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LIQUIDUS PHASE RELATIONSHIPS IN THE SYSTEM CaO–CO_2–H_2O to 40 KILOBARS PRESSURE WITH PETROLOGICAL APPLICATIONS

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ABSTRACT. Two melting reactions, (i) $CaCO_3 + Ca(OH)_2 =$ liquid and (ii) $CaCO_3 + Ca(OH)_2 +$ vapor $=$ liquid, have been extended from 4 kb to 40 kb using piston-cylinder apparatus. Points measured for reaction (i) are: 655°C at 4 kb, 659°C at 15.5 kb, 662°C at 25 kb, and 666°C at 40.7 kb; and for reaction (ii): 630°C at 4 kb, 565°C at 15.5 kb, 537°C at 25 kb, and 524°C at 40.8 kb. A pressure-temperature projection for the system CaO–CO_2–H_2O is presented, in part schematic, from 300°C to 1500°C and from 1 bar to 40 kb. The carbonate phase changes from calcite to aragonite with increasing pressure. The compositions of the liquid and vapor phases appear to remain quite distinct up to 40 kb, but conditions above a hypothetical second critical end-point for reaction (ii) are illustrated. Textures observed in the quenched liquids are compared with textures described in carbonatites and adduced as evidence supporting a magmatic origin for these carbonatites.

INTRODUCTION

The field evidence that many carbonatites are intrusive and possibly magmatic was generally considered to be incompatible with available experimental data until Wyllie and Tuttle (1960) demonstrated that liquids in the system CaO–CO_2–H_2O precipitate calcite at temperatures down to 640°C through a wide pressure range. They described liquids in this system as "synthetic carbonatite magmas", although they did not claim that natural carbonatite magmas had compositions in this system.

Several additional experimental studies in systems more complex than CaO–CO_2–H_2O have since been undertaken in efforts to elucidate two problems: the physical and chemical nature of carbonatite magmas and the petrogenetic relationships between carbonatites and associated alkalic igneous rocks. Reviews of the experimental results so far obtained were published recently (Wyllie, 1966a, 1966b; Wyllie and Biggar, 1966), and at the same time two books on carbonatites which review the various hypotheses for the origin of carbonatites were published (Tuttle and Gittins, 1966; Heinrich, 1966).

There has been increasing awareness in recent years of possible genetic links between kimberlites and carbonatites, as indicated by the 1964 Symposium organized by the International Mineralogical Association (von Eckermann, 1966). The experimental studies have therefore been extended to pressures corresponding to conditions in the upper mantle, where kimberlites probably originate. As a basis for interpretation of the phase relationships in more complex systems involving carbonates and silicates, the system CaO–CO_2–H_2O has been studied to 40 kb pressure. Results have been presented briefly (Boettcher and Wyllie,

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1967a) and contrasted with results obtained in the same pressure range for the system $CaO–SiO_2–CO_2–H_2O$ (Boettcher and Wyllie, 1967b).

PREVIOUS RESULTS

Wyllie and Tuttle (1960) reviewed in detail the relevant phase relationships published before 1959 for the system $CaO–CO_2–H_2O$ up to 4 kb, added new experimental data, and presented a schematic pressure-temperature projection for the system. This projection, which has been revised and extended in figure 4, should be used as a guide to the reactions discussed in this section. For the low-pressure reactions and the distribution of univariant curves around invariant points, see figure 17 of Wyllie and Tuttle (1960). The earlier results are summarized below, along with additional data published since 1960. The reactions and invariant points are identified by the numbers used in figure 4.

$CaO–CO_2$.—Wyllie and Tuttle (1960) intersected two univariant melting reactions in a 1 kb isobaric section:

$$CaCO_3 + CaO = \text{liquid} \qquad (9)$$

$$CaCO_3 = \text{liquid} + \text{vapor} \qquad (8, \text{below about 5 kb})$$

Baker (1962) studied the low pressure part of the system using DTA methods, locating the invariant point:

$$CaCO_3 + CaO + \text{liquid} + \text{vapor} \qquad (Q_2)$$

at 39.5 bars and 1230°C, which is shown by the square in figure 1. His data points plotted in figure 1 permit construction of the detailed *PT* projection between 1 bar and 200 bars. These results extrapolate to temperatures at 1 kb in agreement with the results of Wyllie and Tuttle (1960, figs. 3 and 14). Extension of the phase relationships in the ternary system to 40 kb introduce aragonite as well as calcite, and we therefore completed a detailed re-examination of the calcite-aragonite phase transition (Boettcher and Wyllie, 1967d, 1968). The revised subsolidus phase diagram for the system $CaO–CO_2$ is shown in figure 2; the reactions involved are:

$$\text{calcite I} = \text{aragonite} \qquad (1)$$

$$\text{calcite II} = \text{aragonite} \qquad (2)$$

$$\text{calcite I} = \text{calcite II} \qquad (3)$$

Previous studies on these transitions were reviewed by Boettcher and Wyllie (1968).

$CaO–H_2O$.—In a 1 kb isobaric section, Wyllie and Tuttle (1960) intersected two univariant melting reactions and one reaction that is univariant by restriction:

$$Ca(OH)_2 + CaO = \text{liquid} \qquad (7)$$

$$Ca(OH)_2 + \text{vapor} = \text{liquid} \qquad (6)$$

$$Ca(OH)_2 = \text{liquid} \qquad \text{indistinguishable from (7)}$$

Extension of these results through the pressure interval 27 bars to 3 kb located two other reactions at pressures below the invariant point for the assemblage:

$$Ca(OH)_2 + CaO + \text{liquid} + \text{vapor} \qquad (Q_6)$$

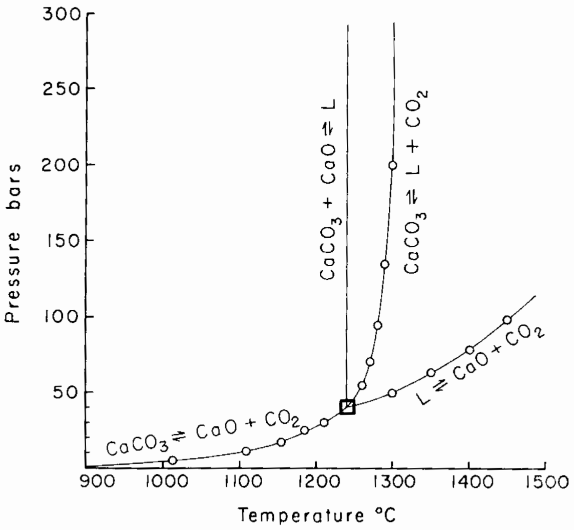


Fig. 1. PT projection of the system $CaO-CO_2$. The open circles represent DTA run points of Baker (1962). See Wyllie and Tuttle (1960, fig. 17).

The detailed phase relationships around Q_6 (see fig. 4) are similar to those around Q_2, the invariant point in figure 1; Q_6 occurs at a higher pressure, about 100 bars (Wyllie and Tuttle, 1960, fig. 12), but still too low to be distinguished from the abscissa in figure 4.

Pistorius (1963) followed what he believed to be the dissociation reaction of portlandite from 3 to 20 kb, but after Wyllie and Tuttle's (1963) review of his evidence, Pistorius added a note that melting was probably the correct interpretation of his results. This was confirmed by Sharp (1964) who located the melting curve for portlandite in the pressure interval 10 to 35 kb, using DTA methods; his previously unpublished results are incorporated into figure 4 as reaction (7), with his permission (personal commun., 1966).

Harker (1964) presented DTA determinations for the melting of portlandite at 1 kb with results about 30°C lower than those reported by Wyllie and Tuttle (1960), and he suggested on this basis that the quenching technique may be misleading in systems where the liquid can not be quenched to a glass. However, it has been established since 1960 that temperatures measured by Wyllie and Tuttle (1960) in cold-seal pressure vessels were too high by 30°C; this was mentioned by Gittins and Tuttle (1964), Wyllie and Haas (1965), and discussed in detail by Wyllie and Raynor (1965). The corrected reaction curves for the system $CaO-H_2O$ below 3 kb are consistent with Sharp's high-pressure measurement of reaction (7). Wyllie and Raynor (1965) also showed that the corrected phase diagram for $CaO-H_2O$ at 1 kb pressure agreed with the DTA measurements of Harker (1964).

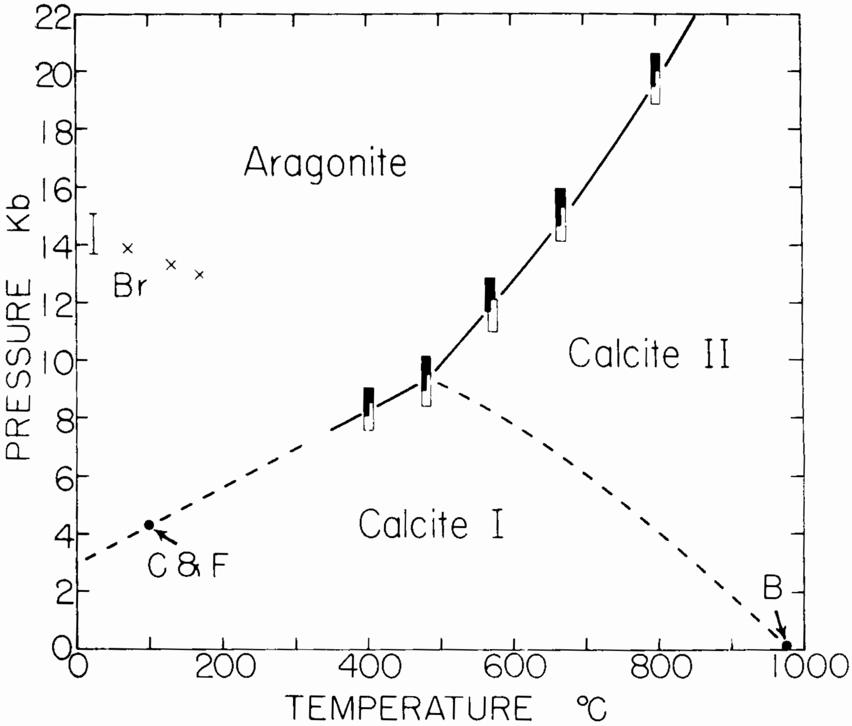


Fig. 2. Phase diagram for the system $CaCO_3$ after Boettcher and Wyllie (1968). Point (B) is from Boeke (1912). Points (Br) lie on the assumed metastable curve for CCI $\rightleftarrows$ CCII (Bridgman, 1939). The point (C&F) represents the transition CCI $\rightleftarrows$ Ar from Crawford and Fyfe (1964).

The solubility of $Ca(OH)_2$ in water at temperatures to 257°C and at pressures to 1.5 kb is very low; it increases with increasing pressure, but it decreases strongly with increasing temperature (Blount and Dickson, 1967).

CaO–CO_2–H_2O.—Wyllie and Tuttle (1960) determined 1 kb isobaric sections for the join $CaCO_3$–$Ca(OH)_2$ and for the ternary system. Figure 5A is a revised version of their figure 9. They followed the univariant reactions through the pressure interval 27 bars to 3 kb (5) and to 4 kb (4):

$$CaCO_3 + Ca(OH)_2 = \text{liquid} \qquad (5)$$

$$CaCO_3 + Ca(OH)_2 + \text{vapor} = \text{liquid} \qquad (4)$$

Their schematic *PT* projection showed how these and low pressure reactions met at the invariant point for the assemblage:

$$CaCO_3 + Ca(OH)_2 + CaO + \text{liquid} + \text{vapor} \qquad (Q_7)$$

The ternary invariant point Q_7 is connected to the binary invariant points Q_6 and Q_2 in figure 4 as shown by Wyllie and Tuttle (1960, figs. 16 and 17). The temperatures of reactions at 1 kb pressure were corrected independently at Leeds University and at The Pennsylvania State University as discussed by Wyllie and Raynor (1965), who also extended the corrected reactions (4) and (5) to 4 kb and established that the invariant point Q_7 lies at a pressure below 10 bars. Wyllie and Tuttle (1960) found that the vapor phase composition in reaction (4) was almost pure H_2O, showing that partition of CO_2 and H_2O between liquid and vapor phases is strongly in favor of the liquid in this system (see the line E_1-V_1 in fig. 5A). They also concluded that only a small proportion of solid material was dissolved in the vapor phase, and the results of Sharp and Kennedy (1965) in the system $CaO–CO_2–H_2O$ confirm very low solubilities in the aqueous vapor phase at pressures to 1.4 kb and temperatures to 600°C. The solubility of calcite in the vapor phase increases with increasing pressure but decreases exponentially with increasing temperature at constant total pressure. In summary, as shown in figure 5A, the low temperature liquid compositions at 1 kb pressure are close to the join $CaCO_3$–$Ca(OH)_2$, and coexisting vapor phase compositions remain close to CO_2–H_2O; there is a wide miscibility gap between the liquid and vapor phase compositions.

EXPERIMENTAL METHOD

Starting materials.—Commercial $CaCO_3$ and $Ca(OH)_2$ were used as source materials. They were prepared as described below, mixed in the desired proportions, blended in a Wig-L-Bug mechanical amalgamator, and stored in a desiccator until used. *$Ca(OH)_2$*: a sample from a new bottle of Baker and Adamson reagent was treated hydrothermally to remove all traces of CaO and was then dried at 240°C for 2 hours. *$CaCO_3$*: two sources of $CaCO_3$ (calcite) were used, most mixtures being prepared from Baker and Adamson reagent. This material contained small amounts of CaO, and Johnson, Matthey, and Co. "Specpure" $CaCO_3$ was therefore used in some runs for comparison. Both materials were dried at 630°C for 49 hours.

Experimental equipment and procedure.—Experiments at 4 kb and below were conducted in cold-seal pressure vessels. Pressures are accurate to ± 5 percent, and temperatures are accurate to ± 5°C for runs of short duration. For experiments at 4 kb and above, a single-stage, piston-cylinder apparatus similar to that described by Boyd and England (1960) was used. Talc served as the pressure-transmitting medium in furnace assemblies of 0.5-inch diameter. All runs, including calibration experiments, were carried out using piston-advance pressure conditions. Temperature was applied after final pressure was attained. The magnitude of the correction for friction was determined as −13 percent of the nominal indicated gauge pressure at 25°C using the BiI-BiII transition at 25.4 kb as a standard. Silicone-grease-based MoS_2 ("Molykote") was used as a lubricant between the steel liner of the pressure vessel and the lead foil surrounding the furnace assembly, necessitating a temperature correction for friction. Following the melting curve of LiCl as a function of pressure (determined in gas apparatus by Clark, 1959), using DTA techniques (Newton, 1965), the value of friction was determined at temperatures up to 850°C, where the correction for friction is −7 percent. The measured values (750° to 850°C) lay on a linear correction curve between 25°C and 850°C. Temperatures were measured with chromel-alumel thermocouples on a proportional controller-recorder and are considered to be precise to ± 5°C, excluding correction for the pressure coefficient on output emf. At pressures up to 40 kb, this correction for chromel-alumel thermocouples is probably less than + 10°C (Wentorf, 1966, p. 979). At the end of each run, temperatures were quenched in several seconds at nearly constant pressure by switching off electrical power to the apparatus. Starting materials (about 5 mg) were encapsulated in welded gold and platinum for use in the cold-seal vessels and piston-cylinder, respectively. Capsules were weighed before and after runs to insure that closed-system conditions prevailed during the experiments. The rapid attainment of equilibrium in this system has been discussed by Wyllie and Tuttle (1960) and Boettcher and Wyllie (1968).

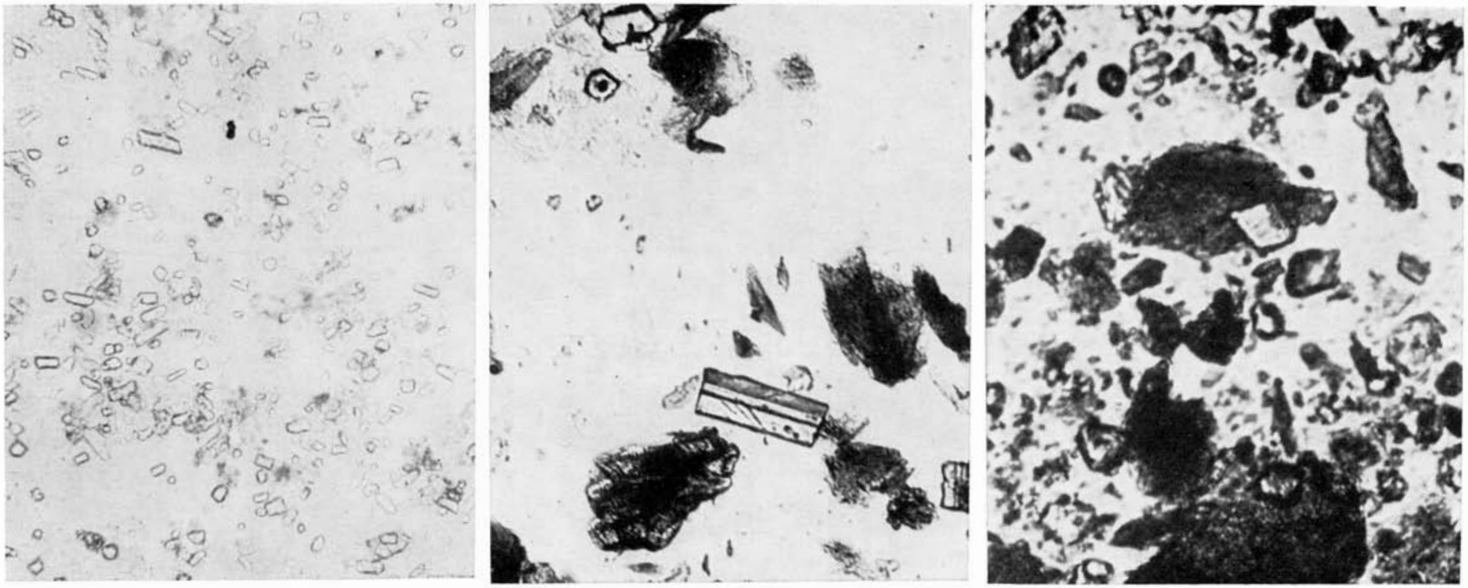
Identification of phases.—The equilibrium phases encountered during the investigation of this system are calcite ($CaCO_3$), aragonite ($CaCO_3$), portlandite ($Ca(OH)_2$), liquid, and vapor. Detailed procedures for the investigation of capsules and run products in similar experiments have been outlined by Wyllie and Tuttle (1960) and Boettcher and Wyllie (1968).

Portlandite occurred as colorless crystals with perfect basal cleavage and uniaxial negative interference figures. The crystals were characteristically rounded when quenched from an assemblage containing liquid, but hexagonal basal sections occurred in subsolidus runs. The presence of liquid, longer run durations, and higher vapor pressures all favored the development of larger crystals. Portlandite that crystallized from liquid during a quench characteristically showed irregular extinction and twinning. However, in runs at pressures of 20 kb and greater, subsolidus portlandite also exhibited well-developed lamellar twinning; such twinning was absent in subsolidus runs at pressure of 15 kb and below. This feature has also been noted by us in the systems $CaO\text{–}SiO_2\text{–}CO_2\text{–}H_2O$, $CaO\text{–}MgO\text{–}CO_2\text{–}H_2O$, and $CaO\text{–}MgO\text{–}SiO_2\text{–}CO_2\text{–}H_2O$, which suggests that portlandite undergoes a phase transition between 15 and 20 kb at temperatures on the order of 600°C.

Calcite in subsolidus runs occurred as small, well-developed rhombs, but larger, more rounded crystals formed in the presence of a liquid (pl. 1-C). Only calcite I was recognized in the quenched products; calcite II inverted during the quench from its stability field (Boettcher and Wyllie, 1968).

Aragonite occurred in several distinctive shapes, depending upon *P-T-X* conditions (Boettcher and Wyllie, 1968), but near the melting curves of figure 3, aragonite formed acicular to stubby, pseudohexagonal prisms, as shown in plate 1-A. Large prisms were produced in the presence of liquid, and these prisms were often hollow as the result of mismatch between the sector-twinned segments (see pl. 1-B). At pressures

PLATE 1



A. B. C.

Photomicrographs of quench products in the system $CaO–CO_2–H_2O$; fragments mounted in immersion oils. These are quenched from the stability fields: (A) Ar + CH + V; (B) Ar + L + V; and (C) CC + L + V. The dark material in (B) and (C) represents quenched liquid. Width of each photograph is 0.3 mm.

above about 25 kb, increased pressure favored smaller aragonite crystals. Aragonite quenched from near the calcite-aragonite boundary usually inverted to calcite on the quench, producing biaxial calcite with complexly twinned aragonite morphology (Boettcher and Wyllie, 1967c, 1968).

Liquid could not be quenched to a glass, although glasses have been obtained under certain conditions in the system $CaO–SiO_2–CO_2–H_2O$ (Boettcher and Wyllie, in preparation) and in the system $CaCO_3–CaF_2–BaSO_4–H_2O$ (Kuellmer, Visocky, and Tuttle, 1966). The nature of the quenched liquid changes with bulk composition and with the polymorphic form of $CaCO_3$ present under run conditions. Liquids quenched from the calcite field appeared as brown, fine-grained aggregates of dendritic calcite and portlandite. Liquids quenched from the aragonite stability field contained acicular crystals of aragonite or calcite inverted from aragonite. Plate 1 shows photomicrographs of products quenched from the stability field of aragonite + portlandite + vapor (1-A), aragonite + liquid + vapor (1-B), and calcite + liquid + vapor (1-C). The individual crystals comprising the quenched liquid are not resolvable at the magnification of the photomicrographs.

Vapor in our runs is rich in H_2O and poor in CO_2, and therefore the capsules at the end of a run were flattened whether or not vapor was present. A capsule that contained H_2O-rich vapor during run conditions contained visible water when opened after the run. Physical evidence for the presence of a trace of vapor was difficult to detect, and saturation conditions for liquids were determined by phase rule considerations, as described in the Results Section. At pressures above about 15 kb, the solubility of solids in the vapor phase increased sufficiently for distinct vapor deposits to be recognized in the quenched assemblages, using the petrographic microscope. These deposits consist of isotropic to weakly birefringent, fine-grained aggregates, easily distinguishable from the quenched liquid phase, which is strongly birefringent because of the dendritic crystalline carbonate.

RESULTS

General remarks.—Wyllie and Tuttle (1960) have discussed and illustrated the representation of phase relationships involving crystals, liquids and vapors in the system $CaO–CO_2–H_2O$, using isobaric *TX* prisms and projections from the prisms. Repetition is unnecessary, and in this paper we shall present results in *PT* projections of univariant reactions and in isobaric polythermal equilibrium diagrams projected onto the bases of TX prisms.

An abbreviated notation is used for the sake of simplicity. Phases are denoted by the symbols: lime – C, calcite = CC, aragonite = Ar, portlandite = CH, liquid = L, and vapor = V. We prefer to use the term "vapor" rather than "gas" for the phase composed largely of the volatile components CO_2 and H_2O. A miscibility gap (abbreviation MG) separates the liquid and vapor phases in this system at least up to 40 kb pressures; theoretically, the miscibility gap L + V is capable of closing through a "fluid" phase with compositions and properties continuously transitional between liquid and vapor; fluid phase = F.

The notation of Greig (1955) is used to designate the phase elements of the phase diagrams. According to this notation, a one-phase element is denoted by the symbol for the element: thus, the range of *P, T,* and *X* occupied by liquid is denoted by L. A liquidus, defined as the range of *P, T,* and *X* for a liquid that can either exist by itself or coexist in equilibrium with a crystalline phase, is denoted by the symbol L(crystal); the liquidus with calcite as the primary crystalline phase is denoted by L(CC). A ternary liquidus field boundary lies between two isobaric liquidus surfaces, and liquids with compositions on the boundary are simultaneously saturated with respect to two crystalline phases: the field boundary separating the isobaric surfaces L(CH) and L(Ar) is denoted by the symbol L(CH,Ar), as shown in figure 5C.

Univariant melting curves to 40 kilobars pressure.—The definitive runs for the reactions $CaCO_3 + Ca(OH)_2 + V \rightleftarrows L$ and $CaCO_3 + Ca(OH)_2 \rightleftarrows L$ are shown in figure 3 and listed in table 1. Run points are indicated by rectangles, the size of which indicates uncertainty in the precision of temperature and pressure measurements. The curves were bracketed at 4 kb using both the piston-cylinder and cold-seal pressure apparatus, with close agreement, despite the possible pressure errors involved in piston-cylinder apparatus at low pressures.

The melting reaction $CaCO_3 + Ca(OH)_2 = L$ proceeds very rapidly, and the curve is almost linear and very insensitive to pressure; therefore it provides an excellent temperature-calibration reaction for high pressure apparatus. The transition calcite II = aragonite is also rapid in the presence of a liquid phase, and it extends through the pressure interval 12 kb to 40 kb in the temperature interval 600°C to 1300°C. These two reactions in the system $CaO–CO_2–H_2O$ may thus prove very useful as calibrants for both temperature and pressure in piston-cylinder apparatus, using either static quench methods or DTA methods.

Bradley (1962) developed thermodynamic calculations for the melting of salt mixtures, based on ideal mixtures of ions and undissociated molecules, and concluded that the melting of $CaCO_3 + Ca(OH)_2$ as determined experimentally by Wyllie and Tuttle (1960) was ideal at a total pressure of 1 kb. The observation that the solidus temperature for this reaction is nearly independent of pressure, together with the relative pressure insensitivity of the reaction $Ca(OH)_2 \rightleftarrows L$ (fig. 4), indicates either that ideality persists to 40 kb pressure or that the activity coefficients of $Ca(OH)_2$ and $CaCO_3$ are nearly equal under these conditions of temperature and pressure.

The new results plotted in figure 3, together with the previous work already discussed, provide figure 4, a complete *PT* projection for the system $CaO–CO_2–H_2O$, in part schematic. The positions of the univariant curves that involve a liquid phase in the system $CaO–CO_2$ are estimated

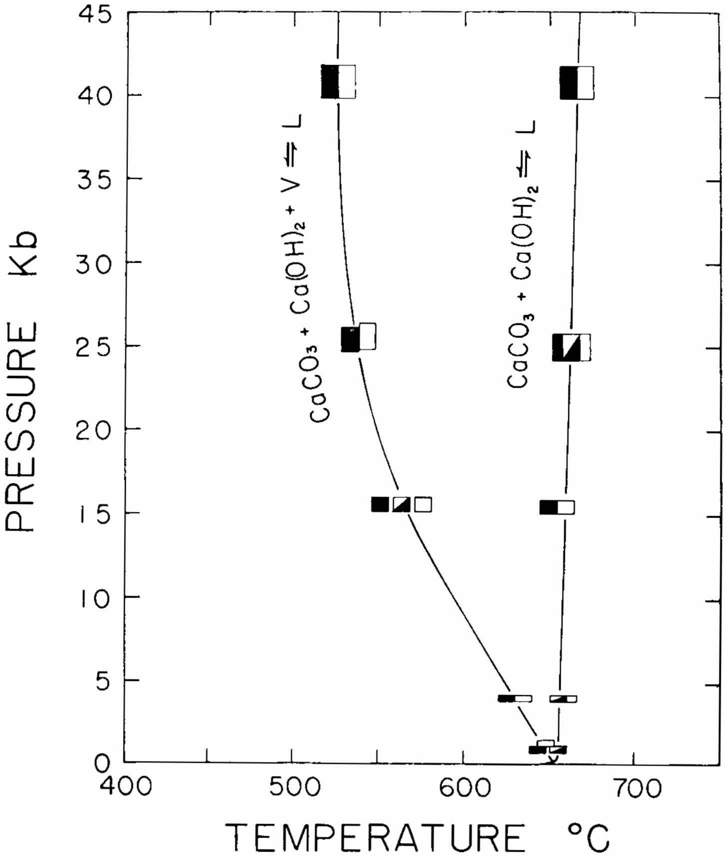


Fig. 3. PT projections for the univariant melting reactions $CaCO_3 + Ca(OH)_2 + V \rightleftarrows L$ and $CaCO_3 + Ca(OH)_2 \rightleftarrows L$. Individual runs are indicated by rectangles, the size of which indicates uncertainty in pressure and temperature precision. Solid rectangles represent subsolidus runs; open rectangles represent hypersolidus runs.

at the high temperature group of dashed lines. Details of the reactions around the invariant point Q_2 are illustrated in figure 1 and in figure 14 of Wyllie and Tuttle (1960). The positions of the univariant curves that involve a liquid phase in the system $CaO–H_2O$ are shown extending from the invariant point Q_6 in figure 4. Details of the reactions around the invariant point are illustrated in figure 12 of Wyllie and Tuttle (1960). The newly measured reactions in the system $CaO–CO_2–H_2O$, transferred from figure 3, rise above the invariant point Q_7, details of which were illustrated by Wyllie and Tuttle (1960) in figures 15, 16, and 17. The revised phase diagram for the polymorphs of $CaCO_3$ (Boettcher and Wyllie, 1968) is also shown in figure 4, and various invariant points are generated where the solid-solid transition boundaries intersect other reaction curves. No inflections in curves (4) and (5) were measured at their intersections with the curve for the calcite II-aragonite transition (figs. 4 and 5) although they must exist. The negative ΔV of the reaction calcite II $\rightarrow$ aragonite apparently is nearly compensated by the concomitant decrease in entropy, producing little change in dP/dT. Equations for the univariant reactions shown in figure 4 are given on the diagram. Complete details for the invariant points shown in figure 4 are listed in table 2, along with the phase assemblages, estimated pressures and temperatures, and the source of the information.

TABLE 1

Definitive experiments in the system $CaO-CO_2-H_2O$ for univariant melting reactions (4) and (5), as plotted in figure 3

Run*	Composition, weight percent			Pressure, kb	Temperature, °C	Time, min.	Results	
	Crystal mixture		H_2O				Quench products by X-ray	Interpreted phases at P and T by X-ray and optics
	$CaCO_3$	$Ca(OH)_2$						
J	35	65	0	1.0	649	10	CC, CH	CC + CH
A	35	65	0	1.0	655	10	CC, CH	CC + CH + L
H	35	65	0	4.0	655	10	CC, CH	CC + CH + L
G	35	65	0	4.0	660	10	CC, CH	CH + L
36	35	65	0	3.6	654	8	CC, CH	CC + CH
15	35	65	0	3.6	663	8	CC, CH	CH + L
12	35	65	0	15.4	650	7	CC, CH	Ar + CH
11	35	65	0	15.4	660	7	CC, CH	CH + L
9	35	65	0	24.9	656	6	Ar, CH	Ar + CH
7	35	65	0	24.9	662	7	Ar, CH	Ar + CH + L
8	35	65	0	24.9	668	7	Ar, CH	CH + L
13	35	65	0	40.7	660	8	Ar, CH	Ar + CH
14	35	65	0	40.7	670	8	Ar, CH	CH + L
C	35	65	29	1.0	643	10	CC, CH	CC + CH + V
I	35	65	25	1.0	648	10	CC, CH	CH + L + V
E	35	65	25	4.0	625	10	CC, CH	CC + CH + V
D	35	65	26	4.0	635	10	CC, CH	CH + L + V
16	35	65	20	3.6	630	10	CC, CH	CC + CH + L + V
21	35	65	21	3.6	640	10	CC, CH	CH + L + V
20	35	65	24	15.5	550	7	Ar, CH	Ar + CH + V
24	35	65	23	15.5	563	7	Ar, CH	Ar + CH + L + V
23	35	65	20	15.5	575	7	Ar, CH	CH + L + V
26	35	65	24	25.2	532	8	Ar, CH	Ar + CH + V
27	35	65	25	25.4	542	12	Ar, CC, CH	Ar + CH + L
168	40	60	24	25.4	545	10	Ar, CC, CH	Ar + CH + L
29	35	65	23	25.5	549	12	Ar, CC, CH	Ar + CH + L
22	35	65	29	40.8	520	6	Ar, CH	Ar + CH + V
37	25	75	18	40.8	530	8	Ar, CH	Ar + CH + L

*Runs labeled with letters were made in cold-seal pressure vessels, and those with numbers in piston-cylinder apparatus.

Abbreviations: CC, calcite; Ar, aragonite; CH, portlandite; L, liquid; V, vapor.

Compositions of liquid and vapor phases.—The compositions of liquid and vapor phases cannot be determined from the *PT* projections of figures 3 and 4; the necessary supplementary diagrams required to complete the phase relationships are the isobaric polythermal projections of figure 5. Figure 5A is the revised version of Wyllie and Tuttle's (1960) figure 9, with the temperature corrections discussed by Wyllie and Raynor (1965). The binary solidus reaction from figures 3 and 4:

$$CaCO_3 + Ca(OH)_2 = \text{liquid} \qquad (5)$$

is represented in figure 5A by the dashed line CC-CH, with the eutectic liquid occurring at the temperature maximum on the field boundary L(CC,CH) where it crosses the join. The ternary solidus reaction

$$CaCO_3 + Ca(OH)_2 + \text{vapor} = \text{liquid} \qquad (4)$$

is represented by the four-phase tie-figure CC + CH + L(E_1) + V(V_1), occurring at 645°C at 1 kb pressure in figure 5A. The liquid, E_1, corresponds to the binary liquid L(CC,CH) with a small proportion of dissolved H_2O; and the vapor, V_1, is almost pure H_2O with a small portion of dissolved CaO and CO_2. The line for the vaporus field boundary, *gf*, is indistinguishable from the $H_2O–CO_2$ join at this scale in figure 5A (Sharp and Kennedy, 1965); it has been distorted for clarity.

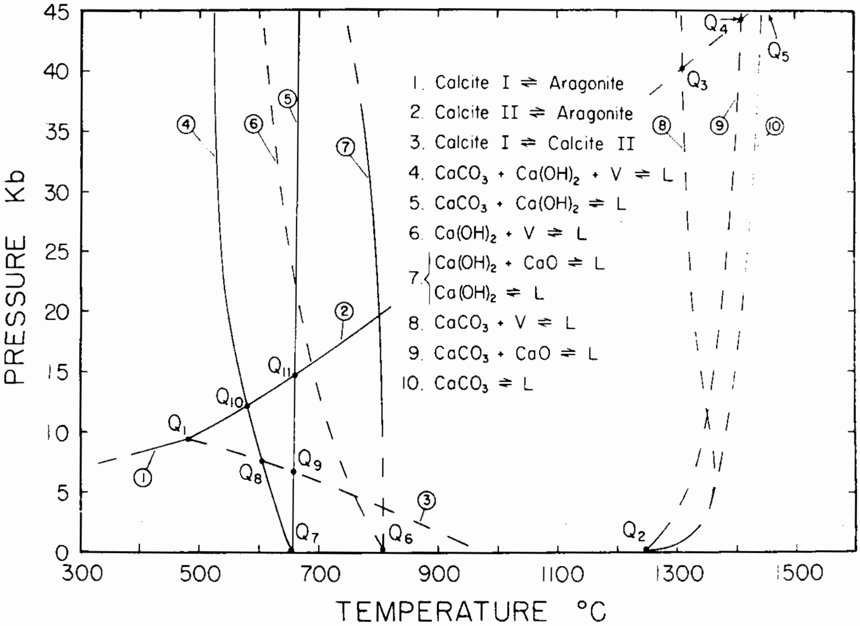


Fig. 4. PT projection for the system $CaO-CO_2-H_2O$, in part schematic, based on figures 1 and 2, plate 1, and the experimental data cited in the text. See table 2 for a list of the phase assemblages represented by the 11 invariant points, Q.

The main features of figure 5A are the liquidus surface divided by field boundaries into the three fields L(C), L(CC), and L(CH); the vaporus surface divided into two fields V(CC) and V(CH) by the field boundary V(CC,CH) extending down in temperature from V_1; and the wide miscibility gap between the liquids L(CH,V) and L(CC,V) along the boundaries aE_1d, and the vapors V(CH,L) and V(CC,L) along the boundaries gV_1f.

Figure 5B is a partly schematic polythermal projection at 25 kb, which represents in general form the phase diagram at pressures between 1 and 40 kb. Figure 4 shows that the temperature of the binary isobaric invariant liquid on the join CC–CH, the liquid L(CC,CH) in reaction (5), is insensitive to pressure, and the ternary liquid L(CC,CH,C) probably exists at a temperature slightly below this (Wyllie and Tuttle, 1960, figs. 15 and 17). Therefore, it is assumed in figure 5 that the positions of the field boundaries L(CH,C) and L(CC,C) along *bc* do not change significantly with increasing pressure; measured or estimated temperatures at any pressure between 1 and 40 kb for the binary liquids *b* (reaction 7) and *c* (reaction 9) can be obtained from the *PT* projection, figure 4.

The main effect of increasing pressure, as shown in figure 5B, is to increase the solubility of the volatile components in the liquids along the boundaries aE_1d. The temperatures of the liquids *a* (reaction 6) and *d* (reaction 8) at 25 kb were estimated from figure 4, and the temperature of E_1V_1 (reaction 4 in fig. 4) was measured directly (fig. 3). The point x in the field L(CH) of figure 5B represents one of the mixtures used in the experiments, and the results listed in table 1 confirm that the mixture x lies within the vapor-deficient region of the system at 25 kb.

TABLE 2

Invariant points in the system CaO-CO_2-H_2O

System	Point in figure 4	Phase assemblage	Pressure, kb	Temperature, °C	Source*
$CaCO_3$	Q1	CCI, CCII, Ar	9.4	480	1
CaO-CO_2	Q2	C, CCII, L, V	0.395	1230	2, 4
CaO-CO_2	Q3	CCII, Ar, L, V	(40)	(1310)	3
CaO-CO_2	Q4	C, CCII, Ar, L	(44)	(1410)	3
$CaCO_3$	Q5	CCII, Ar, L	(47)	(1440)	3
CaO-H_2O	Q6	C, CH, L, V	0.1	780	4, 5
CaO-CO_2-H_2O	Q7	C, CCI, CH, L, V	<0.01	640	4, 5
CaO-CO_2-H_2O	Q8	CCI, CCII, CH, L, V	(7.7)	(605)	1, 3
$CaCO_3$-$Ca(OH)_2$	Q9	CCI, CCII, CH, L	(6.7)	(656)	1, 3
CaO-CO_2-H_2O	Q10	CCII, Ar, CH, L, V	12.2	580	1, 3
$CaCO_3$-$Ca(OH)_2$	Q11	CCII, Ar, CH, L	14.5	659	1, 3

*(1) Boettcher and Wyllie, 1968; (2) Baker, 1962; (3) this paper, figure 4; (4) Wyllie and Tuttle, 1960; (5) Wyllie and Raynor, 1965.

Abbreviations: CC, calcite; Ar, aragonite; CH, portlandite; C, lime; L, liquid; V, vapor.

Values in parentheses are estimates taken from figure 4.

It is difficult to confirm the presence of a trace of vapor, as already mentioned, and similarly it is difficult to confirm that vapor was absent, on the basis of physical evidence. The fact that composition x in figure 6B lies in the vapor-deficient region was established by phase rule considerations. Run 26 is subsolidus, and the three phases Ar + CH + L were positively identified in runs 27 and 29 (table 1). It is possible that run 27 contained in addition a trace of unidentified vapor, in small quantities, if its temperature corresponds to the solidus (reaction 4). However, four phases can coexist in equilibrium at only one temperature in an isobaric ternary system, and, therefore, there can be no vapor phase present in runs 168 and 29. This means that the boundary L(CH,V), or aE_1, lies on the vapor side of point x in figure 5B; its precise position is unknown. The results in table 1 confirm that the point x lies on the vapor side of the boundary aE_1 at 15.5 kb.

Calculations based on our experimental data, using Bradley's (1962) procedure and assuming ideality, indicate that the liquid composition E_1 at 25 kb should contain 20 wt percent H_2O (relative to the join $CaCO_3$–$Ca(OH)_2$). There are many uncertainties in the calculation at this pressure. The experimental data give a value of more than 25 wt percent. Agreement of results with calculations based on assumptions of ideality does not prove that a system behaves ideally.

The composition of the liquid E_1 in terms of $CaCO_3/Ca(OH)_2$ has been determined at 1 kb (fig. 5A), but its precise composition has not

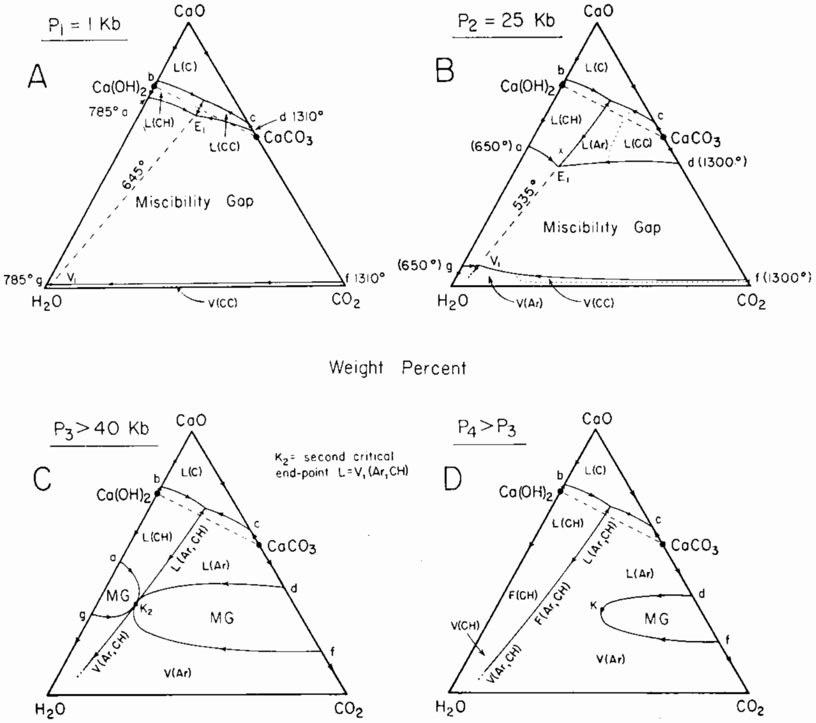


Fig. 5. Isobaric, polythermal diagrams for the system $CaO–CO_2–H_2O$, in part schematic. A is modified from Wyllie and Tuttle (1960). Temperatures in parentheses are estimated. See text for explanation. X in figure B marks the composition used in runs at 25kb (see table 1). C and D are hypothetical diagrams. Justification for use of the term "miscibility gap" (MG) between "fluid" phases was discussed by Roedder and Coombs (1967, p. 419).

been determined at higher pressures. Our preferred interpretation of the available data (table 1) is that the curve L(Ar,CH) traces a path of nearly constant $CaCO_3/Ca(OH)_2$ ratio toward H_2O and toward V_1 (nearly pure H_2O in fig. 5A). It is assumed in figure 5B that, concomitant with the increased solubility of volatiles in the liquid E_1, there is increased solubility of solids in the vapor V_1. Certainly, increase of pressure above 1 kb with simultaneous decrease of temperature would initially cause V_1 to move toward E_1 (Sharp and Kennedy, 1965).

Figure 4 also shows that the ternary reactions at 25 kb lie within the stability field of aragonite, whereas the melting reactions in the system $CaO–CO_2$ remain in the field of calcite. Therefore, dotted isotherms divide the liquidus surface $L(CaCO_3)$ in figure 5B into two fields, L(Ar) and L(CC), and the vaporus surface $V(CaCO_3)$ into two surfaces, V(Ar) and V(CC).

The compositions of the liquid E_1 and the vapor V_1 at 40 kb are not known. By extrapolation from figures 5A and 5B and from the fact that the temperature of reaction (4) continues to decrease with increasing pressure (figs. 3 and 4), it may be safely concluded that the miscibility gap between aE_1d and gV_1f continues to decrease in width. However, at 40 kb the compositions of liquid and vapor phases remain quite distinct. Microscopic examination of subsolidus runs at 40 kb reveals little vapor phase deposits, and the capsules are not puffed by CO_2 after a quench; these observations indicate that the vapor V_1 remains fairly close to the H_2O corner of the system. The system at 40 kb is probably not greatly changed from the diagram shown in figure 5B for 25 kb.

At even higher pressures, there are two possibilities. The miscibility gap between liquids and vapors may persist indefinitely, and perhaps widen, with the solidus reaction (4 in figs. 3 and 4) passing through a minimum in temperature and then achieving a positive slope (dP/dT); this is the behavior discussed and illustrated for silicate-water systems by Smith (1963, figs. 12-35 and 12-38). Alternatively, the compositions of liquid E_1 and vapor V_1 may continue to approach each other with increasing pressure, until they become coincident at a second critical end-point K_2, illustrated schematically in figure 5C. The field boundaries L(Ar,CH) and V(Ar,CH) meet and pass smoothly through the point K_2 which is designated by the symbol L=V,(Ar,CH). The miscibility gap is here divided into two portions. With increasing pressure above P_3, the two miscibility gaps would decrease in size. Each is closed at a critical point K, which moves progressively away from the position of K_2 at pressure P_3. In figure 5D, for example, the boundaries L(Ar,V) and V(Ar,L) which extend from *d* and *f*, respectively, meet smoothly at the critical point K, designated by the symbol L=V,(Ar). The liquidus field boundary L(Ar,CH) passes continuously, with decreasing temperature, into the vaporus field boundary V(Ar,CH); the transition is made along a portion of the field boundary designated F(Ar,CH), with the fluid phase being indeterminate between liquid and vapor.

PETROLOGICAL APPLICATIONS

Neither these experiments nor field and petrographic studies of carbonatites provide realistic estimates of the composition of natural carbonatite magmas from which carbonatite rocks were deposited. The importance of alkalis in some carbonatite magmas, which had been emphasized by von Eckermann (1948), may now be confirmed by the eruption of lavas from Oldoinyo Lengai, which are composed essentially of carbonates of sodium and calcium, with less than 2 percent of dissolved silica. Eruptions of natrocarbonatite from this volcano have recently been reviewed by Dawson (1966). Koster van Groos and Wyllie (1963, 1966, 1968) have discovered that sodium carbonate liquids are immiscible with some silicate liquids, which suggests that liquid immiscibility may play a role in the development of carbonatite magmas. The relationship between natrocarbonatite magmas and calcitic or dolomitic carbonatite rocks is as yet undetermined, and the system CaO–CO_2–H_2O remains a basis for interpretation of the phase relationships in more complex carbonate-silicate systems. A pressure of 40 kb corresponds to a depth within the Earth of approximately 125 km, which is well into the upper mantle and equivalent to the probable depth of origin of kimberlites. Even under these conditions, the compositions of the liquid and vapor phases in the system $CaO–CO_2–H_2O$ remain quite distinct, although they have moved significantly closer together than at 1 kb (figs. 5A and 5B). Therefore, following Wyllie and Tuttle (1960), we conclude that a vapor or gaseous phase containing dissolved solid material is not the major intrusive agent during the formation of most large carbonatite masses. The effect of additional components may limit this conclusion to lower pressures because Boettcher and Wyllie (1967b) have located a second critical end-point on the solidus for the system $CaO–SiO_2–CO_2–H_2O$ at 33 kb, which indicates that addition of SiO_2 to the system produces marked increase in the solubility of solids in the vapor phase. However, the solubility appears to remain low up to 10 kb pressure, which covers conditions within the average continental crust.

A new feature introduced by extending the solidus to high pressures is the crystallization of aragonite from the synthetic carbonatite magma above the invariant point Q_{10} in figure 4 (see fig. 5B), at pressures greater than 12 kb, which corresponds to conditions in the upper mantle just below the continental crust. Aragonite does occur rarely in veins and fissures cutting carbonatite intrusions, but it appears to be late and possibly supergene (von Eckermann, 1948, p. 87; Heinrich, 1966, p. 171-172). It cannot be considered to have crystallized from a carbonatite magma within its stability field. Boettcher and Wyllie (1967c, 1968) noted that aragonite quenched from positions near the calcite-aragonite transition boundary may invert to biaxial calcite during the quench. Biaxial calcite is also known in carbonatites (Paulitsch and Ambs, 1966), and this does not always appear to be related to mechanical postcrystallization deformation (Heinrich, 1966). However, the high pressures required for aragonite to crystallize from the synthetic carbonatite magma (fig. 4) indicate that biaxial calcite in carbonatites is not likely to have been produced by inversion of aragonite that grew within its stability field.

Textural evidence for the existence of intrusive carbonatite magmas is not abundant, and Wyllie and Tuttle (1960) were not aware of any compelling evidence when they published their work on $CaO–CO_2–H_2O$. However, there are now several textures described in the literature that can reasonably be interpreted as indicating the crystallization of a carbonatite magma. Particularly convincing is the description and illustration by Zhabin and Cherepivskaya (1965) of the narrow carbonatite dikes occurring in the Maymecha-Kotuy petrographic province in Siberia. These dikes have a porphyritic and trachytoid texture, with tabular calcite phenocrysts set in a "microgranular granoblastic mesostasis of calcite, dolomite and apatite". The phenocrysts constitute 60 to 80 percent by volume of the dikes. The dikes also have narrow "microgranular chill zones", along the sharp, dike-country rock contacts. Other examples of porphyritic texture and chilled margins are also known.

Wyllie and Tuttle (1960, fig. 2) sketched a synthetic texture with large rhombs or rounded crystals of calcite enclosed in fine-grained quenched liquid; a photomicrograph of similar textures is shown in plate 1-C, although the details of the quenched liquids cannot be distinguished. Johnson (1961, p. 128) described porphyritic beforsite from Southern Rhodesia with very large dolomite phenocrysts set in a fine-grained matrix of "fibrous dolomite". Gittins (1963) also described similar textures and concluded that they "represent a quenched liquid that carried carbonate crystals in suspension at the time of its emplacement". Heinrich (1966, p. 217) has tabulated other examples of "porphyritic" carbonatites with carbonate phenocrysts, but he notes that some of the phenocrysts could equally well be interpreted as late metacrysts.

Von Eckermann (1948) referred to chilled margins of dike rocks in the Alnö complex, and Heinrich (1966, p. 219) reported chilled margins from several small carbonatite intrusions in Colorado. Other evidence for the occurrence of liquid carbonatite magmas is provided by Girault's (1966) illustration in a photomicrograph of dendritic calcite from a point near the margin of the Oka carbonatite complex. Calcite dendrites produced in the system CaO–CO_2–H_2O are regarded as positive evidence for the former existence of a liquid phase. The magnification of the photomicrographs in plate 1 is too low for the texture of the quenched liquids to be distinguished, but these were described in detail and illustrated in sketches by Wyllie and Tuttle (1960, fig. 2). Girault's (1966) natural dendrites are similar to the synthetic examples.

The habit of apatite in some carbonatites may yield information about the conditions of formation of carbonatites. Wyllie, Cox, and Bigger (1962) published photomicrographs of apatite formed in the system CaO–CaF_2–P_2O_5–CO_2–H_2O. Apatite in equilibrium with liquid or vapor formed stubby prisms, whereas apatite precipitated from the liquid phase during a quench formed acicular prisms often skeletal, clustered in sheaf-like form. They proposed that acicular apatite in carbonatites might be useful as a criterion for the former presence of a liquid magma. Heinrich (1966, p. 177) reported that in some carbonatites, apatite does form radial or parallel clusters of very slender prisms, rather than the more usual ovoid grains. Barth and Ramberg (1966) have also described clusters of apatite needles in sovite dikes in the Fen complex and reproduced one of Brögger's (1921) drawings to illustrate the texture. Girault (1966) described in detail two habits of apatite from the Oka carbonatite which correspond very closely to the two habits obtained in the experiments (Wyllie, Cox, and Bigger, 1962), and he included this among his evidence that the Oka carbonatite had a magmatic origin. This conclusion is consistent with the experimental work of Watkinson and Wyllie (1966), which confirms that fractional crystallization of a nepheline-rich liquid in the system $NaAlSiO_4$–$CaCO_3$–H_2O would yield a residual liquid precipitating calcite, and that the sequence of mineral assemblages produced is very similar to the rock sequence occurring at the Oka complex.

Wyllie and Tuttle (1960) remarked that the growing interest in carbonatites was indicated by the publication in 1956 of three wide-ranging reviews of carbonatites by Campbell Smith (1956), Pecora (1956), and Agard (1956). Development of this interest was marked by the publication in 1966 of two books on the geology of carbonatites (Heinrich, 1966; Tuttle and Gittins, 1966) and an international symposium volume dealing with the kimberlites and carbonatites (von Eckermann, 1966). These three volumes contain several chapters reviewing experimental studies of silicate-carbonate systems. Additional field and experimental studies are required before we can decide which came first, the silicate magma or the carbonatite magma (see Heinrich, 1966, p. 288-296).

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REFERENCES

Agard, J., 1956, Les gites mineraux associes aux roches alcalines et aux carbonatites: Univ. Nancy, Sci. de la Terre, v. 4, p. 105-151.

Baker, E. H., 1962, Calcium oxide-carbon dioxide system in the pressure range 1-300 atmospheres: Chem. Soc. Jour., p. 464-470.

Barth, T. F. W., and Ramberg, I. B., 1966, The Fen circular complex, *in* Tuttle, O. F., and Gittins, J., eds., Carbonatites: New York, Intersci. Publishers, p. 225-257.

Blount, G. W., and Dickson, F. W., 1967, The solubility of portlandite ($Ca(OH)_2$) in water to 257° and at pressures to 1500 bars: Am. Geophys. Union Trans., v. 48, p. 249-250.

Boeke, H. E., 1912, Die Schmelzerscheinungen und die umkehrare umwandlung des calciumcarbonats: Neues Jahrb. Mineralogie Geologie, v. 1, p. 91-212.

Boettcher, A. L., and Wyllie, P. J., 1967a, Melting relations in the system $CaO-CO_2-H_2O$ to 40 Kb: Am. Geophys. Union Trans., v. 48, p. 250.

——— 1967b, A second critical endpoint terminating the univariant solidus reaction in the system $CaO-SiO_2-CO_2-H_2O$ at 32 ± 3 Kb and 515°C: Am. Geophys. Union Trans., v. 48, p. 250.

——— 1967c, Biaxial calcite inverted from aragonite: Am. Mineralogist, v. 52, p. 1527-1529.

——— 1967d, Revision of the calcite-aragonite transition, with the location of a triple point between calcite I, calcite II, and aragonite: Nature, v. 213, p. 792-793.

——— 1968, The calcite-aragonite transition measured in the system $CaO-CO_2-H_2O$: Jour. Geology, v. 76, p. 314-330.

Boyd, F. R., and England, J. L., 1960, Apparatus for phase-equilibrium measurements at temperatures up to 50 kilobars and temperatures up to 1750°: Jour. Geophys. Research, v. 65, p. 741-748.

Bradley, R. S., 1962, Thermodynamic calculations on phase equilibria involving fused salts. Part I. General theory and application to equilibria involving calcium carbonate at high pressure: Am. Jour. Sci., v. 260, p. 374-382.

Bridgman, P. W., 1939, The high-pressure behaviour of miscellaneous minerals: Am Jour. Sci., v. 237, p. 7-18.

Brögger, W. C., 1921, Die Eruptivgesteine des Kristianiagebietes. IV. Das Fengebiet in Telemarken, Norwegen: Norske Vidensk. Skr. Math.-Naturv. XI., 1920, no. 9, p. 1-408.

Clark, S. P., 1959, Effect of pressure on the melting points of eight alkali halides: Jour. Chem. Physics, v. 31, p. 1526-1531.

Crawford, W. A., and Fyfe, W. S., 1964, Calcite-aragonite equilibrium at 100°C: Science, v. 144, p. 1569-1570.

Dawson, J. B., 1966, Oldoinyo Lengai—an active volcano with sodium carbonatite lava flows, *in* Tuttle, O. F., and Gittins, J. eds., Carbonatites: New York, Intersci. Publishers, p. 155-168.

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

——— 1966, Kimberlite-carbonatite symposium: Mineralog. Soc. India, IMA v., p. 1-148.

Girault, J., 1966, Genese et geochimie de l'apatite et de la calcite dans les roches liees au complexe carbonatique et hyperalcalin d'Oka (Canada): Soc. Française Mineralog. Bull., v. 84, p. 496-513.

Gittins, J., 1963, Further evidence for the existence of carbonatite magmas: Canadian Mineralogist, v. 7, p. 817.

Gittins, J., and Tuttle, O. F., 1964, The system CaF_2–$Ca(OH)_2$–$CaCO_3$: Am. Jour. Sci., v. 262, p. 66-75.

Greig, J. W., 1955, Sulfides, selenides, and tellurides: Carnegie Inst. Washington Year Book 54, p. 129-134.

Harker, R. I., 1964, Differential thermal analysis in closed systems at high hydrostatic pressure: Am. Mineralogist, v. 49, p. 1741-1747.

Heinrich, E. W., 1966, The geology of Carbonatites: Chicago, Rand McNally and Co., 608 p.

Johnson, R. L., 1961, The geology of the Dorowa and Shawa carbonatite complexes, Southern Rhodesia: Geol. Soc. South Africa Proc., v. 64, p. 101-145.

Koster van Groos, A. F., and Wyllie, P. J., 1963, Experimental data bearing on the role of liquid immiscibility in the genesis of carbonatites: Nature, v. 199, p. 801-802.

——— 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.

——— 1968, 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.

Kuellmer, F. J., Visocky, A. P., and Tuttle, O. F., 1966, Preliminary survey of the system barite–calcite–fluorite at 500 bars, *in* Tuttle, O. F., and Gittins, J., eds., Carbonatites: New York, Intersci. Publishers, p. 353-364.

Newton, R. C., 1965, The thermal stability of zoisite: Jour. Geology, v. 73, p. 431-441

Paulitsh, P., and Ambs, H., 1966, Carbonatites, their fabric, chemistry and their genesis: Mineralog. Soc. India, IMA v., p. 140-147.

Pecora, W. T., 1956, Carbonatites: a review: Geol. Soc. America Bull., v. 67, p. 1537-1556.

Pistorius, C. W. F. T., 1963, Thermal decomposition of portlandite and xonotlite to high pressures and temperatures: Am. Jour. Sci., v. 261, p. 79-87.

Roedder, E., and Coombs, D. S., 1967, Immiscibility in granitic melts, indicated by fluid inclusions in ejected granitic blocks from Ascension Island: Jour. Petrology, v. 8, p. 417-451.

Sharp, W. E., ms, 1964, The system CaO–CO_2–H_2O in the two phase region calcite + aqueous solution and its application to the origin of quartz-calcite veins: Ph.D. thesis, Univ. California, Los Angeles.

Sharp, W. E., and Kennedy, G. C., 1965, The system CaO–CO_2–H_2O in the two-phase region calcite + aqueous solution: Jour. Geology, v. 73, p. 391-403.

Smith, F. G., 1963, Physical geochemistry: Reading, Mass., Addison-Wesley Publishing Co., Inc., 624 p.

Smith, W. Campbell, 1956, A review of some problems of African carbonatites: Geol. Soc. London Quart. Jour., v. 112, p. 189-219.

Tuttle, O. F., and Gittins, J., 1966, Carbonatites: New York, Intersci. Publishers, 591 p.

Watkinson, D. H., and Wyllie, P. J., 1966, Carbonatites as derivatives of nephelinitic magma: experimental evidence [abs.]: Geol. Soc. America Spec. Paper 101, p. 238.

Wentorf, R. H., Jr., 1966, Solutions of carbon at high pressure: Bunsengesellschaft Physical Chemistry Ber., v. 70, p. 975-982.

Wyllie, P. J., 1966a, Experimental studies of carbonatite problems: The origin and differentiation of carbonatite magmas, *in* Tuttle, O. F., and Gittins, J., eds., Carbonatites: New York, Intersci. Publishers, p. 311-352.

——— 1966b, Experimental data bearing on the petrogenetic links between kimberlites and carbonatites: Mineralog. Soc. India, IMA v., p. 67-82.

Wyllie, P. J., and Biggar, G. M., 1966, Fractional crystallization in the "carbonatite systems" CaO–MgO–CO_2–H_2O and CaO–CaF_2–P_2O_5–CO_2–H_2O: Mineralog. Soc. India, IMA v., p. 92-105.

Wyllie, P. J., Cox, K. G., and Biggar, G. M., 1962, The habit of apatite in synthetic and igneous systems: Jour. Petrology, v. 1, p. 1-46.

Wyllie, P. J., and Haas, J. L., 1965, The system CaO–SiO_2–CO_2–H_2O: I. Melting relationships with excess vapor at 1 kilobar pressure: Geochim. et Cosmochim. Acta, v. 29, p. 871-892.

Wyllie, P. J., and Raynor, E. J., 1965, D.T.A. and quenching methods in the system CaO–CO_2–H_2O: Am. Mineralogist, v. 50, p. 2077-2082.

Wyllie, P. J., and Tuttle, O. F., 1960, The system CaO–CO_2–H_2O and the origin of carbonatites: Jour. Petrology, v. 1, p. 1-46.

——— 1963, The quenching technique in non-quenchable systems: A discussion concerning the alleged thermal decomposition of portlandite at high pressures: Am. Jour. Sci., v. 261, p. 983-988.

Zhabin, A. G., and Cherepivskaya, G. Y., 1965, Carbonatite dikes as related to ultrabasic-alkalic extrusive igneous activity: Akad. Nauk SSSR Doklady, v. 160, p. 135-138.