö Island: Sveriges geol. undersökning, no. 36, 176 p.

———— 1961, The petrogenesis of the Alnö alkaline rocks: Uppsala Univ. Geol. Inst. Bull., v. 40, p. 25-36.

Eggler, D. H., 1973, Role of CO_2 in melting processes in the mantle: Carnegie Inst. Washington Year Book 72, p. 457-467.

Erickson, R. L., and Blade, L. V., 1963, Geochemistry and petrology of the alkalic igneous complex at Magnet Cove, Arkansas: U.S. Geol. Survey Prof. Paper 425, 94 p.

Garson, M. S., 1962, The Tundulu carbonatite ring-complex in southern Nyasaland: Malawi Geol. Survey Mem. 2, 248 p.

Goldsmith, J. R., and Newton, R. C., 1969, P-T-X relations in the system $CaCO_3$-$MgCO_3$ at high temperatures and pressures: Am. Jour. Sci., v. 269-A, Schairer v., p. 160-190.

Green, D. H., 1973, Contrasted melting relations in a pyrolite upper mantle under mid-oceanic ridge, stable crust and island arc environments: Tectonophysics, v. 17, p. 285-297.

Green, D. H., and Ringwood, A. E., 1967, The genesis of basaltic magmas: Contr. Mineralogy Petrology, v. 15, p. 103-190.

Harker, R. I., and Tuttle, O. F., 1955, Studies in the system CaO–MgO–CO_2 Part 1. The thermal dissociation of calcite, dolomite and magnesite: Am. Jour. Sci., v. 253, p. 209-224.

Heinrich, E. W., 1966, The geology of carbonatites: Chicago, Rand McNally & Co., 555 p.

Hill, E. T., and Boettcher, A. L., 1970, Water in the earth's mantle: melting curves of basalt-water and basalt-water-carbon dioxide: Science, v. 167, p. 980-982.

Holmes, Arthur, 1952, The potash ankaratrite-melaleucitite lavas of Nabugando and Mbuga craters, southwest Uganda: Geol. Soc. Edinburgh Trans., v. 15, p. 187-213.

Irving, A. J., and Wyllie, P. J., 1973, Melting relationships in CaO–CO_2 and MgO–CO_2 to 36 kilobars with comments on CO_2 in the mantle: Earth Planetary Sci. Letters, v. 20, p. 220-225.

Johannes, Wilhelm, 1969, An experimental investigation of the system MgO–SiO_2–H_2O–CO_2: Am. Jour. Sci., v. 267, p. 1083-1104.

King, B. C., 1965, Petrogenesis of the alkaline igneous rock suites of the volcanic and intrusive centres of eastern Uganda: Jour. Petrology, v. 6, p. 67-100.

King, B. C., and Sutherland, D. S., 1960, Alkaline rocks of eastern and southern Afrika, Parts I, II and III: Sci. Prog., v. 48, p. 298-321, 504-524, 709-720.

Koster van Groos, A. F., and Wyllie, P. J., 1966, Liquid immiscibility in the system Na_2O–Al_2O_3–SiO_2–CO_2 at pressures to 1 kilobar: Am. Jour. Sci., v. 264, p. 234-255.

———— 1968a, Liquid immiscibility in the join $NaAlSi_3O_8$–Na_2CO_3–H_2O and its bearing on the genesis of carbonatites: Am. Jour. Sci., v. 266, p. 932-967.

———— 1968b, Melting relationships in the system $NaAlSi_3O_8$–NaF–H_2O to 4 kilobars pressure: Jour. Geology, v. 76, p. 50-70.

———— 1969, Melting relationships in the system $NaAlSi_3O_8$–NaCl–H_2O at one kilobar pressure, with petrological applications: Jour. Geology, v. 77, p. 581-605.

———— 1973, Liquid immiscibility in the join $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3–H_2O: Am. Jour. Sci., v. 273, p. 465-487.

Kröger, C., and Fingas, E., 1935, Über die Systeme Alkalioxyd–CaO–Al_2O_3–SiO_2–CO_2. V. Die stabilen Gleichgewichte im System Na_2O–SiO_2–CO_2 und die CO_2-Drucke der Einwirkung von K_2CO_3 auf K_2SiO_3: Zeitschr. Anorg. Allg. Chemie, v. 225, p. 1-23.

Levin, E. M., Robbins, C. R., and McMurdie, H. F., 1964, Phase diagrams for ceramists: Columbus, Ohio, Am. Ceramic Soc. Inc., 601 p.

Luth, W. C., and Ingamells, C. O., 1965, Gel preparation of starting materials for hydrothermal experimentation: Am. Mineralogist, v. 50, p. 255-258.

Luth, W. C., and Tuttle, O. F., 1963, Externally heated cold-seal pressure vessels for use to 10,000 bars and 750°C: Am. Mineralogist, v. 48, p. 1401-1403.

McGetchin, T. R., and Besancon, J. R., 1973, Carbonate inclusions in mantle-derived pyropes: Earth Planetary Sci. Letters, v. 18, p. 408-410.

McGetchin, T. R., and Nikhanj, Y. S., 1973, Carbonatite-kimbelite relations in the Cane Valley diatreme, San Juan County, Utah: Jour. Geophys. Research, v. 78, p. 1854-1869.

Morey, G. W., and Fleischer, M., 1940, Equilibrium between vapor and liquid phases in the system CO_2–H_2O–K_2O–SiO_2: Geol. Soc. America Bull., v. 51, p. 1035-1058.

Mysen, B., 1973, Melting in a hydrous mantle: Phase relations of mantle peridotite with controlled water and oxygen fugacities: Carnegie Inst. Washington Year Book 72, p. 467-478.

Noble, D. C., 1965, Gold Flat member of the Thirsty Canyon Tuff-a pantellerite ash-flow sheet in southern Nevada: U.S. Geol. Survey Prof. Paper 525B, p. 85-90.

Roedder, E., 1965, Liquid CO_2 inclusions in olivine-bearing nodules and phenocrysts from basalts: Am. Mineralogist, v. 50, p. 1746-1782.

Schuiling, R. D., 1961, Formation of pegmatitic carbonatite in a syenite-marble contact: Nature, v. 192, p. 1289.

Shand, S. J., 1945, The present status of Daly's hypothesis of the alkaline rocks: Am. Jour. Sci., v. 243-A (Daly v.), p. 495-507.

Tomkeieff, S. I., 1961, Alkalic ultrabasic rock and carbonatites in the U.S.S.R.: Internat. Geol. Rev., v. 3, p. 739-758.

Tuttle, O. F., 1949, Two pressure vessels for silicate-water studies: Geol. Soc. America Bull., v. 60, p. 1727-1729.

Walter, L. S., Wyllie, P. J., and Tuttle, O. F., 1962, The system MgO–CO_2–H_2O at high temperatures and pressures: Jour. Petrology, v. 3, p. 49-64.

Watkinson, D. H., and Wyllie, P. J., 1969, Phase equilibria studies bearing on the limestone-assimilation hypothesis: Geol. Soc. America Bull., v. 80, p. 1565-1576.

———— 1971, Experimental study of the composition join $NaAlSiO_4$–$CaCO_3$–H_2O and the genesis of alkalic rock carbonatite complexes: Jour. Petrology., v. 12, p. 357-378.

Weidner, J. R., 1972, Equilibria in the system Fe–C–O part I: Siderite–magnetite–carbon vapor equilibrium from 500 to 10,000 bars: Am. Jour. Sci., v. 272, p. 735-751.

Wyllie, P. J., and Boettcher, A. L., 1969, Liquidus phase relationships in the system CaO–CO_2–H_2O to 40 kilobars pressure with petrological applications: Am. Jour. Sci., v. 269-A, Schairer v., p. 489-508.

Wyllie, P. J., and Tuttle, O. F., 1959, Effect of carbon dioxide on the melting of granite and feldspars: Am. Jour. Sci., v. 257, p. 648-655.

———— 1960, The system CaO–CO_2–H_2O and the origin of carbonatites: Jour. Petrology, v. 1, p. 1-46.

Yoder, H. S., and Tilley, C. E., 1962, Origin of basalts magmas: an experimental study of natural and synthetic rock systems: Jour. Petrology, v. 3, p. 342-532.