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LIQUID IMMISCIBILITY IN THE JOIN $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3–H_2O

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ABSTRACT. The phase relationships in the six component system $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3–H_2O were determined between 650° and 950°C and 1 kb pressure along the joins $Ab_{80}An_{20}$–Na_2CO_3 and $Ab_{50}An_{50}$–Na_2CO_3 both with 10 percent H_2O present. The phase relationships are complex. Crystalline phases encountered were plagioclase, nepheline, noselite, cancrinite, wollastonite, sodium carbonate, and sodium calcium carbonate. The solidus was intersected at minimally 695°C.

The most important feature is the presence of a two-liquid field above 750°C, separating a carbonate-poor silicate liquid and a silicate-poor carbonate liquid. Electron microprobe analyses of the quenched silicate liquid and atomic absorption data for the quenched carbonate liquid show that the silicate liquid is peralkaline and strongly undersaturated in silica and that the coexisting carbonate liquid is strongly enriched in calcium.

A third fluid phase present with these two liquids is an aqueous vapor phase enriched with sodium silicate and CO_2.

It is concluded that in this system three fluid phases coexist that correlate well with the natural occurring undersaturated alkalic urtite–ijolite–melteigite rock series, the carbonatites, and the associated metasomatic fenites of the carbonatite-alkalic rock complexes.

INTRODUCTION

Since it was established that carbonate liquids can exist at geologically reasonable temperatures and pressures (Wyllie and Tuttle, 1960), the phase relations in several systems have been determined in attempts to elucidate the origin of and the relationships between carbonatites and the associated alkalic complexes (Franz and Wyllie, 1967; Watkinson and Wyllie, 1971; Koster van Groos and Wyllie, 1966, 1968). Following von Eckermann (1948) who thought that carbonatite magmas are alkali-rich melts, an idea that was emphasized later by the occurrence of natro-carbonate lava flows from Oldonyo Lengai (Dawson, 1962), we studied the joins $NaAlSi_3O_8$–Na_2CO_3 and $NaAlSi_3O_8$–Na_2CO_3–H_2O (Koster van Groos and Wyllie, 1966, 1968). In these joins a wide miscibility gap was recognized between silicate-rich and carbonate-rich liquids, explaining how a presumably highly reactive natro-carbonate melt could form in nature.

Carbonatites, however, are composed mainly of calcite and do not contain sodium carbonate. Even the natro-carbonate lavas from Oldonyo Lengai contain 12.8 percent $CaCO_3$ (Dawson, 1962). So, in order to investigate the effect of lime on the miscibility gap and to determine the distribution of CaO between the coexisting liquids, we studied the section plagioclase–Na_2CO_3–H_2O along two joins, containing the plagioclase compositions $Ab_{80}An_{20}$ and $Ab_{50}An_{50}$. These compositions and all others in this paper are expressed in weight percent.

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PREVIOUS EXPERIMENTAL STUDIES

According to Niggli's (1920) results for the system Na_2CO_3–$CaCO_3$, Na_2CO_3 can dissolve about 30 percent $CaCO_3$ in solid solution before the intermediate compound $Na_2Ca(CO_3)_2$ becomes stable.

In the reciprocal system Na_2CO_3–$CaCO_3$–$CaAl_2Si_2O_8$–$NaAlSiO_4$, a solid-solution series of cancrinite is present at the liquidus (Eitel, 1925, 1954). The end-members are Ca-cancrinite ($3NaAlSiO_4 \cdot CaCO_3$) and Na-cancrinite ($3NaAlSiO_4 \cdot Na_2CO_3$).

Edgar and Burley (1963) showed that the Na_2CO_3-rich end-member of the cancrinite series converts to a nosean structure at temperatures above 600°C and at H_2O pressures between 0.6 and 2 kb pressure. Later, Edgar (1964) determined that the CaO-rich end-member can exist at temperatures as high as 800°C at 1 kb H_2O pressure.

Watkinson and Wyllie (1965, 1969, 1971) studied a series of joins through the system CaO–Na_2O–Al_2O_3–SiO_2–CO_2–H_2O. They found a high-temperature thermal barrier on the liquidus of the join $NaAlSi_3O_8$–$CaCO_3$–H_2O between silicate and carbonate liquids, but in the join $NaAlSiO_4$–$CaCO_3$–H_2O (Watkinson and Wyllie, 1971), the liquid phase is continuous from nepheline- rich to carbonate-rich compositions at moderate temperatures.

Koster van Groos and Wyllie (1966) showed that in the system Na_2O–Al_2O_3–SiO_2–CO_2 a wide miscibility gap between silicate-rich and carbonate-rich liquids is intersected along the join $NaAlSi_3O_8$–Na_2CO_3 at moderate CO_2 pressures. Figure 1 shows schematically the extent of this miscibility gap in the quaternary system, modified from the published diagram by incorporation of recent results (Koster van Groos, unpub. data), which indicate that this miscibility gap persists at Al_2O_3-poorer compositions and possibly extends to the bounding system Na_2O–SiO_2–CO_2.

Two liquids were also encountered in the join $NaAlSi_3O_8$–Na_2CO_3–H_2O (Koster van Groos and Wyllie, 1968). Figure 2 shows the phase relationships with 10 percent H_2O present at 1 kb pressure. The solidus and the compositional range of the phase fields containing both liquids are shown by the heavy lines. The silicate-rich liquid can precipitate cancrinite and is, therefore, undersaturated with SiO_2. The coexisting H_2O–CO_2 vapor phase is assumed to be enriched with Na_2O and SiO_2.

EXPERIMENTAL METHOD

Starting Materials

Reagent grade sodium carbonate was dried to constant weight at 550°C. Gels of two plagioclase compositions, which we will refer to as $Ab_{80}An_{20}$ and $Ab_{50}An_{50}$, were prepared using standard methods (Luth and Ingamells, 1965). The dried starting materials were ground to pass 200 mesh, mixed in a mechanical shaker for 15 minutes, and stored in a desiccator. The composition of the dry starting mixtures is shown in figure 3.

Apparatus and Method

All runs were made in cold-seal pressure vessels (Tuttle, 1949), using standard quenching techniques (Wyllie and Tuttle, 1960; Koster van Groos and Wyllie, 1968). Bulk compositions were made by pipetting a known weight of distilled water in a gold tube and adding the required weight of the anhydrous starting mixture to obtain an H_2O content of 10 percent. Temperature measurements are believed accurate to ± 5°C; pressure, measured with commercial bourdon-type gauges, is accurate to within 5 percent.

The vessel was quenched rapidly in cold water at the end of a run, in order to minimize complications caused by the growth of crystalline phases during a quench. Nevertheless, the growth of a noselite-like phase during quenching remained a problem.

The usual tests to determine whether equilibrium was established confirmed that the time of duration of the runs was more than adequate.

Identification of the Phases

The equilibrium phase assemblages were determined using the appearance of the capsule, the physical characteristics of the sample after

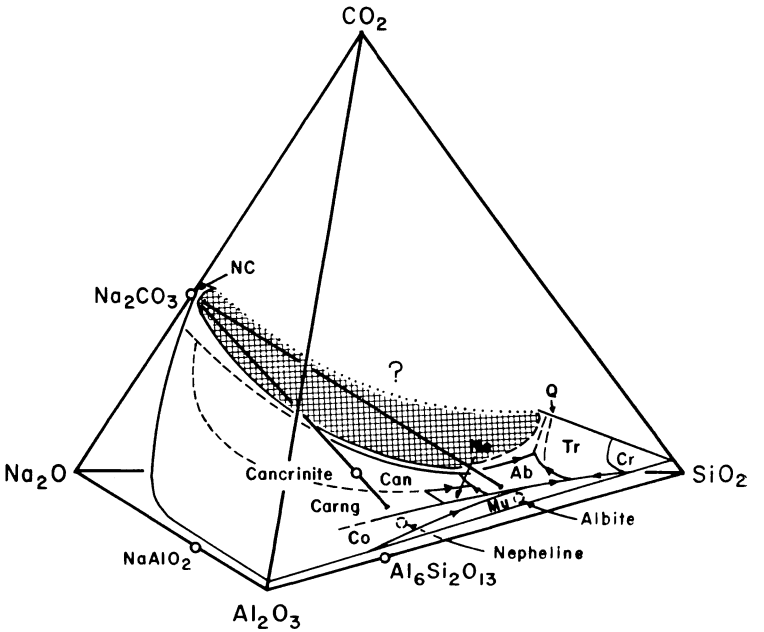

Fig. 1. Schematic diagram of the vapor-saturated liquidus surface in the system Na_2O–Al_2O_3–SiO_2–CO_2 at 1 kb pressure. The field of liquid immiscibility is shaded. Abbreviations: Ab = albite, Carng = carnegieite, Can = cancrinite, Co = corundum, Cr = cristoballite, Mu = mullite, Ne = nepheline, NC = sodium carbonate, Q = quartz, Tr = tridymite.

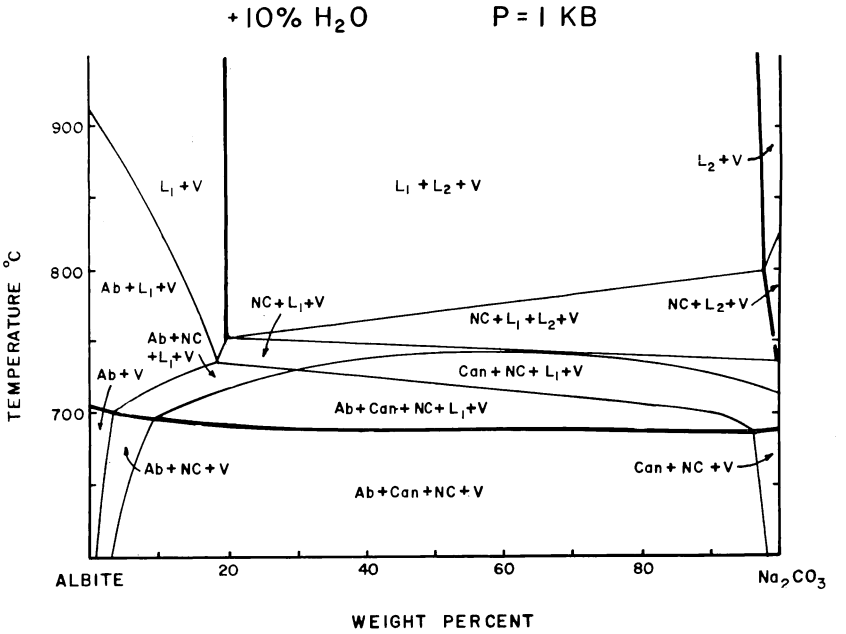

Fig. 2. The join $NaAlSi_3O_8$–Na_2CO_3 with 10 percent H_2O at 1 kb pressure. The heavy lines indicate the solidus and the extent of the two-liquid field. Abbreviations: L_1 = silica-rich liquid, L_2 = carbonate-rich liquid, V = vapor, for other abbreviations see table 1.

it was removed from the capsule, petrographic study of the crushed sample, and X-ray powder diffraction patterns. Refractive indices were measured in sodium light. They are assumed to be accurate to ± 0.001. An attempt was made to determine the composition of the liquid phases by atomic absorption and electron microprobe methods.

The phases encountered are listed in table 1 and described below.

Plagioclase occurred as small lath-shaped crystals, up to 0.05 mm long, of unknown composition.

Nepheline formed short hexgonal prisms, up to 0.2 mm long.

Noselite.—An isotropic crystalline phase with the refractive index varying between 1.480 and 1.488 occurred over a large part of the join. Usually the crystals were very small, about 0.01 mm, but they reached sizes up to 0.1 mm in runs rich in Na_2CO_3. The X-ray reflections and the optical properties define it as a member of the sodalite group and match most closely those of noselite. It is probably the Na_2CO_3–$CaCO_3$ bearing analog of noselite ($3NaAlSiO_4 \cdot Na_2SO_4$).

Cancrinite occurred as short prisms, up to 0.5 mm long, with the refractive indices N_o = 1.518 and N_e = 1.508. During quenching cancrinite microlites crystallized. Continued growth of these microlites in the glass at room temperature was observed over several months.

Wollastonite formed small columnar crystals up to 0.2 mm long. This phase is easily recognized because of its high refractive index and habit.

Sodium carbonate formed very fine-grained crystalline aggregates. Semi-angular carbonate-rich inclusions in silicate glass were interpreted to represent primary sodium carbonate, and spherical carbonate inclusions were interpreted as quenched liquid. We did not find other criteria to distinguish primary sodium carbonate from quenched liquid carbonate. Its refractive index, estimated to be $N_o = 1.530$, was difficult to measure because of its habit.

Sodium calcium carbonate.—In some runs a calcite-like phase was present in the fine-grained carbonate aggregates. The refractive index $N_o = 1.548$ agrees with the refractive index of sodium calcium carbonate. The amount present was too small for confirmation by X-ray diffraction.

Silicate-rich liquid.—The silicate-rich liquid L_1 quenched to a colorless glass. This glass is bluish in high-temperature runs, probably because a trace of cobalt diffused through the walls of the gold capsule from the pressure vessel. The refractive index varies between 1.497 and 1.537. It often devitrifies partially during the quench, forming microlites of cancrinite.

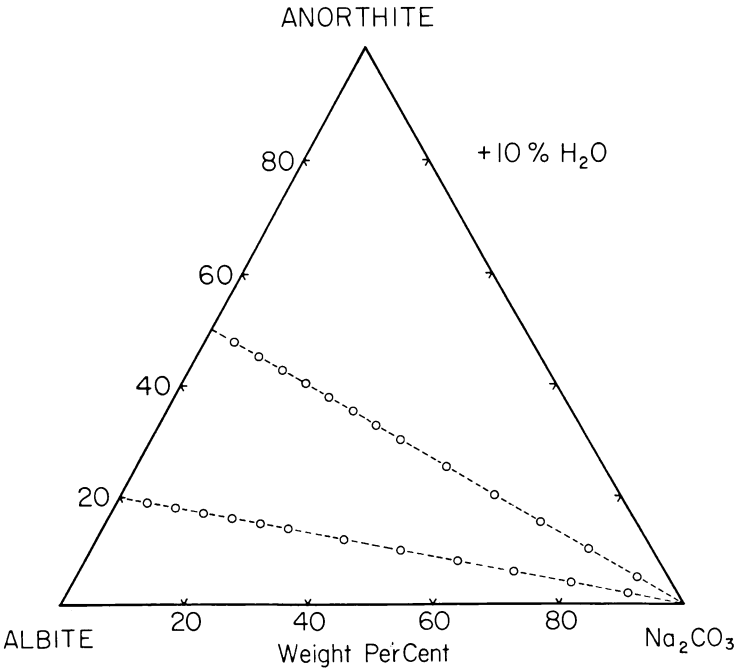

Fig. 3. The composition join $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3. The circles indicate the composition of the dry starting mixtures. The dashed lines indicate the joins investigated.

TABLE 1
List of the phases encountered in experimental study

Phase	Symbol	Assumed composition
Plagioclase	Pl	$NaAlSi_3O_8$–$CaAl_2Si_2O_8$
Nepheline	Ne	$NaAlSiO_4$
Noselite	No	$3NaAlSiO_4 \cdot (Na_2CO_3, CaCO_3)$
Cancrinite	Can	$3NaAlSiO_4 \cdot (Na_2CO_3, CaCO_3)$
Wollastonite	Wo	$CaSiO_3$
Sodium carbonate	NC	Na_2CO_3
Sodium calcium carbonate		$Na_2Ca(CO_3)_2$
Silicate-rich liquid	L_1	Variable
Carbonate-rich liquid	L_2	Variable
Vapor	V	Variable

Carbonate-rich liquid.—The carbonate-rich liquid L_2 did not quench to a glass but formed fine-grained crystalline aggregates, which were indistinguishable from primary sodium carbonate. Because the melting temperature of sodium carbonate in the presence of excess H_4O is 750°C at 1 kb pressure with 20 percent H_2O dissolved in the liquid (Koster van Groos and Wyllie, 1968), this crystalline aggregate must represent a quenched liquid when the run was at a higher temperature. Also, we assumed that spherical inclusions of the fine-grained carbonate in silicate-rich glass represented a quenched liquid. Sometimes crystals of sodium calcium carbonate were found in the quenched liquid, indicating that the liquid contained at least 30 percent $CaCO_3$ (Niggli, 1920).

Vapor is present in all runs. This is indicated by the physical character of the quenched capsules and by the presence of small isotropic spheres with a low index of refraction, about 1.47, which is recognized as a standard quench product of a vapor phase in silicate-H_2O systems. The presence of CO_2 in the vapor phase is indicated because the capsules were puffed after the runs, caused by the gas under pressure.

Analytical Procedure

An attempt was made to determine the compositions of the silicate-rich liquid with the electron microprobe and the compositions of the carbonate-rich liquid with atomic absorption.

Only high-temperature runs were selected so that silicate glass was abundant. The samples, each with a total weight of approximately 30 mg, were crushed in a small mortar, and the carbonate phase was dissolved in 1 ml of diluted acetic acid. When effervescence ceased, the liquid was removed, and the residue was washed carefully five times with 1 ml distilled and deionized water. The rinsing solution was added to the acetic acid solution. Microscopic inspection showed that all carbonate was removed with the exception of carbonate spheres mantled by by the silicate-rich liquid. The solution were diluted and filtered, and the Ca/Na ratio was determined using standard atomic absorption techniques. Most likely the vapor deposits dissolved in the acetic acid solution also. Considering the higher solubility of sodium silicates in H_2O-rich vapor as compared with calcium silicates, it would seem likely that

the Ca/Na ratio of the solution would decrease with the addition of the dissolved vapor deposits.

The silicate-rich residue was analyzed with the electron microprobe. Standards were homogeneous glasses made by melting a series of synthetic mixtures of plagioclase composition. The silicate residue of the samples was not homogeneous. Small crystals of plagioclase, wollastonite, and noselite were sometimes abundant, complicating the analysis. A more serious difficulty was the very rapid boil-off of sodium of the hydrated and carbonated samples, even at low currents and large spot size. Therefore, it can be expected that the sodium analyses are probably on the low side. The hole burned in the polished surface of the sample by the electron beam also caused an inaccuracy in the values obtained for the other elements.

About 30 analyses were made from run. This allowed us to discard analyses that showed either high lime and silicate contents, assumed to be caused by the presence of wollastonite, or extremely high sodium contents which were probably caused by the presence of noselite or the occurrence of very small spheres of sodium carbonate under the polished glass surface.

RESULTS

Phase Relationships

The phase fields intersected by the joins $Ab_{80}An_{20}$–Na_2CO_3 and $Ab_{50}An_{50}$–Na_2CO_3 both with 10 percent H_2O present at 1 kb pressure are shown in figures 4 and 5. The critical runs are listed in tables 2 and 3. Both joins lie in the system CaO–Na_2O–Al_2O_3–SiO_2–CO_2–H_2O. There is no indication that the phase relationships in these joins are simplified by compositional restrictions limiting the number of degrees of freedom. Only the end-members of the joins have a composition lying on the join. All the phases with the exception of wollastonite form continuous solution series in the solid, liquid, or vapor state.

The liquidus in the join $Ab_{80}An_{20}$–Na_2CO_3 is intersected over a wide range of compositions at 900°C; in the join $Ab_{50}An_{50}$–Na_2CO_3 the liquidus is not reached at 950°C, the highest temperature possible with our apparatus. The solidus, indicated with a heavy line, is intersected at about 690°C in figure 4; in figure 5 the solidus is intersected at minimally 725°C.

The upper stability of plagioclase decreases sharply with the addition of Na_2CO_3. Phase fields containing plagioclase extend to the composition $Pl_{73}NC_{27}$ in figure 4 and to the composition $Pl_{78}NC_{22}$ in figure 5. The composition of the small plagioclase crystals was not determined; it is probably enriched with albite at lower temperatures and when more Na_2CO_3 is present in the starting mixture. Plagioclase and sodium carbonate do not occur together.

The stability field of nepheline is intersected by the join $Ab_{50}An_{50}$–Na_2CO_3 only. It is stable at compositions with up to 28 percent Na_2CO_3

TABLE 2

Critical runs in the join $Ab_{80}An_{20}$–Na_2CO_3 with 10 percent H_2O present at 1 kb pressure. See table 1 for abbreviations.

Composition in wt %	Temperature °C	Time in hrs	Interpreted phase assemblage
$Pl_{95}NC_5$	925	2	L_1+V
	885	80	L_1+V
	850	80	$Pl+L_1+V$
	820	65	$Pl+L_1+V$
	720	76	$Pl+L_1+V$
	710	400	$Pl+L_1+V$
	690	240	$Pl+Can+V$
	685	190	$Pl+Can+V$
	655	270	$Pl+Can+V$
$Pl_{90}NC_{10}$	925	2	L_1+V
	885	80	L_1+V
	820	65	$Wo+L_1+V$
	790	72	$Pl+Wo+L_1+V$
	775	38	$Pl+Wo+L_1+V$
	730	30	$Pl+Wo+L_1+V$
	720	400	$Pl+Wo+Can+L_1+V$
	695	78	$Pl+Wo+Can+L_1+V$
	685	380	$Pl+Wo+Can+V$
	655	270	$Pl+Wo+Can+V$
$Pl_{85}NC_{15}$	925	2	$Wo+L_1+V$
	885	80	$Wo+L_1+V$
	820	65	$Wo+L_1+V$
	800	24	$Wo+L_1+V$
	775	38	$Wo+No+L_1+V$
	760	48	$Wo+No+L_1+V$
	740	48	$Wo+No+L_1+V$
	730	38	$Pl+Wo+Can+L_1+V$
	720	76	$Pl+Wo+Can+L_1+V$
	710	80	$Pl+Wo+Can+L_1+V$
	655	270	$Pl+Wo+Can+V$
$Pl_{80}NC_{20}$	925	2	L_1+V
	910	3	L_1+V
	890	104	L_1+V
	850	55	$Wo+No+L_1+V$
	800	24	$Wo+No+L_1+V$
	775	38	$Wo+No+L_1+V$
	760	48	$Wo+No+L_1+V$
	740	48	$Wo+No+L_1+V$
	730	38	$Wo+Can+L_1+V$
	720	400	$Wo+Can+L_1+V$
	695	78	$Pl+Wo+Can+L_1+V$
	685	380	$Pl+Wo+Can+V$
	655	270	$Pl+Wo+Can+V$
$Pl_{75}NC_{25}$	925	2	L_1+V
	890	18	$No+L_1+V$
	800	24	$No+L_1+V$
	775	38	$No+L_1+V$
	760	48	$No+L_1+V$
	740	48	$Wo+No+L_1+V$
	720	76	$Wo+Can+L_1+V$
	710	400	$Wo+Can+L_1+V$
	655	270	$Pl+Wo+Can+V$
$Pl_{70}NC_{30}$	925	1	L_1+L_2+V
	910	3	L_1+L_2+V
	890	104	$No+L_1+L_2+V$

TABLE 2 (continued)

Composition in wt %	Temperature °C	Time in hrs	Interpreted phase assemblage
$Pl_{70}NC_{30}$	800	24	No+L_1+L_2+V
	760	48	No+L_1+L_2+V
	740	48	No+L_1+L_2+V
	730	270	Can+L_1+L_2+V
	710	400	Can+NC+L_1+V
	695	78	Can+NC+L_1+V
	685	380	Wo+Can+NC+V
	655	270	Wo+Can+NC+V
$Pl_{60}NC_{40}$	925	1	L_1+L_2+V
	910	3	L_1+L_2+V
	890	104	No+L_1+L_2+V
	775	240	No+L_1+L_2+V
	750	123	No+L_1+L_2+V
	730	270	Can+NC+L_1+L_2+V
	695	270	Can+NC+L_1+V
	655	270	Can+NC+V
$Pl_{50}NC_{50}$	750	123	No+L_1+L_2+V
	730	270	Can+NC+L_1+V
	695	270	Can+NC+L_1+V
	685	380	Can+NC+V
	655	270	Can+NC+V
$Pl_{40}NC_{60}$	925	1	L_1+L_2+V
	910	3	L_1+L_2+V
	890	18	No+L_1+L_2+V
	850	80	No+L_1+L_2+V
	790	72	No+L_1+L_2+V
	775	240	No+L_1+L_2+V
	750	123	No+L_1+L_2+V
	730	270	No+NC+L_1+V
	720	104	Can+NC+L_1+V
	695	270	Can+NC+L_1+V
	685	190	Can+NC+L_1+V
	655	48	Can+NC+V
$Pl_{30}NC_{70}$	750	123	No+L_1+L_2+V
	730	270	No+NC+L_1+V
	720	400	Can+NC+L_1+V
	710	125	Can+NC+L_1+V
	695	270	Can+NC+L_1+V
	685	190	Can+NC+L_1+V
	655	48	Can+NC+V
$Pl_{20}NC_{80}$	925	1	L_1+L_2+V
	890	104	No+L_1+L_2+V
	850	80	No+L_1+L_2+V
	790	72	No+L_1+L_2+V
	775	240	No+L_1+L_2+V
	765	100	No+L_1+L_2+V
	750	123	No+L_1+L_2+V
	720	400	No+NC+L_1+V
	710	125	Can+No+NC+L_1+V
	685	190	Can+NC+L_1+V
	655	48	Can+NC+V
$Pl_{10}NC_{90}$	925	1	L_1+L_2+V
	890	18	No+L_1+L_2+V
	850	52	No+L_1+L_2+V
	775	240	No+L_1+L_2+V
	730	38	No+NC+L_1+V
	710	400	No+NC+V
	685	380	No+NC+V

TABLE 3

Runs in the join $Ab_{50}An_{50}$–Na_2CO_3 with 10 percent H_2O at 1 kb pressure. See table 1 for abbreviations.

Composition in wt %	Temperature °C	Time in hrs	Interpreted phase assemblage
$Pl_{95}NC_5$	950	2	Pl+Ne+L_1+V
	890	84	Pl+Ne+Wo+L_1+V
	795	110	Pl+Ne+Wo+V
	750	240	Pl+Ne+Wo+V
	680	380	Pl+Ne+Wo+V
$Pl_{90}NC_{10}$	950	2	Pl+Ne+Wo+L_1+V
	890	84	Pl+Ne+Wo+L_1+V
	795	110	Pl+Ne+Wo+V
	750	240	Pl+Ne+Wo+V
	680	380	Pl+Ne+Wo+V
$Pl_{85}NC_{15}$	950	2	Ne+Wo+L_1+V
	890	84	Ne+Wo+L_1+V
	795	110	Pl+Ne+Wo+L_1+V
	750	240	Pl+Ne+Wo+V
	680	380	Pl+Ne+Wo+Can+V
$Pl_{80}NC_{20}$	950	2	Ne+Wo+L_1+V
	910	96	Ne+Wo+L_1+V
	890	84	Ne+Wo+L_1+V
	795	110	Ne+Wo+L_1+V
	750	380	Pl+Ne+Wo+Can+L_1+V
	680	380	Pl+Ne+Wo+Can+V
$Pl_{75}NC_{25}$	950	2	Ne+Wo+No+L_1+V
	910	96	Ne+Wo+No+L_1+V
	890	84	Ne+Wo+No+L_1+V
	795	110	Ne+Wo+No+L_1+V
	755	240	Ne+Wo+No+Can+L_1+V
	680	380	Ne+Wo+Can+V
$Pl_{70}NC_{30}$	950	2	Wo+No+L_1+V
	910	96	Wo+No+L_1+V
	890	84	Wo+No+L_1+V
	800	110	Wo+No+L_1+V
	755	240	Wo+No+Can+L_1+V
	720	700	Wo+No+Can+V
	680	380	Wo+Can+NC+V
$Pl_{65}NC_{35}$	950	1	No+L_1+L_2+V
	910	96	No+Wo+L_1+L_2+V
	890	84	Wo+No+L_1+L_2+V
	800	110	Wo+No+Can+L_1+L_2+V
	755	240	Wo+No+Can+L_1+L_2+V
	720	700	Wo+No+Can+NC+V
	690	190	Wo+No+Can+NC+V
$Pl_{60}NC_{40}$	950	1	No+L_1+L_2+V
	910	96	No+L_1+L_2+V
	800	110	No+L_1+L_2+V
	755	240	Wo+No+Can+L_1+L_2+V
	720	700	Wo+No+Can+NC+V
	690	190	Wo+No+Can+NC+V
$Pl_{50}NC_{50}$	950	1	No+L_1+L_2+V
	800	110	No+Can+L_1+L_2+V
	755	240	No+Can+L_1+L_2+V
	720	700	No+Can+NC+V
	690	190	No+Can+NC+V
$Pl_{40}NC_{60}$	950	1	No+L_1+L_2+V
	800	110	No+Can+L_1+L_2+V
	740	240	No+Can+NC+L_1+V
	720	700	No+Can+NC+V

TABLE 3 (continued)

Composition in wt %	Temperature °C	Time in hrs	Interpreted phase assemblage
$Pl_{30}NC_{70}$	950	1	No+L_1+L_2+V
	910	96	No+L_1+L_2+V
	800	110	No+Can+L_1+L_2+V
	720	700	No+Can+NC+L_1+V
$Pl_{20}NC_{80}$	950	1	No+L_2+V
	910	96	No+L_2+V
	740	240	No+NC+V
	720	700	No+NC+V
	690	190	No+Can+NC+V
$Pl_{10}NC_{90}$	950	1	No+L_2+V
	740	240	No+NC+V
	690	190	No+NC+V

and at all temperatures examined. Nepheline and sodium carbonate do not occur together.

The sodalite-group mineral, which we call noselite, occurs at compositions with more than 12 percent Na_2CO_3 in the join $Ab_{80}An_{20}$–Na_2CO_3 and more than 23 percent Na_2CO_3 in the join $Ab_{50}An_{50}$–Na_2CO_3. It converts to cancrinite between 740° and 700°C in the join $Ab_{80}An_{20}$–

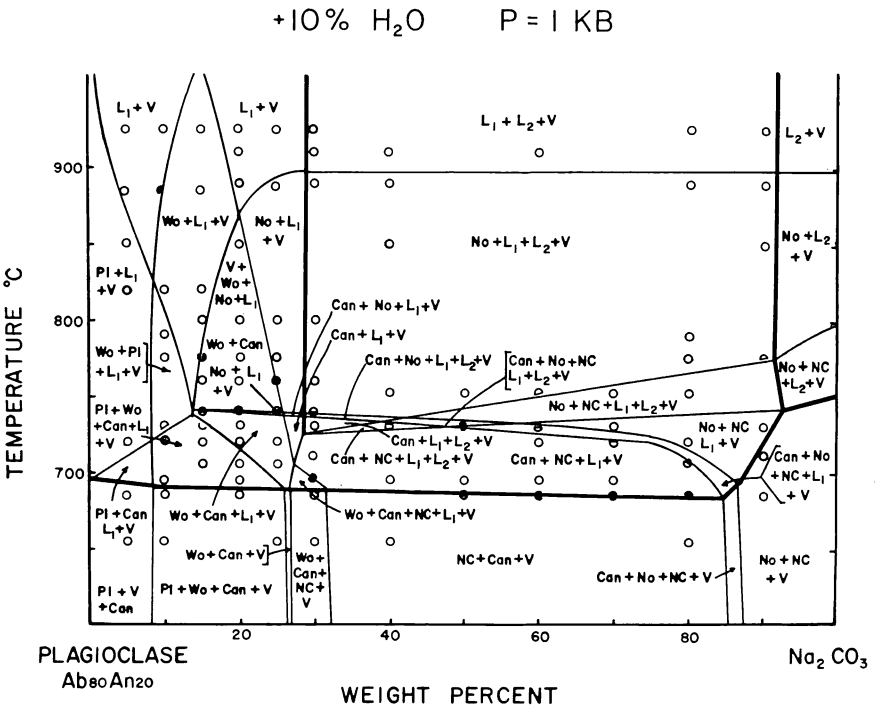

Fig. 4. The join $Ab_{80}An_{20}$–Na_2CO_3 with 10 percent H_2O at 1 kb pressure. The circles indicate the critical runs. For abbreviations see table 1.

Na_2CO_3, while it coexists with cancrinite over almost the full range of the cancrinite stability field in the join $Ab_{50}An_{50}$–Na_2CO_3. Noselite is present at temperatures in excess of 950°C in the join $Ab_{50}An_{50}$–Na_2CO_3, while the upper stability lies at about 900°C in the join $Ab_{80}An_{20}$–Na_2CO_3.

In the join $Ab_{80}An_{20}$–Na_2CO_3 no cancrinite is found above 750°C, but in the join $Ab_{50}An_{50}$–Na_2CO_3 it is stable at temperatures in excess of 800°C.

Both joins contain wollastonite. Its stability range is enhanced in the more CaO-rich join. Wollastonite is present at compositions containing between 8 and 32 percent Na_2CO_3 in the join $Ab_{80}An_{20}$–Na_2CO_3 as compared to compositions containing between 2 and 42 percent Na_2CO_3 in the join $Ab_{50}An_{50}$–Na_2CO_3.

A silicate-rich liquid (L_1) is present over most of the joins. Its composition is highly variable with temperature and composition of the starting material as is indicated by the refractive indices of the glasses representing the quenched liquid L_1. The refractive index (R.I.) of glasses from runs at 925°C are listed in table 4 and shown graphically in figure 6. In the join $Ab_{80}An_{20}$–Na_2CO_3 the refractive index of the glasses increases from 1.501 at the composition $Pl_{95}NC_5$ to 1.517 at the composition

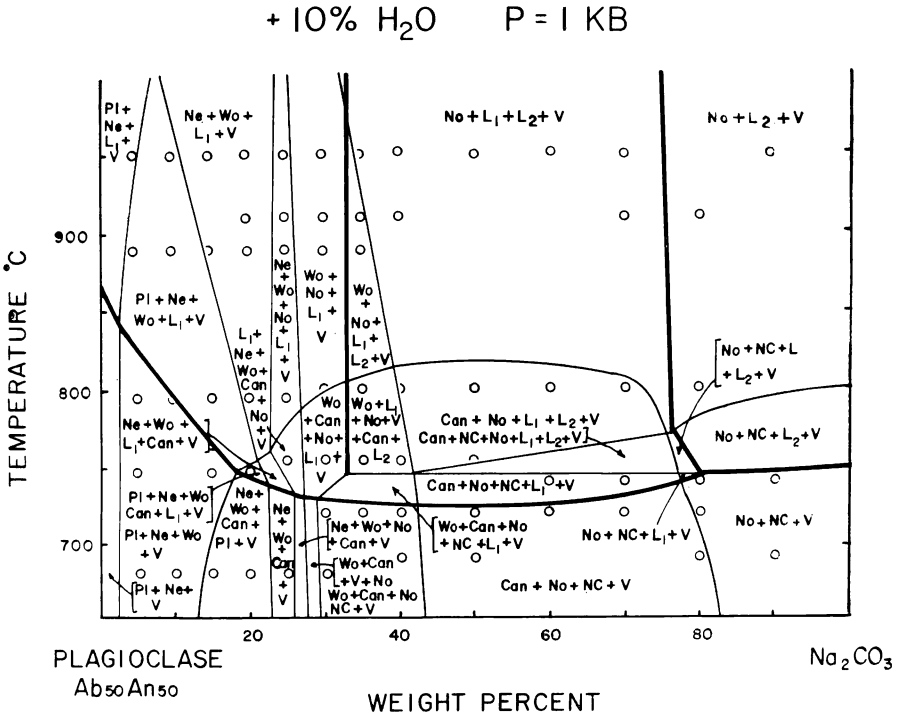

Fig. 5. The join $Ab_{50}An_{50}$–Na_2CO_3 with 10 percent H_2O at 1 kb pressure. The circles represent all runs made in this join. For abbreviations see table 1.

TABLE 4

Refractive index of glasses from runs in the composition joins $Ab_{80}An_{20}$–NC and $Ab_{50}An_{50}$–NC both with 10 percent H_2O present at kb pressure and 925°C, accuracy ± 0.001. The phase assemblage of the runs is given also. For abbreviations see table 1.

Composition	Interpreted phase assemblage	R.I.
The join $Ab_{80}An_{20}$–Na_2CO_3:		
$Pl_{95}NC_5$	L_1+V	1.501
$Pl_{90}NC_{10}$	L_1+V	1.507
$Pl_{85}NC_{15}$	Wo+L_1+V	1.513
$Pl_{80}NC_{20}$	L_1+V	1.516
$Pl_{75}NC_{25}$	L_1+V	1.517
$Pl_{70}NC_{30}$	L_1+L_2+V	1.513
$Pl_{65}NC_{35}$	L_1+L_2+V	1.508
$Pl_{60}NC_{40}$	L_1+L_2+V	1.508
$Pl_{50}NC_{50}$	L_1+L_2+V	1.508
The join $Ab_{50}An_{50}$–Na_2CO_3:		
$Pl_{95}NC_5$	Pl+Ne+L_1+V	1.510
$Pl_{90}NC_{10}$	Pl+Ne+Wo+L_1+V	1.522
$Pl_{85}NC_{15}$	Ne+Wo+L_1+V	1.530
$Pl_{80}NC_{20}$	Ne+Wo+L_1+V	1.535
$Pl_{75}NC_{25}$	Ne+Wo+No+L_1+V	1.537
$Pl_{70}NC_{30}$	Wo+No+L_1+V	1.536
$Pl_{65}NC_{35}$	No+L_1+L_2+V	1.524
$Pl_{60}NC_{40}$	No+L_1+L_2+V	1.502
$Pl_{50}NC_{50}$	No+L_1+L_2+V	1.498

$Pl_{75}NC_{25}$. When the two-liquid field is intersected the refractive index of the glass decreases sharply to 1.508 and remains at this value for mixtures richer in Na_2CO_3. The variation of the refractive index of the glasses is even more pronounced in the join $Ab_{50}An_{50}$–Na_2CO_3, rising from 1.510 at the composition $Pl_{95}NC_5$ to 1.537 at the composition $Pl_{70}NC_{30}$ and decreasing to 1.497 within the two-liquid field.

Primary sodium carbonate occurs in both joins in runs containing more than 25 percent Na_2CO_3. The upper stability limit for sodium carbonate varies between 725° and 800°C.

The fine-grained carbonate material representing the quenched carbonate-rich liquid (L_2) is present at compositions containing minimally 28 percent Na_2CO_3 in the join $Ab_{80}An_{20}$–Na_2CO_3 and 33 percent Na_2CO_3 in the join $Ab_{50}An_{50}$–Na_2CO_3.

In runs with the composition $Pl_{65}NC_{35}$ and $Pl_{60}NC_{40}$ of the join $Ab_{50}An_{50}$–Na_2CO_3, large crystals were found with a refractory index N_o = 1.548. These are probably sodium calcium carbonate crystals, grown during the quench. Their presence indicates that in these runs the carbonate-rich liquid contained more than 30 percent Ca_2CO_3 (Niggli, 1920).

Analytical Data

The quenched silicate-rich liquids (L_1) were analyzed with the electron microprobe. The results are listed in table 5, together with the composition of the starting materials. The analyses are not very satisfactory, even when corrected for both the H_2O content, which is probably between 3 and 5 percent, and the CO_2 content, which is unknown but probably very small.

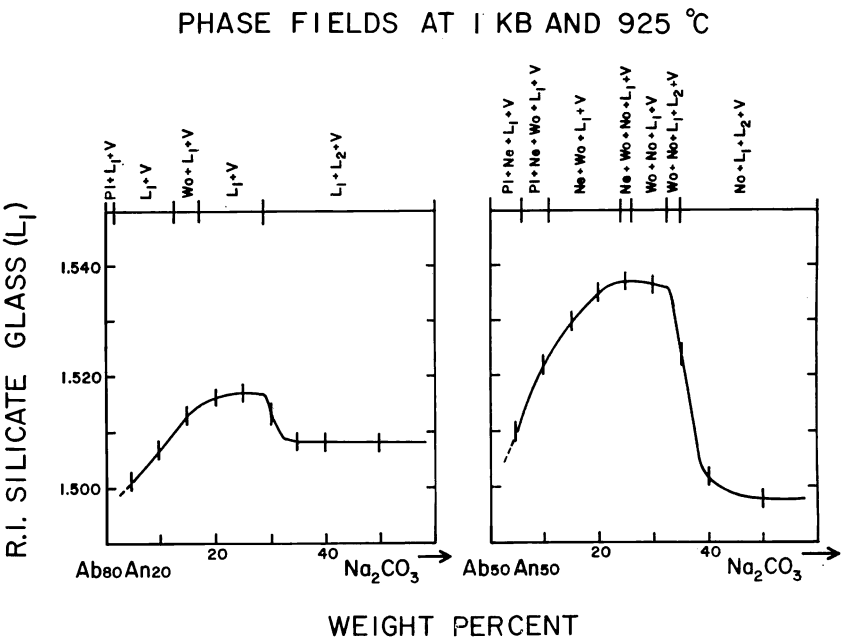

Fig. 6. The refractive indices (R.I.) of the silicate glasses of the joins $Ab_{80}An_{20}$–Na_2CO_3 and $Ab_{50}An_{50}$–Na_2CO_3. The length of the vertical lines indicate the accuracy of the measurements, ± 0.001. The phase fields intersected in these joins are indicated also.

The composition of the silicate-rich liquids varies greatly. They become strongly alkalic and undersaturated in runs rich in Na_2CO_3. The CaO content of the silicate liquid is low in the presence of wollastonite, which is to be expected, and very low when the carbonate-rich liquid is present.

With increasing Na_2CO_3 content, the starting compositions of these joins become peralkaline (mole Na_2O > mole Al_2O_3) at the composition $Pl_{90}NC_{10}$ and $Pl_{80}NC_{20}$ in respectively the join $Ab_{80}An_{20}$–Na_2CO_3 and $Ab_{50}An_{50}$–Na_2CO_3, while the analyses of L_1 indicate that the silicate liquid becomes peralkaline when the two-liquid field is intersected. This indicates that the vapor phase coexisting with the silicate-rich liquid, in absence of the carbonate-rich liquid L_2, is enriched in Na_2O.

The CaO/Na_2O ratio of the quenched carbonate-rich liquid was determined by atomic absorption. The results are listed in table 6, together with the CaO/Na_2O ratio of the starting materials and the silica-rich glasses. These ratios are plotted in figure 7 also: for the starting compositions by a dotted line, for the carbonate-rich liquid L_2 by a dashed line, and for the silicate-rich liquid L_1 by a full line.

The CaO/Na_2O ratios of the quenched carbonate-rich liquids are probably somewhat higher than the analyses indicate, because the solu-

TABLE 5

Electron microprobe analysis of the quenched silicate-rich (L_1) liquid of: (A) the join $Ab_{80}An_{20}$–Na_2CO_3 and (B) the join $Ab_{50}An_{50}$–Na_2CO_3 together with the composition of the starting material (mix).

Sample		CaO	Na_2O	Al_2O_3	SiO_2	CO_2	total
A. The join $Ab_{80}An_{20}$–Na_2CO_3 at 925°C							
$Pl_{95}NC_5$	L_1	2.3	4.3	20.0	64.2	n.d.	88.5
	mix	4.01	11.8	21.92	60.17	2.08	100.0
$Pl_{90}NC_{10}$	L_1	2.7	7.0	18.8	62.6	n.d.	88.4
	mix	3.80	14.26	20.76	57.01	4.16	100.0
$Pl_{85}NC_{15}$	L_1	3.6	6.5	19.1	59.1	n.d.	88.3
	mix	3.59	16.72	19.61	53.84	6.23	100.0
$Pl_{80}NC_{20}$	L_1	3.5	7.1	20.2	60.3	n.d.	91.1
	mix	3.34	19.18	18.46	50.67	8.30	100.0
$Pl_{75}NC_{25}$	L_1	3.6	12.5	18.7	56.2	n.d.	92.0
	mix	3.17	21.63	17.30	47.51	10.38	100.0
$Pl_{70}NC_{30}$	L_1	2.8	21.0	19.9	55.2	n.d.	98.9
	mix	2.96	24.09	16.15	44.34	12.45	100.0
$Pl_{60}NC_{40}$	L_1	1.8	21.0	18.0	56.0	n.d.	96.6
	mix	2.53	29.01	13.84	38.00	16.60	100.0
$Pl_{50}NC_{50}$	L_1	1.4	15.6	19.2	49.3	n.d.	85.5
	mix	2.11	33.92	11.54	31.67	20.76	100.0
$Pl_{40}NC_{60}$	L_1	0.8	21.9	22.5	53.0	n.d.	98.2
	mix	1.69	38.83	9.28	25.34	24.91	100.0
$Pl_{30}NC_{70}$	L_1	0.4	15.5	18.7	47.0	n.d.	81.6
	mix	1.27	43.75	6.92	19.00	29.06	100.0
$Pl_{20}NC_{80}$	L_1	0.0	18.0	27.4	40.0	n.d.	85.4
	mix	0.84	48.67	4.61	12.67	33.20	100.0
$Pl_{10}NC_{90}$	L_1	not enough glass present for analysis					
	mix	0.42	53.58	2.31	6.33	37.36	100.0
B. The join $Ab_{50}An_{50}$–Na_2CO_3 at 950°C							
$Pl_{95}NC_5$	L_1	8.5	6.2	23.3	53.2	n.d.	92.1
	mix	9.85	8.38	26.91	52.77	2.08	100.0
$Pl_{90}NC_{10}$	L_1	6.8	9.1	24.2	52.0	n.d.	92.1
	mix	9.33	11.02	25.50	50.00	4.16	100.0
$Pl_{85}NC_{15}$	L_1	5.7	13.0	24.0	49.5	n.d.	92.2
	mix	8.81	13.65	24.08	47.22	6.23	100.0
$Pl_{80}NC_{20}$	L_1	2.1	15.5	27.3	45.5	n.d.	90.4
	mix	8.30	16.29	22.66	44.44	8.30	100.0
$Pl_{75}NC_{25}$	L_1	2.3	18.9	26.5	44.5	n.d.	92.2
	mix	7.78	18.93	21.25	41.66	10.38	100.0
$Pl_{65}NC_{35}$	L_1	1.0	14.8	26.5	38.0	n.d.	80.3
	mix	6.74	24.20	18.41	36.11	14.53	100.0
$Pl_{60}NC_{40}$	L_1	0.5	19.0	22.6	39.1	n.d.	81.2
	mix	6.22	26.84	17.00	33.33	16.60	100.0
$Pl_{50}NC_{50}$	L_1	0.2	17.7	21.6	39.5	n.d.	79.0
	mix	5.19	32.12	14.17	27.78	20.76	100.0
$Pl_{40}NC_{60}$	L_1	0.2	18.1	23.0	40.5	n.d.	81.8
	mix	4.15	37.40	11.33	22.22	24.91	100.0
$Pl_{30}NC_{70}$	L_1	0.3	14.8	27.8	39.5	n.d.	82.4
	mix	3.11	43.27	8.50	16.66	29.06	100.0
$Pl_{20}NC_{80}$		no glass present					
	mix	2.07	47.94	5.67	11.11	33.20	100.0
$Pl_{10}NC_{90}$		no glass present					
	mix	1.04	53.22	2.83	5.56	37.36	100.0

tions with the dissolved carbonates also contain some or all of the vapor phase enriched with Na_2O, as was discussed earlier.

The analyses of both quenched liquids show that the carbonate-rich liquid is enriched and the silicate-rich liquid impoverished in CaO, as compared with the starting mixtures. The carbonate-rich liquids from the compositions containing 35 and 40 percent Na_2CO_3 of the join $Ab_{50}An_{50}$–Na_2CO_3 are strongly enriched with CaO. The amount of L_2 in these runs is relatively small, which probably accounts for the high concentration of CaO.

DISCUSSION OF THE RESULTS

The results presented in this paper show that the field of liquid immiscibility extends from the join $NaAlSi_3O_8$–Na_2CO_3–H_2O (Koster van Groos and Wyllie, 1968) into the join $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3–H_2O. This is shown in figure 8 for compositions containing 10 percent H_2O. This figure represents a composition join through a very complex six-component system and is not a pseudo-ternary system. The two-liquid field is drawn in such a way that the join $Ab_{35}An_{65}$–Na_2CO_3 would not intersect this field, although no data are available to substantiate this. It is possible that even the bounding join anorthite–Na_2CO_3 intersects the two-liquid field. However, Eitel (1925) does not mention the presence of two liquids in his study of the reciprocal system $CaAl_2Si_2O_8$–$NaAlSiO_4$–Na_2CO_3–$CaCO_3$. He found that cancrinite coexists with a carbonate-rich liquid at high temperatures. The latter would be similar to our results for compositions very rich in Na_2CO_3, which contain the assemblage No + L_2.

TABLE 6

The CaO/Na_2O ratios of the silicate-rich liquid L_1 (determined by electron microprobe), the carbonate-rich liquid L_2 (determined by atomic absorption), and the starting mixtures for: (A) the join $Ab_{80}An_{20}$–Na_2CO_3 and (B) the join $Ab_{50}An_{50}$–Na_2CO_3.

Composition	(A) The join $Ab_{80}An_{20}$–Na_2CO_3			(B) The join $Ab_{50}An_{50}$–Na_2CO_3		
	CaO/Na_2O L_1	CaO/Na_2O L_2	CaO/Na_2O mixture	CaO/Na_2O L_1	CaO/Na_2O L_2	CaO/Na_2O mixture
$Pl_{95}NC_5$	0.53	—	0.34	1.37	—	1.18
$Pl_{90}NC_{10}$	0.39	—	0.27	0.75	—	0.85
$Pl_{85}NC_{10}$	0.55	—	0.21	0.44	—	0.64
$Pl_{80}NC_{20}$	0.49	—	0.18	0.14	—	0.51
$Pl_{75}NC_{20}$	0.29	—	0.15	0.12	—	0.41
$Pl_{70}NC_{25}$	0.13	0.17	0.12	0.21	—	0.34
$Pl_{65}NC_{35}$	—	—	—	0.068	0.81	0.28
$Pl_{60}NC_{40}$	0.086	0.10	0.087	0.026	0.73	0.23
$Pl_{50}NC_{50}$	0.089	0.074	0.062	0.011	0.18	0.16
$Pl_{40}NC_{60}$	0.036	0.051	0.044	0.011	0.13	0.11
$Pl_{30}NC_{70}$	0.025	0.035	0.029	0.020	0.10	0.073
$Pl_{20}NC_{80}$	0.00	0.024	0.017	—	0.064	0.043
$Pl_{10}NC_{90}$	—	0.013	0.008	—	0.032	0.020

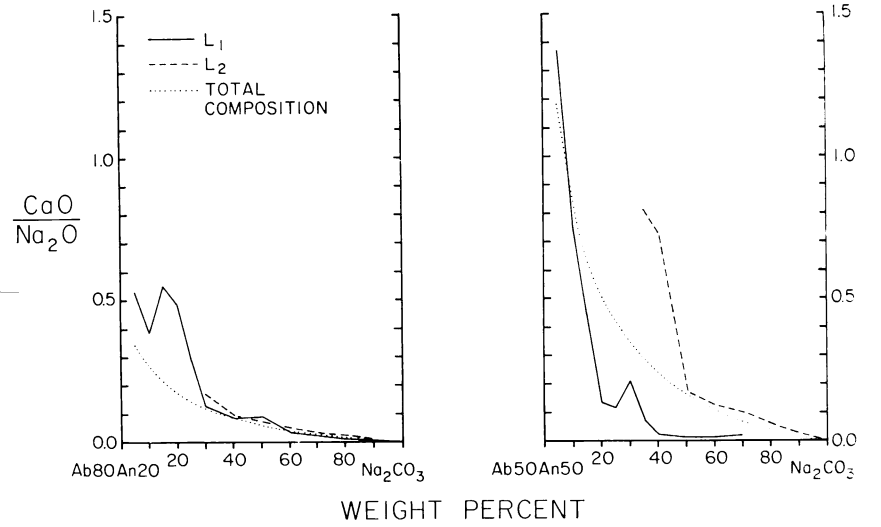

Fig. 7. Graphic representation of the CaO/Na_2O ratio of the silicate-rich liquid (L_1), the carbonate-rich liquid (I_2), and the starting mixtures.

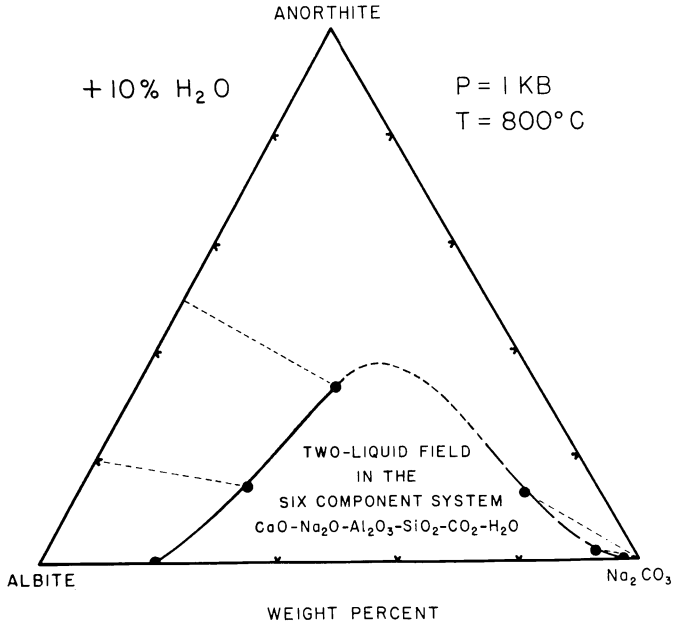

Fig. 8. A schematic diagram showing the extent of the two-liquid field in the join $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3 with 10 percent H_2O present, at 800°C and 1 kb pressure. The dashed lines indicate the position of the joins investigated. The solid circles indicate the positions of the intersections of the two-liquid field with the joins.

In these joins it is possible to understand the occurrence of the various phase assemblages, using inferred reactions between the phases. This is facilitated by considering the plagioclase end-member of a join and discussing the effect of continuously adding Na_2CO_3 at, for example, 850°C. Thus, when Na_2CO_3 is added to the plagioclase $Ab_{80}An_{20}$, a reaction may take place such as

$$Pl_{ss} + Na_2CO_3 \rightleftharpoons Pl_{ss} + L_1 + V \tag{1}$$

while in the join $Ab_{50}An_{50}$–Na_2CO_3 a reaction may occur such as

$$Pl_{ss} + Na_2CO_3 \rightleftharpoons Pl_{ss} + Ne + L_1 + V. \tag{2}$$

Both reactions are probably a combination of

$$\underset{(Pl)}{CaAl_2Si_2O_8} + Na_2CO_3 \rightleftharpoons \underbrace{2NaAlSiO_4 + CaO}_{(L_1)} + \underset{(V)}{CO_2} \tag{3}$$

and

$$\underset{(Pl)}{NaAlSi_3O_8} + Na_2CO_3 \rightleftharpoons \underbrace{NaAlSiO_4 + Na_2O + 2SiO_2}_{(L_1)} + \underset{(V)}{CO_2}. \tag{4}$$

The amount of $NaAlSiO_4$ produced in these reactions apparently immediately saturates the silicate liquid of the join $Ab_{50}An_{50}$–Na_2CO_3 with it, for nepheline (Ne) becomes a stable phase.

A continuous increase of Na_2CO_3 produces enough CaO and SiO_2 in the liquid L_1 (reactions 3, 4) to form wollastonite.

$$\underbrace{CaO + SiO_2}_{(L_1)} \rightleftharpoons \underset{(Wo)}{CaSiO_3}. \tag{5}$$

This is substantiated by the decrease of the CaO content of the silicate liquid, see table 5. When all plagioclase has reacted, additional Na_2CO_3 may react with the liquid

$$\underset{(L_1)}{3NaAlSiO_4} + Na_2CO_3 \rightleftharpoons \underset{(No)}{3NaAlSiO_4 \cdot Na_2CO_3}. \tag{6}$$

This reaction is similar to

$$\underset{(Ne)}{3NaAlSiO_4} + Na_2CO_3 \rightleftharpoons \underset{(No)}{3NaAlSiO_4 \cdot Na_2CO_3}. \tag{7}$$

These series of reactions explain why plagioclase and nepheline are not found together with sodium carbonate. The silicate liquid is probably continuously enriched in sodium following a reaction such as

$$Na_2CO_3 \rightleftharpoons \underset{(L_1)}{Na_2O} + \underset{(V)}{CO_2}. \tag{8}$$

This sodium-enriched silicate liquid is capable of dissolving wollastonite, reversing reaction (5).

When the CO_2 pressure in the vapor phase becomes high enough, reaction (8) ceases, and Na_2CO_3 forms the second liquid L_2.

The CO_2 pressure in the vapor phase is apparently high enough to cause the reaction

$$\underset{(L_1)}{CaO} + \underset{(V)}{CO_2} \rightleftharpoons \underset{(L_2)}{CaCO_3}. \qquad (9)$$

The analyses (table 6) show that this reaction is very effective in the join $Ab_{50}An_{50}$–Na_2CO_3.

Almost all these reactions involve CO_2 which goes into the vapor phase. These reactions, therefore, will be strongly pressure dependent. It would seem likely that an increase in pressure will increase the compositional range of the two-liquid field by stabilizing Na_2CO_3, see reaction (8), and favor the fractionation of CaO toward the carbonate liquid L_2 through reaction (9).

Following the phase rule $F = C - P + 2$, a six-component system is isobaric invariant when seven phases coexist. In this study we encountered only one seven-phase assemblage. It lies in the join $Ab_{50}An_{50}$–Na_2CO_3 between the compositions $Pl_{67}NC_{33}$ and $Pl_{58}NC_{42}$ at 740°C ± 15°C. The reaction intersected here is interpreted to be

$$Wo + No + Can + NC + L_1 + V \rightleftharpoons L_2. \qquad (10)$$

The compositions of all phases are defined in this assemblage at the selected pressure of 1 kb.

Several six-phase assemblages are intersected by these joins. In the join $Ab_{80}An_{20}$–Na_2CO_3 only one six-phase assemblage, Can + No + NC + L_1 + L_2 + V, is intersected between the compositions $Pl_{60}NC_{40}$ at approximately 740°C. A series of six-phase assemblages is encountered at about the same temperature in the join $Ab_{50}An_{50}$–Na_2CO_3.

All other phase fields intersected by these joins contain five, four, or three phases. The compositions of the various phases in these fields are not necessarily constant. The analytical data of the two coexisting liquids clearly illustrate this (fig. 7).

It is possible that the composition of one phase varies little, while the composition of the other phases shows a great deal of variation. For example, the carbonate-rich liquids from the samples $Pl_{60}NC_{40}$ of the join $Ab_{80}An_{20}$–Na_2CO_3 and $Pl_{30}NC_{70}$ of the join $Ab_{50}An_{50}$–Na_2CO_3 have the same CaO/Na_2O ratio, 0.10, indicating a very similar composition. The coexisting silicate-rich liquids have, however, entirely different compositions (table 5).

This study shows that the carbonate-rich liquid is strongly enriched in CaO. This is particularly evident in samples in which the quantity of the carbonate-rich liquid is small. In the sample $Pl_{70}NC_{30}$ of the join $Ab_{80}An_{20}$–Na_2CO_3 the CaO/Na_2O ratio is 0.17, indicating that the liquid has a composition with 15 percent $CaCO_3$, 85 percent Na_2CO_3. In the join $Ab_{50}An_{50}$–Na_2CO_3 the carbonate-rich liquids are even more enriched in CaO, as is shown in figure 7. Here a run with the composition $Pl_{65}NC_{35}$

contains a carbonate-rich liquid with the composition 46 percent $CaCO_3$, 54 percent Na_2CO_3. The latter result was indicated by the presence of sodium calcium carbonate crystals in the quenched carbonate-rich liquid.

The peralkaline nature of the silicate-rich liquid coexisting with the carbonate liquid is very interesting. The only exception is the liquid L_1 from the sample $Pl_{65}NC_{35}$ of the join $Ab_{50}An_{50}$–Na_2CO_3. However, considering the difficulties in obtaining good sodium analyses with the electron microprobe for these glasses, it is possible that this liquid may be peralkaline also.

The peralkaline nature of these silicate liquids is illustrated by the C.I.P.W. norm of the following two examples. The quenched silicate-rich liquid of sample $Pl_{70}NC_{30}$ of the join $Ab_{80}An_{20}$–Na_2CO_3 is: Ab = 45.0, Ne = 31.5, Ns = 17.7, Cs = 5.8; the norm of the quenched liquid L_1 of the sample $Pl_{60}NC_{40}$ of the join $Ab_{50}An_{50}$–Na_2CO_3 is: Ab = 19.8, Ne = 66.5, Ns = 12.6, and Cs = 1.1.

These norms illustrate that an increase in the vapor pressure may increase the amount of CaO in the carbonate-rich liquid by further reversing reaction (9).

The path of crystallization of the liquids is difficult to determine because the liquids do not lie within the composition joins and because the composition of the liquids changes continuously, precipitating crystalline phases of unknown composition. It is possible to make some general remarks on the path of crystallization, if we start with liquids of known composition. For example, assume that a phase assemblage with the composition $Pl_{60}NC_{40}$ from the join $Ab_{50}An_{50}$–Na_2CO_3 is cooled from 950°C. Furthermore, let us assume that the liquids are saturated with an aqueous vapor phase at 1 kb pressure. Thirdly, we will only consider the case in which the two liquids become effectively separated, preventing reaction between them.

The carbonate liquid has a composition of $CaCO_3$ = 43.3 percent, Na_2CO_3 = 56.7 percent, if the silicate content is neglected. The solubility of H_2O is probably in the order of 20 percent (Koster van Groos and Wyllie, 1968). Upon cooling, sodium carbonate and sodium calcium carbonate will crystallize, and a vapor phase will form. The solubility of Na_2CO_3 in the vapor phase increases during the cooling, while $CaCO_3$ remains rather insoluble (Koster van Groos and Wyllie, 1968; Wyllie and Tuttle, 1960). The crystalline phases will then become further enriched with $CaCO_3$.

The composition of the silicate-rich liquid (table 5) coexisting with the previously discussed carbonate liquid is, expressed in the C.I.P.W. norm, Ab = 19.8, Ne = 66.5, Cs = 1.1, Ns = 12.6. The H_2O content of this liquid is probably between 3 and 5 percent. The amount of CO_2 in the liquid is assumed to be small. During cooling nepheline will form, together with noselite or cancrinite, if some carbonate was dissolved in the liquid. With further cooling wollastonite and albite will precipitate, enriching the liquid in Na_2O and SiO_2. Because an H_2O-rich vapor phase and sodium metasilicate are very soluble in each other (Morey and

Hesselgesser, 1952) forming a low temperature phase assemblage L + V, it would seem likely that the liquid phase in question would persist to low temperatures and become very rich in Na_2SiO_3. The vapor phase at low temperatures is composed mainly of H_2O and CO_2 but enriched in Na_2CO_3 and Na_2SiO_3.

In conclusion, the experimental results of this study show that three fluid phases can coexist in the join $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–Na_2CO_3 with 10 percent H_2O present at 1 kb pressure. These phases are:

1. A silicate-rich liquid which is peralkaline and strongly undersaturated with SiO_2. The liquid has a low CaO content.
2. A carbonate-rich liquid containing appreciable amounts of Na_2CO_3 and strongly enriched in CaO compared to the silicate-rich liquid.
3. A vapor phase composed of H_2O and CO_2 and strongly enriched in Na_2O and, to a lesser extent, in SiO_2.

PETROLOGICAL APPLICATIONS

The petrology of alkalic-rock carbonatite complexes is very complicated. The specific rock types, mineralogy, and chemistry vary from location to location. Nevertheless, the main features of these complexes are fairly constant. The carbonatite, which may contain calcite, dolomite, ankerite, and a small amount of a variety of alkali-rich minerals, is associated with silicate-rich rocks like fenites, nepheline syenites, and strongly undersaturated rocks such as the urtite-ijolite-melteigite series, composed mainly of nepheline and pyroxene, the latter ranging from diopside to aegerine diopside. Heinrich (1966, p. 45) observed that . . . "If any particular group of rocks may be especially characteristic of the carbonatite ring complexes, the urtite-ijolite-melteigite series certainly qualifies. . . .".

The results presented in this paper are on a small part of the system CaO–Na_2O–Al_2O_3–SiO_2–CO_2–H_2O. The composition of the magmas involved in the genesis of carbonatites and the associated alkalic rocks is much more complex, containing in addition MgO, FeO, Fe_2O_3, K_2O, and others.

The stability of the carbonates $CaCO_3$, $MgCO_3$, and $FeCO_3$ is strongly pressure dependent at elevated temperatures (Harker and Tuttle, 1955; French, 1971). Of these carbonates $CaCO_3$ is the most stable, and $FeCO_3$ the least.

According to our discussion an increase of CO_2 pressure favors the presence of CaO in a carbonate-rich liquid, coexisting with a silicate-rich liquid. It is to be expected that this is also valid for MgO and FeO, but to a lesser degree. Thus, if a significant amount of CaO is present in the silicate liquid coexisting with a carbonate-rich liquid, then it would be reasonable to expect that the carbonate liquid would be poor in MgO and FeO. The presence of MgO and FeO in the alkalic silicate liquid would stabilize a diopsidic pyroxene or aegirine rather than wollastonite. Only at much higher CO_2 pressures would dolomite and ankerite become stable in the carbonate liquid.

The three fluid phases recognized in this experimental study seem to correlate well with the naturally occurring rock assemblages, the silicate-rich liquid with the alkalic nepheline syenites and especially with the urtite-melteigite series, the carbonate-liquid with the carbonatites, and the Na_2O and SiO_2 enriched vapor phase with the fenitizing agents accompanying the emplacements of these rocks. The low SiO_2 content of the carbonatite magma and the alkalic nature of the associated rocks are very satisfactorily explained.

We conclude that the formation of carbonatite-alkalic rock complexes can be explained by the thesis that at high pressures, deep in the Earth's crust and especially in the mantle, concentration of CO_2 may occur. The presence of CO_2 in the mantle is certainly established by the occurrence of CO_2-rich inclusions in olivine-bearing nodules (Roedder, 1965) and by the high carbonate content of kimberlites. To concentrate CO_2 in the mantle by diffusion is very unlikely. Therefore, we assume that this concentration takes place by rising of CO_2-rich vapor bubbles in a magmatic environment. These vapor bubbles will probably contain some H_2O and readily dissolve alkali and some CaO (Iijama, 1961). Thus, it seems possible that higher levels can become enriched with CO_2 and alkali and CaO. Possibly a carbonate-rich liquid phase could separate at this stage, dissolving some MgO and FeO.

The presence of carbonate-rich globules in melilite-rich basalt and kimberlite (von Eckermann, 1961) and in sills and dikes with an ultrabasic character (Ferguson and Currie, 1971) illustrate the feasibility of this process.

A subsequent reaction of this carbonate-rich melt and the vapor phase with silicates and melts at higher levels in the mantle could form the undersaturated rock series associated with carbonatite complexes.

The high concentration of volatiles in carbonate-rich liquids, due to the inherent presence of CO_2 and the high solubility of H_2O, is illustrated by the explosive features of many carbonatite complexes (von Eckermann, 1948).

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REFERENCES

Dawson, J. B., 1962, Sodium carbonate lavas from Oldoinyo Lengai, Tanganyika: Nature, v. 195, p. 1075-1076.

Eckermann, Harry 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.

Edgar, A. D., 1964, Studies on cancrinites: II. Stability fields and cell dimensions of calcium and potassium-rich cancrinites: Canadian Mineralogist, v. 8, p. 53-67.

Edgar, A. D., and Burley, B. J., 1963, Studies on cancrinites: I. Polymorphism in sodium carbonate rich cancrinite-natrodavyne: Canadian Mineralogist, v. 7, p. 613-642.

Eitel, W. H. J., 1925, Über die Synthese der Feldspatvertreter: Leipzig, Akad. Verlagsges., 258 p.

———— 1954, The physical chemistry of the silicates: Chicago, Chicago Univ. Press, 1592 p.

Ferguson, I., and Currie, K. L., 1971, Evidence of liquid immiscibility in alkaline ultrabasic dikes at Callander Bay, Ontario: Jour. Petrology, v. 12, p. 566-574.

Franz, G. W., and Wyllie, P. J., 1967, Experimental studies in the system CaO–MgO–SiO_2–CO_2–H_2O, *in* Wyllie, P. J., ed., Ultramafic and related rocks: New York, John Wiley & Sons, p. 323-326.

French, B. M., 1971, Stability relations of siderite ($FeCO_3$) in the system iron–carbon–oxygen: Am. Jour. Sci., v. 271, p. 37-78.

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

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

Iiyama, J. T., 1961, Étude préliminaire de la solubilité du basalte dans l'eau à haute température: Soc. franç. minéralogie Bull., v. 84, p. 128-130.

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.

———— 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.

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

Morey, G. W., and Hesselgesser, J. M., 1952, The system H_2O–Na_2O–SiO_2 at 400°C: Am. Jour. Sci., Bowen v., p. 343-371.

Niggli, P., 1920, Die leichtfluchtigen Bestandteile im Magma: Leipzig, B. G. Teubner Verlag, 272 p.

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

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

Watkinson, D. H., and Wyllie, P. J., 1965, Phase relationships in the join $NaAlSiO_4$–$CaCO_3$–(25%)H_2O and the origin of some carbonatite-alkalic rock complexes: Canadian Mineralogist, v. 8, p. 402-403.

———— 1969, Phase equilibrium 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 carbonatites complexes: Jour. Petrology, v. 12, p. 357-378.

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