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Contributions to Mineralogy and Petrology

Peralkaline nephelinites

II. Low pressure fractionation and the hypersodic lavas of Oldoinyo L'engai

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Abstract. Two fractionation trends in sodic alkaline ultramafic liquids have been predicted from experiments in subsystems of the join Di-Ak-Ne-Lc-Qz. The products of these trends are equated with contrasting suites of peralkaline nephelinites from two nephelinite-carbonatite volcanos of the south Gregory Rift, Shombole (southern Kenya) and Oldoinyo L'engai (northern Tanzania). In both trends, peralkalinity is interpreted to result from fractional crystallization of aluminous clinopyroxene. The "Shombole trend" has olivine nephelinite as its parental magma, and the differentiation products are mildly peralkaline [$(Na+K)/Al \approx 1.15$] nephelinites. It is the most common lineage observed in nephelinite-carbonatite centres. The "Oldoinyo L'engai trend" has melilitite or olivine-melilite nephelinite as its parental magma, and produces extremely peralkaline [$(Na+K)/Al = 1.4–2.3$] wollastonite- and combeite- ($Na_2Ca_2Si_3O_9$) bearing nephelinites. The presence of a reaction relation between wollastonite and liquid to produce combeite, indicated by corroded wollastonite phenocrysts armoured by combeite in some nephelinites from Oldoinyo L'engai, is confirmed by melting experiments. Combeite nephelinites from Oldoinyo L'engai were erupted simultaneously with natrocarbonatite ash, and are very similar in composition to silicate liquids that have been shown by experiment to be immiscible with natrocarbonatite. Because the L'engai trend is rarely expressed at extrusive centres (combeite has been recorded at only three localities), and combeite nephelinites are highly evolved magmas, it is unlikely that natrocarbonatite is primary to other carbonatite types. It is proposed that carbonatite liquid is exsolved at crustal pressures from a wide range of nephelinitic liquids: Mg-rich carbonatite from primitive, olivine-bearing alkaline ultramafic liquids, Ca-rich carbonatite from olivine-free nephelinites of low peralkalinity, and natrocarbonatite from strongly peralkaline combeite nephelinites.

Introduction

Silica-undersaturated alkaline magmas present unique petrogenetic problems due to the effects of physical processes that are rare or inefficient in basaltic magmas. These processes include extreme metasomatic enrichment of the source region, liquid immiscibility, and considerable subsolidus adjustment of the composition of intrusive rocks by reaction with fenitizing fluids. Crystal fractionation may produce unusual compositional trends due to the presence of phenocryst minerals such as perovskite and melanite.

Many nephelinites and their intrusive equivalents (ijolites) from carbonatite-bearing complexes are peralkaline (e.g., Barth and Ramberg 1966; Bailey and Schairer 1966). Peralkalinity in igneous rocks has been attributed to subsolidus reaction with metasomatic fluids (Taylor et al. 1980), an alkali-enriched source region (Bailey 1978), contamination by saline chemical sediments or brines (Schneiderhöhn 1948, in Wimmenauer 1966; Currie et al. 1986) and crystal fractionation (Nash et al. 1969; MacDonald 1974). Major element trends in alkali basalts, which can produce peralkaline derivatives (e.g., Baker et al. 1977), have been attributed to crystallization along cotectics that have been experimentally reproduced (Sack et al. 1987), but the phase equilibria of nephelinitic liquids are less well understood. Experiments with peralkaline undersaturated rocks have been performed by Piotrowski and Edgar (1970) and Sood and Edgar (1970), but primarily for the purpose of measuring the crystallization intervals of various alkaline rock types. Relevant synthetic systems have been studied by Schairer and Yoder (1960: the system Di-Ne-Ab), Onuma and Yagi (1967: Di-Ne-Ak), Platt and Edgar (1972: Di-Ne-Or), Gupta et al. (1973: Di-Ne-Ak-Lc), and Onuma and Yamamoto (1976: Di-Ne-Ak-Qz).

This paper, the second of two on evolved alkaline ultramafic rocks from Shombole and Oldoinyo L'engai, East Africa (Fig. 1), examines the origin and evolution of peralkaline nephelinites utilizing data given by Peterson (1989) (hereafter referred to as Part I). In Part I, it was shown that the nephelinites of Shombole and Oldoinyo L'engai contrast strongly in their alkali contents and mineralogy, although the physical processes in both centres must have been similar, as evidenced by similarities in phenocryst zoning profiles and in eruptive style. Both centres are dominated by evolved, Mg-poor nephelinites and phonolites; carbonatite also occurs at both centres. At Oldoinyo L'engai, the carbonatite (natrocarbonatite lava) and many of the silicate lavas have unusually high Na_2O+K_2O (35% and 18% respectively), whereas the nephelinites of Shombole are less alkaline (averaging 12% Na_2O+K_2O) and the carbonatites, which are mainly dikes of melanite sövite, are calcic. Shombole-type nephelinites are common in East African alkaline centres, but strongly alkaline L'engai-type nephelinites are very rare.

As noted in Part I, there has been little detailed petrological study of the silicate lavas of carbonatite-bearing extru-

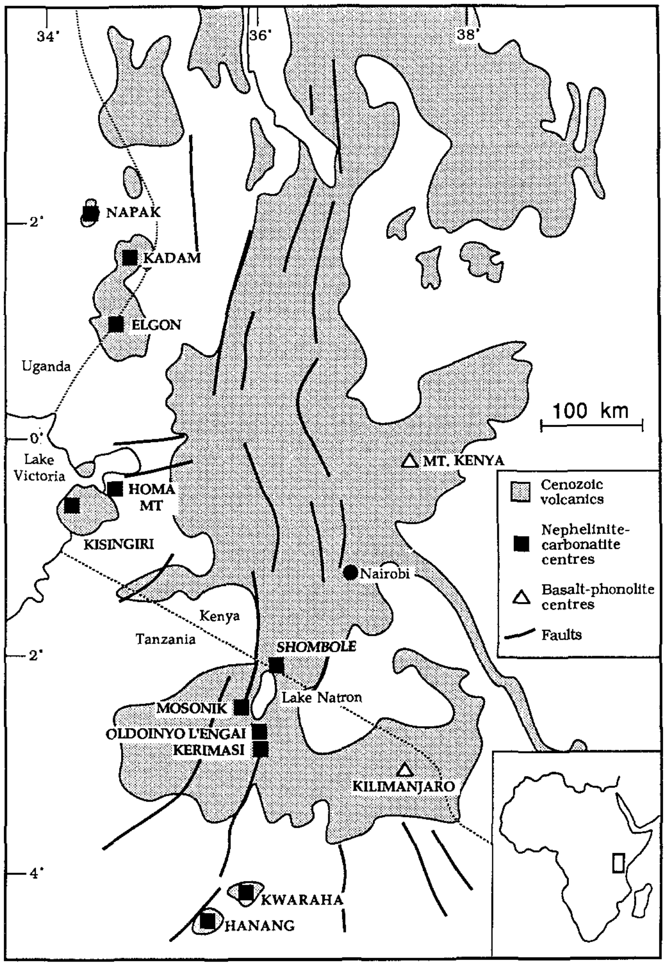


Fig. 1. Locations of major Cenozoic nephelinite-carbonatite eruptive centres of the East African Rift. Geology from Baker et al. (1972) and Cahen and Snelling (1984)

sive alkaline centres, and it is the thesis of this paper that two differentiation trends occur, which were first postulated by Onuma and Yamamoto (1976). In the first ("Shombole trend"), low-Mg ($<3\%$ MgO) moderately peralkaline nephelinites [$(Na+K)/Al \approx 1.15$] are produced by fractionation of olivine and aluminous clinopyroxene from olivine nephelinites, and peralkalinity remains approximately constant after nepheline and sodic clinopyroxene begin to crystallize. In the second ("Oldoinyo L'engai trend"), the parental liquids are melilite-bearing nephelinites that yield strongly peralkaline liquids [$(Na+K)/Al \geq 1.4$], which increase in peralkalinity as differentiation proceeds, producing rocks of extreme composition and unusual mineralogy. The degree of peralkalinity of nephelinites, among other factors such as Mg content and pressure, influences the possible composition of carbonatites derived from them by liquid immiscibility.

The nomenclature of alkaline ultramafic rocks has not been fully systematized. The terminology used here is similar to that of Le Bas (1977, page 34). 'Nephelinite' is a lava with clinopyroxene and nepheline on the liquidus, that commonly contains accessory minerals such as perovskite, melanite, and sphene. With increasing SiO_2 content of the liquid and the appearance of sanidine, nephelinites grade into phonolitic nephelinites and phonolites. Melanephelinite is a variety of nephelinite with colour index > 50. Nephelinites characterized by the presence of particular phenocryst phases in addition to clinopyroxene and nepheline are qualified by mineral names (e.g., melilite nephelinites, wollastonite nephelinites). The terms olivine nephelinite and olivine-melilite nephelinite imply the presence of nepheline phenocrysts, but many Mg-rich rocks of this association are erupted at temperatures above the nepheline liquidus, which occurs at about 1050°–1100° C, and therefore lack nepheline phenocrysts; some melanephelinites also lack nepheline. Melilitites contain phenocrysts of melilite and clinopyroxene. The complete association, including carbonatites, will be referred to as alkaline ultramafic rocks. These will be considered distinct from other alkaline and ultramafic, but potassic lavas such as ugandites.

Phase equilibria of primitive alkaline ultramafic liquids

Peralkaline nephelinites, which are the dominant lavas in small nephelinite-carbonatite centres such as Shombole and Oldoinyo L'engai, have strongly depleted compatible element compositions and are enriched in Zr, F, and Cl, indicating they represent fractionated magmas (Part I). Olivine and olivine-melilite nephelinites, although volumetrically subordinate, are present at most centres of this type (e.g., Kisingiri, Kenya: Le Bas 1977; Mount Elgon, Uganda: King 1965; Kwaraha, Tanzania: Gerasimovsky et al. 1972). Intrusive equivalents of these lavas, and related cumulates, are similarly less common than ijolites, but appear in some complexes (e.g., peridotite at Jacupiranga: Melcher 1966; uncompahgrite at Iron Hill: Nash 1972). Olivine nephelinites were probably erupted at the same time as the Shombole lavas from fissures and small cones near the western (Nguruman) escarpment of the Gregory Rift 30 km north of Shombole (the Loisiumurto volcanics: Crossley 1979). Several writers have concluded that olivine and/or olivine-melilite nephelinite is the parental magma of alkaline ultramafic complexes (e.g., Fen, Norway: Mitchell and Brunfelt 1975; the Kaiserstuhl, Rhine Graben:Wimmenauer 1966).

Crystallization of synthetic alkaline ultramafic systems

Any discussion of the crystallization of natural alkaline ultramafic liquids is hampered by the lack of experimental investigations of phase equilibria at pressures corresponding to the lower continental crust (about 5–10 kbar). This is, presumably, where considerable fractionation of mafic magmas occurs in the continental rift environment. Virtually all carbonatites are found in continental rifts or grabens (e.g., Woolley 1987). Experimental work has been done utilizing model mantle compositions, and mafic alkaline lavas, that shows that primitive alkaline ultramafic liquids can be produced by small ($\leq 5\%$) degrees of partial melting of peridotite or pyrolite. Their production is favoured by high volatile content, high CO_2/H_2O, and high pressure (Wallace and Green 1988; Olafsson and Eggler 1983; Brey 1978; Brey and Green 1977). The phase relationships in peridotite-CO_2-H_2O at mantle pressures near the solidus are reasonably well-understood (Olafsson and Eggler 1983; Eggler 1978, 1987; Wyllie 1977, 1978, 1987). This paper is primarily concerned with the production of highly evolved peralkaline nephelinites, however, so low-pressure data are likely to be more appropriate. For example, the experimental results of Baker and Wyllie (1988) show that, at 25 kbar and 1200° C, the 2-liquid (silicate +

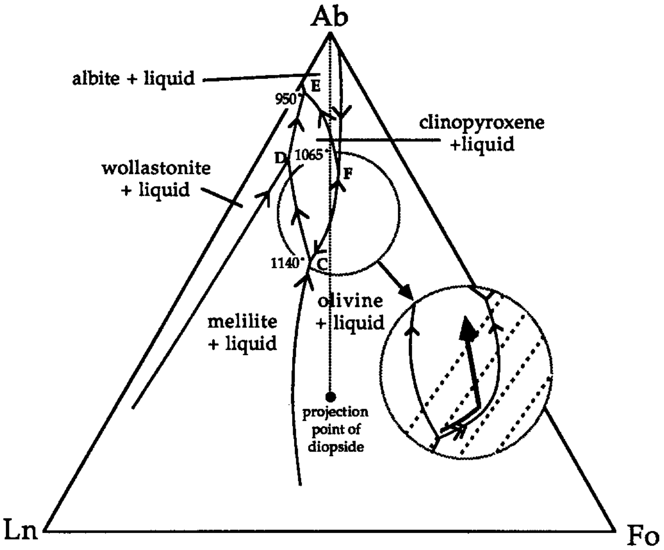


Fig. 2. Schematic projection of cotectics of alkaline ultramafic liquids onto the plane Ab-Ln-Fo (after Yoder 1979). Nepheline may be present in addition to the phase indicated for each liquidus field. The *inset* shows the cotectics which appear if C is a distributary reaction point, superimposed on lines of constant Fo content, and also one possible fractionation path leading to nephelinites (*heavy line*). The reaction relation between olivine and liquid to produce clinopyroxene in alkaline ultramafic liquids implies that the olivine-cpx cotectic must move towards the Fo apex with decreasing temperature for part of its length, as has been indicated. See text for discussion

carbonate) field for nephelinite-carbonatite joins is small relative to that at 5–7 kbar (Kjarsgaard and Hamilton 1988) and exists only for extremely sodic bulk compositions. Hence, any nephelinite which demonstrably contains immiscible calcic carbonatite, as do some Shombole nephelinites (Part 1) presumably equilibrated at relatively low pressure. Kjarsgaard and Hamilton (1989) have shown that exsolution of calcic carbonatite from moderately peralkaline nephelinites occurs in the pressure range of 2–6 kbars. The upper and lower limits to this range have not been defined.

A comprehensive experimental investigation of the phase equilibria of natural alkaline ultramafic liquids at one bar has not been performed, but inferences concerning important crystal-liquid relationships can be made from the results of experiments in related synthetic systems. A reaction between olivine and liquid to produce clinopyroxene occurs in the system Ne-Di-Qz (Schairer and Yoder 1960) and in Ne-Di-Sa (Platt and Edgar 1972), which suggests the sequence olivine nephelinite→nephelinite. Olivine reacts with liquid to produce clinopyroxene and melilite in the system Ne-Di-Ak (Onuma and Yagi 1967), which led these authors to suggest the evolutionary trend: olivine melilitite→olivine-melilite nephelinite→melilite nephelinite. Platt and Edgar (1972) suggested that melilite nephelinites further fractionate to produce wollastonite nephelinites by a melilite-liquid reaction that occurs as the liquid becomes enriched in SiO_2. The system Ne-Di-Ak-Qz (Onuma and Yamamoto 1976) displays all of these relations, and clearly shows the possibility of two trends in alkaline ultramafic liquids, indicated by the presence or absence of melilite. The trends diverge at a low-variance point where liquid coexists with olivine, melilite, clinopyroxene, and occasionally nepheline.

Yoder (1979) has combined the results of these and other experiments that offer insight into the crystallization paths of alkaline ultramafic liquids. His figure 13-4, a schematic projection of liquidus surfaces from Ne onto the plane Ab-Ln-Fo, is adapted here as Fig. 2. Because not all of the liquids will be saturated with nepheline, some crystallization paths are not represented in this diagram, but the nature of the two differentiation trends is well displayed. The nephelinite/melanephelinite field (clinopyroxene + liquid) is bounded by cotectics adjoining the liquidus fields of olivine, melilite, wollastonite, and feldspar.

Liquids saturated with melilite and olivine (± nepheline) may move along the melilite-olivine cotectic until the point C (Fig. 2) is reached, where clinopyroxene begins to crystallize. The nature of this point is in doubt. Yoder presumes that a thermal divide exists where the Ab-Di join intersects the olivine-clinopyroxene cotectic to the right of C, and that C is a reaction point where liquid dissolves previously crystallized olivine and subsequently moves away along the melilite-clinopyroxene cotectic. He notes, however, that the experimental uncertainty in the determination of the temperature of point C (1140° ± 5° C) and the presumed thermal maximum on the olivine-clinopyroxene cotectic (1138° ± 3° C) does not preclude the possibility that point C is a distributary reaction point (inset to Fig. 2). Liquids obtained from olivine-melilite nephelinites could then move along either side of the nephelinite field, depending on the relative amounts of olivine and melilite available for reaction. The nature of point C may well depend on the presence of additional components in the liquid, on solid solution in the phenocryst phases, and on the pressure.

Liquids crystallizing along the olivine-clinopyroxene cotectic (olivine nephelinites) will enter the nephelinite field via an olivine-liquid reaction, which will be hastened by fractionation of olivine. Note that this relationship requires the cotectic to move towards the Fo apex (regardless of the nature of point C), as has been indicated in the inset to Fig. 2. Liquids on the melilite-clinopyroxene cotectic (melilite nephelinites) could eventually reach the point D where a reaction to eliminate melilite and produce wollastonite occurs. These magmas in general will be rich in normative larnite, which is evidenced as modal melilite and CaTs-rich clinopyroxene.

Compositional trends in natural alkaline ultramafic liquids

In Fig. 3, the compositions of natural alkaline ultramafic lavas have been projected from Ne onto the plane Ab-Ln-Fo. The method of projection is described in the Appendix. The data base includes both oceanic and continental alkaline ultramafic rocks, the latter dominating the data for nephelinites; approximately $^2/_3$ of the analyses in the nephelinite field are from Shombole (Part I; see figure caption for additional references). Note that, since many authors do not publish petrographic descriptions with chemical analyses, the phenocryst populations of many lavas included in the melilitite field are uncertain and the term melilitite is necessarily used in a general sense in the following discussion. Many of the lavas placed in the melilitite field will be olivine melilitites and some others will be melilite nephelinites.

The olivine nephelinites occupy a restricted field largely overlapping the nephelinite field and together they form an array pointing away from the Fo apex, consistent with

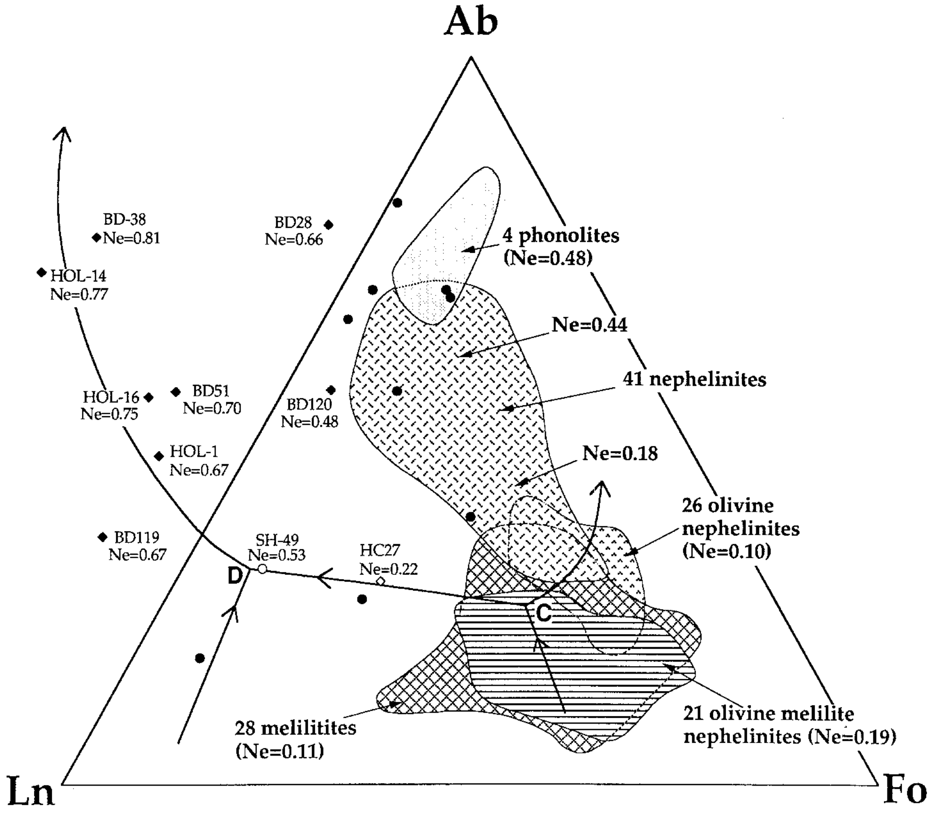


Fig. 3. Projection of the compositions of alkaline ultramafic lavas onto the plane Ab-Ln-Fo. The mean values of *ne* in the tetrahedron Ne-Ab-Ln-Fo are indicated for each field, with nephelinites divided into two populations (low and high *ab*+*ne*). See the text for a description of the individual points plotted in this figure. The data used to define the *shaded fields* are from Alibert et al. (1983), Bailey (1974), Clague and Frey (1982), King and Sutherland (1966), LeBas (1977, 1987), Mitchell and Platt (1983), Strong (1972), Wilkinson and Stolz (1983), and Wimmenauer (1966). No distinction has been made between nepheline-free or nepheline-bearing lavas, since the presence or absence of nepheline is rarely indicated in the data. The melilitite field also contains melilite nephelinites and olivine melilitites, which cannot be distinguished due to incomplete petrographic descriptions. The interpreted locations of critical cotectics have been indicated (c.f. Fig. 2)

a relationship primarily determined by olivine fractionation. The average *ne* value for these fields increases toward phonolites, suggesting that fractionation carries magma compositions toward the Ne apex, ending near $Ne_{50}Ab_{50}$.

Although the melilitite field in part shares the overlap between nephelinite and olivine nephelinite, in fact only 14% of all melilitites have *ab* values as high as the low end of the nephelinite field. In contrast, 57% of melilitites underlie the olivine-melilite nephelinite field, and the overlap area does not intersect that of nephelinite-olivine nephelinite. These relationships suggest: (1) that nephelinites are derived primarily from olivine nephelinites, and (2) melilite-bearing lavas define a separate, more silica-undersaturated population (lower *ab* values), which does not clearly indicate a trend towards any fractionated magmas. The compositional heterogeneity of primitive melilite-bearing lavas relative to olivine nephelinites implies that their generation is more sensitive to compositional and physical variations in the source region (such as pressure), which would result if they were generated at lower degrees of partial melting, or if a previous episode of mantle metasomatism were a necessary condition for their formation.

Also plotted in Fig. 3 are individual analyses of wollastonite nephelinites from Oldoinyo L'engai (filled diamonds) (Dawson 1962; Donaldson et al. 1987; Part I), a wollastonite melanephelinite from Kisingiri, Kenya (HC-27: the open diamond) (Le Bas 1977); and sample SH-49 (open circle), a carbonate-rich perovskite melanephelinite from Shombole. All of these lavas have peralkalinities greater than the mean of the Shombole nephelinites (1.15) (e.g., the average peralkalinity of the eight wollastonite nephelinites from Oldoinyo L'engai is 1.43). The extension of the melilitite field toward Ln is defined by a single sample (K-53: Le Bas 1977) which is a highly peralkaline [$(Na+K)/Al=1.33$] melilitite from Kisingiri, Kenya. The filled circles are additional nephelinites from Oldoinyo L'engai, which are either wollastonite-free or have unreported mineralogies (Dawson 1962; Donaldson et al. 1987). In particular, the filled circle nearest the Ln apex represents analysis #8 of Dawson (1962) of a "nephelinite" for which there is no petrographic description; the peralkalinity of this lava is 1.45. Those filled circles clustering near the shaded nephelinite field all represent moderately peralkaline lavas [average $(Na+K)/Al$ of 1.16].

Superimposed on Fig. 3 is a rearrangement of a portion of the cotectics of Fig. 2 that is consistent with the interpretation that wollastonite nephelinites represent a fractionation trend originating with melilite-bearing liquids, and that 'ordinary' nephelinites extend from the olivine-clinopyroxene cotectic into the clinopyroxene (± nepheline) field. Wollastonite nephelinites have consistently increasing values of *ne* along the wollastonite-clinopyroxene cotectic, supporting the inference that they represent increasingly fractionated magmas. In view of the scattering of the projected points (due perhaps to inadequacies of the projection scheme, incorporation of xenocrysts, or fractionation of immiscible carbonatite) these cotectics must be considered schematic. If a melilite nephelinite-wollastonite nephelinite trend does exist, it seems safe to conclude that: (1) it is uncommon, and (2) it is associated with high peralkalinity.

Note that sample SH-49 from Shombole, which lies on the wollastonite nephelinite trend, does not contain wollastonite. It is anomalous among the Shombole lavas for having a high volume fraction of immiscible carbonatite (9%), and being the most silica-poor (40% SiO_2) and most peralkaline [(Na+K)/Al=1.37] nephelinite in the Shombole suite. This sample possibly indicates that strongly peralkaline and basic nephelinites may have such high CO_2 contents that wollastonite is unstable with respect to a CaO-rich immiscible carbonate liquid. Ongoing experimental work with this sample (Part I; Kjarsgaard and Hamilton 1989) has shown that melilite crystallizes from the composition $(SH\text{-}49)_{90}(CaCO_3)_{10}$ at 950° C and 2 kbar (other phases are nepheline, perovskite, melanite, silicate liquid, and Ca-rich carbonate liquid); a melilite-out reaction has not yet been identified. In view of these results, the melilite-wollastonite reaction point has been placed close to SH-49 in Fig. 3. The inference is that derivatives of melilite-bearing magmas were also erupted at Shombole, but in very minor amounts compared to derivatives of olivine nephelinites. At Oldoinyo L'engai, the derivatives of both types of parental magma are approximately equally represented. Despite this, the term 'L'engai-type nephelinite' will refer to lavas of the wollastonite nephelinite trend only, since these are so well represented at Oldoinyo L'engai.

Wollastonite ijolites and urtites are present in most alkaline ultramafic intrusive centres (e.g., Currie 1975), but equivalent lavas are extremely rare. For example, Le Bas (1977) lists only one analysis of a wollastonite nephelinite (HC-27) at Kisingiri. No nephelinites equivalent to the extremely fractionated and strongly peralkaline lavas of Oldoinyo L'engai have been found at Shombole, but wollastonite does occur as xenocrysts replaced by calcite in some caldera lavas; Peterson (1987, 1988) attributed this wollastonite to Ca-fenitization of intrusive rocks by carbonatite. Moderately peralkaline [(Na+K)/Al≈1.2], late, mingled, wollastonite phonolites associated with sövite dikes and breccias at Shombole have been interpreted as partial melts of ijolite fenites (Peterson 1988), but may be derivatives of nephelinites corresponding to point E in Fig. 2 (Peterson and K. Bell, in preparation).

The trends identified in Fig. 3 are consistent with the crystallization paths envisaged by Yoder (1979) although the natural cotectic geometry is evidently displaced relative to his schematic projection and includes considerable movement of liquids relative to the Ne apex. The great abundance of Shombole-type over L'engai-type nephelinites in alkaline ultramafic centres indicates that, in rifting continental crust, olivine nephelinites preponderate over melilitites and related magmas. Yoder and Velde (1976) report that an extensive search for melilite-liquid reaction textures in over 300 melilite-bearing lavas failed to yield a single example, indicating that few lavas approach or pass the reaction point D where melilite becomes unstable, producing wollastonite nephelinites. Wilkinson and Stolz (1983) report the presence of corroded melilite phenocrysts in olivine-melilite nephelinites from Oahu. They note an increase in normative *wo* in the residual liquids of these lavas and suggest this indicates a tendency to fractionate toward wollastonite-bearing liquids, although wollastonite is not present in any of the lavas or segregated residual liquids.

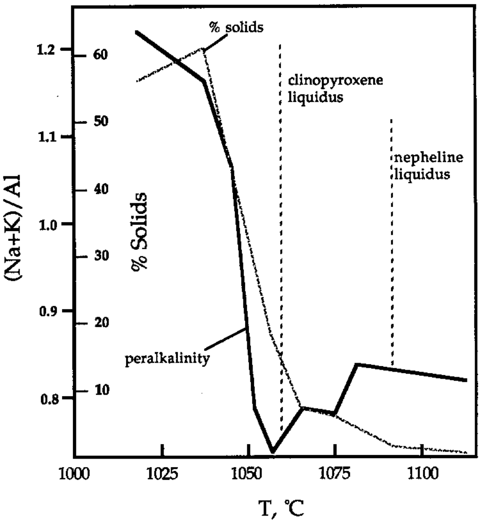


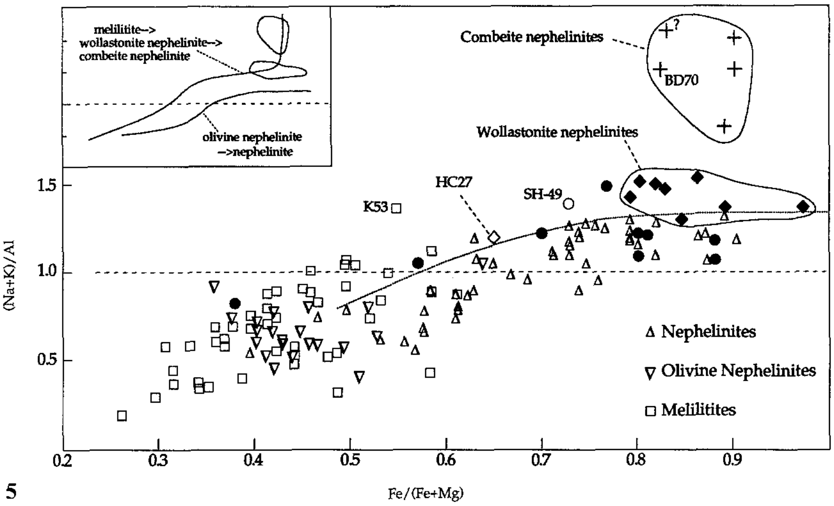
Fig. 4. Melt peralkalinity and percent solids vs temperature for melting experiments with a perovskite ijolite from the Ice River Complex, British Columbia, showing the effect of crystallization of nepheline and clinopyroxene on melt alkali/alumina ratios. The rapid increase in peralkalinity below 1060° is due to removal of Al from the liquid by clinopyroxene with about 13% Al_2O_3 and 7.7% TiO_2. The apparent decrease in crystallinity at the lowest temperature is an artifact of errors in point counting and settling of crystals in the bead. Minor phases appearing in these experiments and their liquidus temperatures are perovskite (1080°), olivine (1075°), and magnetite (1030°) (fO_2=IW). The experimental method is the same as that described in the Appendix to Part I

Further experimental work with natural compositions near the olivine-melilite-clinopyroxene cotectic (point C) is needed to determine which reactions actually occur in magmas, but for the purpose of defining a testable model I identify two differentiation trends in alkaline ultramafic magmas. The most common ("Shombole trend") leads to moderately peralkaline nephelinites [(Na+K)/Al≈1.15] via fractionation of olivine nephelinite. The second ("Oldoinyo L'engai trend") leads to highly peralkaline wollastonite nephelinites [(Na+K)/Al≥1.4] that originate with melilitites and closely related magmas.

Origin of peralkalinity

Velde and Yoder (1976) report that the average (Na+K)/Al ratio and MgO content of lavas with groundmass melilite are 0.69 and 13.52% respectively, and 0.96 and 6.96% for lavas with phenocrysts of melilite. This observation strongly implies that a highly aluminous phase is fractionated from primitive alkaline ultramafic magmas. Fractionation of aluminous plagioclase feldspar is responsible for development of peralkalinity in derivatives of alkali basalt (trachytes and phonolites) (e.g., Baker et al. 1977), but feldspar is absent from alkaline ultramafic rocks. For peralkalinity to develop in alkaline ultramafic melts that initially have (Na+K)/Al<1, fractionation of aluminous clinopyroxene must occur, because other aluminous phases, such as spinel, are basent from or rare in primitive alkaline ultramafic lavas (e.g., Wilkinson and Stolz 1983; McIver 1981).

The clinopyroxenes of the evolved portions of both proposed trends are similar and are nonaluminous diopside-



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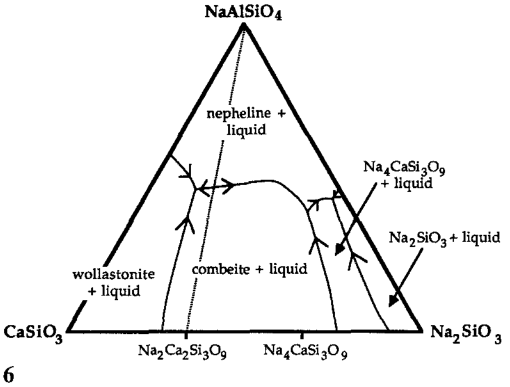

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Fig. 5. Peralkalinity vs Fe/(Fe+Mg) for alkaline ultramafic lavas, including the combeite nephelinites from Oldoinyo L'engai (*crosses* (Part I). The data and symbols are the same as for Fig. 3, except that the olivine melilite nephelinites have been grouped together here with melilitites. The nephelinite labeled as BD70 from Oldoinyo L'engai (Donaldson et al. 1987), placed in the combeite nephelinite field, reportedly contains a phase with the approximate compositon $Na_2CaSi_2O_6$. This is probably combeite, which is a solid solution of $Na_2Ca_2Si_3O_9$ and $Na_4CaSi_3O_9$. The combeite nephelinite labeled with a question mark is sample #7 of Dawson (1962) for which there is no petrographic description, but its peralkalinity is so high (2.38) that it is presumed to contain combeite. The inset shows the idealized paths of the two differentiation trends. They are separated by a dashed line in the main figure that corresponds in part to the lower stability limit of wollastonite with respect to (Na+K)/Al

Fig. 6. Liquidus fields in the system $NaAlSiO_4-CaSiO_3-Na_2SiO_3$ (Ne-Wo-Ns) after Spivak (1944). High-temperature polymorphs of $NaAlSiO_4$ and $CaSiO_3$ have been omitted

hedenbergite-acmite solutions (e.g., Mitchell 1980; Part I), but clinopyroxenes in Mg-rich alkaline rocks can be very aluminous due to solution of $CaAl_2SiO_6$ (CaTs) and $CaTiAl_2O_6$ (Tp) components. Sahama (1976) records clinopyroxenes with up to 9% Al_2O_3 (0.2% Na_2O) in melilitites from Nyiragongo, Zaire. Similar clinopyroxenes with 9.5% Al_2O_3 occur in the cumulate alkali pyroxenites (jacupirangites) of the Ice River Complex, British Columbia (Currie 1975). Mitchell (1980) has documented the entire range of composition of clinopyroxenes from the Fen complex, Norway; the most primitive rock types there (damkjernites) contain pyroxenes with 7.5%–13% Al_2O_3. Peralkaline ijolites are also found at both the Ice River Complex and at Fen. Note that the Al content of these pyroxenes is not a function of high pressure, i.e., the aluminous component is not jadeite and the Na content of aluminous clinopyroxenes from alkaline ultramafic magmas is usually very low.

A suite of lavas from a single centre, documenting the role of aluminous clinopyroxene in the formation of peralkaline nephelinites is unfortunately not available. Peralkalinity produced by crystallization of Al-bearing pyroxene has been noted in residual liquids in the system nepheline-diopside (Yoder and Kushiro 1972), however, the tendency for aluminous clinopyroxene to grow metastably in experimental charges introduces difficulties in the interpretation of these and other results. Crystallization experiments with a perovskite-bearing ijolite (Peterson 1987) do indicate a strong potential for production of peralkaline liquids by crystallization of aluminous clinopyroxene from metaluminous alkaline ultramafic liquids. In Fig. 4, the melt alkalinity and total crystallinity measured in these experiments are plotted against the temperature. Crystallization of nepheline, which is the liquidus phase for this composition (1090° C), initially *decreases* melt alkalinity because the bulk composition has $(Na+K)/Al=0.83$. Below the clinopyroxene liquidus (about 1060° C), melt alkalinity rises steadily, with (Na+K)/Al exceeding 1.2 at 60% solidification. The clinopyroxenes from these experiments have about 13% Al_2O_3 and 7.7% TiO_2.

Alternatively, alkaline ultramafic melts with initial values of (Na+K)/Al slightly greater than one may yield increasingly peralkaline derivative liquids by fractionation of nepheline, which has $(Na+K)/Al \approx 1$. The olivine-melilite nephelinites of Oahu, which have about 11% MgO and 250 ppm Ni, commonly have (Na+K)/Al slightly greater than 1 (Wilkinson and Stolz 1983). It is noteworthy that the clinopyroxenes in these lavas, with $Al_2O_3 < 3\%$, are only weakly aluminous, suggesting a negative correlation between melt peralkalinity and the Al contents of low-pressure pyroxenes. Ijolitic pegmatoids, and in particular one 'mineraloid residuum' from these lavas have higher peralkalinities than the bulk lavas (up to 6.8 for the mineraloid).

A positive correlation between melilite stability, normative larnite, and alkali content in alkaline ultramafic rocks is well documented (Velde and Yoder 1976; Yoder and Velde 1976), so that the enhanced peralkalinity of derivatives of melilite nephelinites relative to those of olivine nephelinites is in part due to initial alkali contents acquired in the source regions. Normative larnite is also an expression of a high CaTs content in clinopyroxene, however, so it is not surprising that the fractionation products of melilite nephelinites can be highly peralkaline.

Fig. 5 shows peralkalinity versus Fe/(Fe+Mg) for all of the compositions in Fig. 3, plus the combeite nephelinites of Oldoinyo L'engai (Part I). The insert shows the two interpreted differentiation paths. The olivine nephelinite trend shows a pronounced increase in peralkalinity at $Fe/(Fe+Mg) \approx 0.6$, and approximately constant peralkalinity $[(Na+K)/Al \approx 1.15]$ for $Fe/(Fe+Mg) \geq 0.7$. The increase occurs shortly after the disappearance of olivine, at Fe/

(Fe + Mg) ≈ 0.55 (neglecting one outlying point at 0.63) and (Na + K)/Al ≈ 0.7. The degree of scatter in the melilitites makes generalizations uncertain, but relative to the olivine nephelinites they have higher average peralkalinity, especially for Fe/(Fe + Mg) ≥ 0.5. The evolved rocks grouped with the melilitites show steady increase in peralkalinity until wollastonite becomes unstable with respect to combeite (see below), whereupon (Na + K)/Al rises rapidly. The replacement of melilite by wollastonite in this trend begins at Fe/(Fe + Mg) ≈ 0.63, and [Na + K]/Al ≈ 1.2.

In Fig. 5, a dashed curve has been drawn separating evolved nephelinites that maintain constant, low peralkalinity (Shombole trend), and those that increase further in peralkalinity as crystallization progresses (Oldoinyo L'engai trend). If peralkalinity is constant, it may be presumed that it is buffered by fractionation of nepheline and sodic clinopyroxene, the only significant Na-K-Al phases present in Shombole-type nephelinites. As discussed in Part I, most of the Na-K-Al variation in the evolved part of both trends is due to differential movement of nepheline and liquid. Above the curve, compositions apparently are sufficiently peralkaline that the ratio of fractionated sodic clinopyroxene/nepheline is not high enough to prevent a rise in peralkalinity. That this should also correspond to a stability boundary for wollastonite may not be coincidental, but defies explanation at present.

In Part I it was suggested that fractionation in the Shombole suite produced increasingly siliceous magmas of nearly constant peralkalinity (ending in phonolites), but that further fractionation of the L'engai wollastonite nephelinites produced extremely peralkaline [(Na + K)/Al ≥ 2] combeite ($Na_2Ca_2Si_3O_9$) bearing nephelinites, which coexisted with immiscible natrocarbonatite magma. The generation of combeite nephelinites is considered in greater detail below.

Crystallization of L'engai-type nephelinites

Textures in a suite of nephelinites from Oldoinyo L'engai that indicate the existence of a reaction relation between wollastonite and liquid to produce combeite were described in Part I. Combeite nephelinites contain both euhedral phenocrysts of combeite and combeite pseudomorphs after euhedral wollastonite phenocrysts. Combeite and wollastonite nephelinites also contain phenocrysts of melanite, sphene, and sodalite, and globules of mixed zeolites and carbonates interpreted as immiscible segregations. These lavas are geochemically very similar to Shombole nephelinites, except for their high peralkalinity and high Zr contents (700 vs 400 ppm).

Experimental work by Spivak (1944) in the system $NaAlSiO_4 - Na_2SiO_3 - CaSiO_3$ (Ne-Ns-Wo) indicates that nepheline, wollastonite, combeite, and liquid coexist at a eutectic (Fig. 6). Combeite melts congruently at one bar (Morey and Bowen 1925), hence, a reaction relation involving production of combeite is not indicated. A peritectic reaction at the point nepheline + wollastonite + combeite + liquid would be indicated, however, if the location of this point shifted to the Ns side of the nepheline-combeite join (which defines a thermal divide where it crosses the combeite-nepheline cotectic in Ne-Ns-Wo). Such a shift could result from solid solution effects in phenocryst phases or the presence of additional components in the liquid (such as K_2O and volatiles).

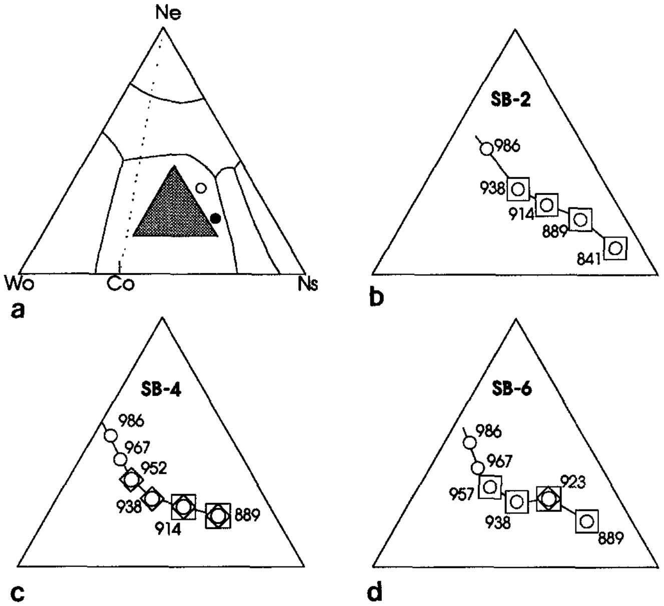

Fig. 7 a–d. Projections onto the plane Ne-Wo-Ns. **a** Locations of glasses from wollastonite nephelinite HOL-16 (*open circle*) and combeite nephelinite HOL-10 (*filled circle*) (tabulated in Part I). The *shaded triangle* indicates the region occupied by (b)–(d). **b–d** Projections of compositions of experimental glasses coexisting with nepheline (*circles*), combeite (*squares*), and wollastonite (*diamonds*). Temperatures in °C are indicated. See text for discussion

Projections of the average compositions of the glasses of wollastonite and combeite nephelinites (tabulated in Part I) onto the plane Ne-Ns-Wo appear in Fig. 7A. The projection was made as follows: *ne* = $Al_2O_3/2$; *ns* = ($Na_2O - Al_2O_3$); *wo* = CaO (molecular). Because no Ca is assigned to other components (e.g., clinopyroxene), and K is not included with Na, this biases projections toward the Ne-Wo join and the wollastonite stability field. The glass compositions plot well to the right of the nepheline-combeite join, indicating that fractionation with any combination of the phases nepheline, wollastonite, and combeite cannot prevent the liquid from moving towards the Ne-Ns join. Fractionation of highly sodic clinopyroxene could reduce the peralkalinity, but extreme and unreasonable amounts would be required. The presence of a reaction relation between wollastonite and liquid was confirmed by experiments with a combeite nephelinite.

Experimental method

Finely ground powder from combeite nephelinite HOL-10 was mixed with varying quantities of sodium bicarbonate, and fused and recrystallized on Pt loops. The sodium bicarbonate serves to induce high peralkalinity at relatively low crystallinities and to replace Na lost during initial fusion and devolatilization. Pt wire 0.25 mm thick was electroplated with Fe in saturated ferrous ammonium sulfate solution and annealed for 24–48 hours at 1250° C below the IW buffer (approximately 10% Fe alloy produced). Loops (0.5 cm diameter) were re-used whenever possible to minimize Fe loss. Runs were from 24 to 48 hours duration, and oxygen fugacity was controlled by $H_2 - CO_2$ gas mixtures. All experiments were run at close to IW which inhibits the growth of clinopyroxene, somewhat altering compositional trends, but yielding cleaner textures to aid analysis. Quench was by airblast, and beads or bead fragments were mounted in epoxy and prepared as microprobe mounts. Identification of phases was made optically (confirmed by microprobe analysis). Loss of Na_2O during probe analysis of glasses (15 keV; 40 µ beam diameter; 10 nA beam current; 20 s counting interval) was corrected using empirically obtained exponential decay factors (maximum 5% relative correction). Temperatures, glass compositions, and phase assemblages are available from the author. Reversals performed during the calibration of a nepheline-liquid geothermometer (Part I) indicate that equilibrium is rapidly attained in these strongly alkaline, low-viscosity liquids.

The results from three representative compositions are projected onto Ne-Ns-Wo in Fig. 7b–7d. All compositions have nepheline on the liquidus (approx. 1070° C). The composition with the highest peralkalinity [SB-2, $(Na+K)/Al=3.03$] crystallizes combeite at 938° C, and wollastonite never appears. The composition of lowest peralkalinity [SB-4, $(Na+K)/Al=2.74$] crystallizes wollastonite at 952° and combeite at 914°. Both remain stable to the lowest run temperature of 889° C. Intermediate compositions display a reaction relation. Compositions SB-6 ($[Na+K]/Al=2.85$) and SB-5 ($[Na+K]/Al=2.87$) (not shown in Fig. 7) display the following sequence: nepheline, nepheline + combeite, nepheline + combeite + wollastonite, nepheline + combeite.

Composition SB-4 is analogous to liquids in Ne-Ns-Wo that approach the eutectic from the left, along the nepheline-wollastonite cotectic. Composition SB-2 is analogous to liquids crystallizing on the nepheline-combeite cotectic, to the right of the nepheline-combeite join. Composition SB-6 displays some of the behaviour expected of liquids which lie between this join and the eutectic: wollastonite can crystallize after the precipitation of combeite. Wollastonite becomes unstable, however, as the liquid composition migrates toward the sodium metasilicate apex, which occurs with falling temperature for all compositions. The peralkalinity of the natural glasses in the wollastonite nephelinites is even more extreme [$(Na+K)/Al\approx4.0$: Part I] than that of the experimental liquids, which should enhance the reaction relation. It is presumed that the wollastonite in composition SB-4 would also have become unstable at some temperature below 889°, but reliable experiments at much lower temperatures unfortunately could not be performed because the gas mixtures used to control $f(O_2)$ did not react well below about 850°.

It is possible, therefore, to interpret the reaction between wollastonite and liquid observed in the lavas as a result of equilibrium crystallization, and it is not necessary to presume, as did Peterson and Marsh (1986) that wollastonite nephelinite had been contaminated by Na-rich material (see Discussion), although this is not precluded by the experimental results. The incompatible elements Zr, Rb, Sr, Ba, F, and Cl are relatively concentrated in the combeite nephelinites, consistent with an origin by fractionation of wollastonite nephelinite.

Discussion

Since the discovery of natrocarbonatite lava in the northern crater of Oldoinyo L'engai (Dawson 1962) a popular view has been that such lava is representative of carbonatite magmas before their emplacement and solidification. Because intrusive carbonatites are comprised mostly of Ca, Mg, and Fe carbonates (aside from rare Sr or REE carbonatites) this view is consistent with the alkali metasomatism so commonly observed around carbonatites. It is assumed that Na and K leave the crystallizing magma in low-temperature, hydrothermal (fenitizing) fluids (e.g., Dawson 1966; Gittins and McKie 1980; Le Bas 1981). The first dissenting voice in this debate was that of Milton (1968), who suggested that bedded trona [$Na_3H(CO_3)_2\cdot2H_2O$], possibly underlying L'engai, had been melted and erupted as 'carbonatite'. Thick trona beds occur in Lake Magadi 100 km north of L'engai and the mineral is common as encrustations along the shore of nearby Lake Natron and many other saline lakes in the Kenya Rift. This model was initially supported by the preliminary results of Peterson and Marsh (1986), but is now superseded by the model presented here. The available radiogenic and stable isotope data strongly indicate an igneous origin for the natrocarbonatite, with no discernible crustal influence (Bell et al. 1973; Javoy et al. 1988). It should be noted that Hans Eugster, based on his knowledge of the sedimentology and stratigraphy of the south Kenya Rift, argued that there was no bedded trona beneath Oldoinyo L'engai (Eugster, personal communication 1986), however, Milton continues to argue for a sedimentary source for natrocarbonatite.

Twyman and Gittins (1987) pointed out that phase equilibria in carbonate systems preclude any possibility of the derivation of Ca- and Fe-carbonatites from natrocarbonatite by crystal fractionation, which was proposed by Le Bas (1987). Twyman and Gittins and also Gittins (1988) alternatively suggested that Mg-rich carbonatites are directly derived from the mantle and are parental to other varieties of carbonatite. Both of these models implicity assume that the variations observed in carbonatite compositions, which are certainly extreme, are due to the combined effects of crystal fractionation and loss of fenitizing fluids, and they also presume the existence of a single, primary carbonatite magma.

The evidence presented here and in Part I supports an alternative to these models, namely, that natrocarbonatite is associated solely with highly evolved combeite nephelinites. As noted previously, combeite nephelinites are virtually identical in composition to silicate liquids shown to coexist with immiscible natrocarbonatite (Freestone and Hamilton 1980; Part I). The proposed differentiation trend leading to combeite nephelinites is rarely expressed at alkaline ultramafic centres, suggesting that natrocarbonatite has little general relevance for the evolution of such complexes. Combeite has been recorded from only three locations in the world: Oldoinyo L'engai; Mount Shaheru, Zaire (Sahama and Hytönen 1957); and the Eifel Province, Germany (location unspecified) (Fischer and Tillmans 1983). The experimental data of Kjarsgaard and Hamilton (1988) and Freestone and Hamilton (1980) indicate that carbonatite liquid may be exsolved from any type of nephelinite, and erupted or emplaced as intrusive bodies after collection in larger bodies of crystallized alkaline silicate magma. Ca-carbonatite can be immiscibly exsolved by Mg-poor Shombole-type nephelinites (Part I; Kjarsgaard and Hamilton 1989).

Some authors have identified former nyerereite [$(Na_{0.82}K_{0.18})_2Ca(CO_3)_2$] phenocrysts, pseudomorphed by calcite, in the tuffaceous deposits of extinct carbonatite volcanoes (Turner 1988; Deans and Roberts 1984; Hay 1983) and have referred to the original material as natrocarbonatite. This is incorrect, however, for primary phenocrysts of calcite are also recognized in all of these deposits, but to date no other carbonatite tuff or lava has been identified which also contains pseudomorphs after the much more Na-rich mineral gregoryite [$(Na_{0.78}K_{0.05})_2Ca_{0.17}CO_3$], an abundant phenocryst mineral in natrocarbonatite from Oldoinyo L'engai. A considerable compositional gap exists between the gregoryite-nyerereite and nyerereite-calcite cotectics in the system $Na_2CO_3-K_2CO_3-CaCO_3$ at 1 kbar (Cooper et al. 1975), and no fractionation path linking the two cotectics exists; they represent quite distinct types of carbonatite magma. All available evidence indicates that the natrocarbonatite of Oldoinyo L'engai is unique.

It is proposed here that rare, highly magnesian olivine-phlogopite-dolomite-calcite carbonatites, such as the Verity carbonatite, British Columbia (Heinrich 1966) are immiscibly exsolved by olivine-bearing alkaline ultramafic magmas. The condition that any phase stable in the carbonate liquid must also be stable in the conjugate silicate liquid requires that, if such carbonatites are derived by liquid immiscibility, they arise from olivine-bearing magmas. It is true that trace melts formed at about 20–30 kbar in carbonated peridotite and pyrolite correspond broadly to Mg-rich carbonatites (e.g., Wallace and Green 1988), but crustal emplacement of Mg-carbonatite could also be mediated by carbonated olivine melilitite (or olivine nephelinite, etc.), which could exsolve an Mg-carbonatite liquid if decompressed (i.e., emplaced in the crust) before undergoing much crystal fractionation. Carbonated alkaline ultramafic silicate melts are produced in greater volumes from the same source composition than are Mg-carbonatites, making them more mobile and more common. Transport of Mg-carbonatite from the mantle to the crust might therefore be more efficient if it is mediated by a silicate parental liquid. The span of carbonatite compositions can be viewed as a continuum reflecting the span of compositions of alkaline ultramafic melts that they are exsolved from, with only minor contributions by subsequent crystal fractionation or loss of fenitizing fluids.

Oceanic occurrences of carbonatites are extremely rare (but see Le Bas 1984). Le Bas (1987) suggested that the essential difference between the evolution of continental and oceanic olivine nephelinites was that dense primary alkaline ultramafic liquid could pond at shallower levels in oceanic crust. Thus, oceanic centres are dominated by primitive magmas. In general, production of carbonatites will occur after extensive crystallization because the melt must become saturated with CO_2; this explains the common association of carbonatites and fractionated nephelinites (or ijolites). Only evolved nephelinites have sufficiently low density (2.5–2.6 g/cm^3) to buoyantly ascend through the upper continental crust and hence their parental magmas are poorly represented in continental alkaline centres. Calculations indicate that melilite-bearing, primitive alkaline ultramafic melts have slightly greater densities (≈ 2.8 g/cm^3) than olivine nephelinites (≈ 2.75 g/cm^3) but any difference in the availability of their differentiation products is more probably due to differences in the depths of their source regions, and the relative volumes of primary magmas produced in continental rift settings. With increasing pressure, melts of peridotite-CO_2 become increasingly rich in normative larnite (Eggler 1978), hence, melilitites and olivine-melilite nephelinites are generated at higher pressures and must travel greater distances to the surface than olivine nephelinites, inhibiting their appearance in continental crust.

Summary

Two possible differentiation trends in sodic alkaline ultramafic liquids are: (1) olivine nephelinite→nephelinite, and (2) olivine-melilite nephelinite (or melilitite)→melilite nephelinite→wollastonite nephelinite→combeite nephelinite. The first trend, occurring at Shombole, southern Kenya, produces mildly peralkaline liquids and is the common one in nephelinite-carbonatite centres. The second trend, occurring at Oldoinyo L'engai, northern Tanzania, leads to strongly peralkaline liquids and passes through three reaction points where olivine, melilite, and wollastonite in turn become unstable, finally producing magmas with the assemblage nepheline + clinopyroxene + combeite. The Oldoinyo L'engai trend is rarely recorded. In both trends, peralkalinity is induced by fractional crystallization of aluminous clinopyroxene, an effect enhanced by the high normative larnite and high initial alkali content of melilite-bearing alkaline ultramafic liquids.

The final magmas produced in the L'engai trend are sufficiently alkaline to coexist with immiscible natrocarbonatite. It was suggested that natrocarbonatite is a variety of carbonatite associated solely with the L'engai trend and is not a viable parental magma for other carbonatites, which are derived themselves by liquid immiscibility from less alkaline and usually more primitive nephelinites. Compared to parental magmas of the Shombole trend, those of the L'engai trend are relatively dense and formed at greater depths, which inhibits their emplacement within continental crust. The unlikelyhood of a magma successfully passing through three peritectic reaction points may also contribute to the rarity of L'engai-type nephelinites.

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Note added in proof

Experimental work by Gee and Sack (1989) confirms that point C in Ab – Ln – Fo is a distributary reaction point and that clinopyroxenes in liquids near C are highly aluminous (6–15% Al_2O_3).

Appendix

The following steps were used to project lava compositions onto the plane Albite-Larnite-Forsterite.

(1) Convert weight percent of SiO_2, TiO_2, Al_2O_3, FeO_{total}, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5 to single-cation mole numbers.
(2) Let $Fe' = Fe + Mn$; $Na' = Na + K$
(3) Ap (apatite) = P/3; $Ca = Ca - 5 \times Ap$
(4) Us (ulvospinel) = Ti; $Fe' = Fe' - 2 \times Us$
(5) If $Na' > Al$, go to step (6), otherwise, go to step (7).
(6) Ne (nepheline) = Al; Ac (acmite) = $Na' - Al$; $Fe' = Fe' - Ac$. CaTs (calcium Tschermak's molecule) = 0. Go to step (8).
(7) $Ne = Na'$; $CaTs = (Al - Na')/2$; $Ca = Ca - CaTs$; $Ac = 0$
(8) Ln (larnite) = Ca/2
(9) Fo (forsterite) = $(Mg + Fe')/2$
(10) $Si = Si - (Ln + Fo + Ne + CaTs + 2 \times Ac)$
(11) Ab (albite) = Si/2
(12) $Ne = Ne - Ab$

This yields a representation of the lava in the component set Ne, Ab, Ln, Fo, Ac, CaTs, and Us.

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