A common origin of carbonatite magmas

Daniel Weidendorfer[1,2]*, Max W. Schmidt[1], and Hannes B. Mattsson[1]

[1]Department of Earth Sciences, ETH Zurich, Clausiusstrasse 25, 8092 Zurich, Switzerland
[2]Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, 595 Charles Young Drive East, Los Angeles, California 90095-1567, USA

ABSTRACT

The more than 500 fossil Ca-carbonatite occurrences on Earth are at odds with the only active East African Rift carbonatite volcano, Oldoinyo Lengai (Tanzania), which produces Na-carbonatite magmas. The volcano's recent major explosive eruptions yielded a mix of nephelinitic and carbonatite melts, supporting the hypothesis that carbonatites and spatially associated peralkaline silicate lavas are related through liquid immiscibility. Nevertheless, previous eruption temperatures of Na-carbonatites were 490–595 °C, which is 250–450 °C lower than for any suitable conjugate silicate liquid. This study demonstrates experimentally that moderately alkaline Ca-carbonatite melts evolve to Na-carbonatites through crystal fractionation. The thermal barrier of the synthetic Na-Ca-carbonate system, held to preclude an evolution from Ca-carbonatites to Na-carbonatites, vanishes in the natural system, where continuous fractionation of calcite + apatite leads to Na-carbonatites, as observed at Oldoinyo Lengai. Furthermore, saturating the Na-carbonatite with minerals present in possible conjugate nephelinites yields a parent carbonatite with total alkali contents of 8–9 wt%, i.e., concentrations that are realistic for immiscible separation from nephelinitic liquids at 1000–1050 °C. Modeling the liquid line of descent along the calcite surface requires a total fractionation of ~48% calcite, ~12% apatite, and ~2 wt% clinopyroxene. SiO_2 solubility only increases from 0.2 to 2.9 wt% at 750–1200 °C, leaving little leeway for crystallization of silicates. The experimental results suggest a moderately alkaline parent to the Oldoinyo Lengai carbonatites and therefore a common origin for carbonatites related to alkaline magmatism.

INTRODUCTION

Na-carbonatite lavas predominantly consist of nyerereite [$Na_2Ca(CO_3)_2$] and gregoryite [$(Na, Ca_x, K)_{2-x}CO_3$] phenocrysts embedded in a heterogeneously quenched matrix of Ba-rich nyerereite, gregoryite, Na-sylvite, fluorite, and quenched Ba-Ca-Sr-Na carbonate solid solutions (Gittins and Jago, 1998). The formation of Na-carbonatites from Ca-rich parent melts is thought to be prohibited by a thermal barrier in the Na-K-Ca-carbonate system (Cooper et al., 1975). Accordingly, fractionation of Ca-rich carbonate melts would terminate in an eutectic, less alkaline than, $(Na,K)_2Ca(CO_3)_2$ (nyerereite-fairchildite solid solution), while the Na-carbonatites are more alkaline than this composition (Figs. 1 and 2B). This led to the suggestion that carbonatite melts parental to the Na-carbonatites must have been chemically close to the erupted compositions (Gittins and Jago, 1998), resulting in theories that encompass direct liquid immiscibility requiring a hidden conjugate silicate melt (Freestone and Hamilton, 1980; Kjarsgaard et al., 1995), melting of Na-evaporites (Milton, 1968) similar to those present on the East African Rift floor today, or a derivation from much deeper (unknown) sources (Keller and Hoefs, 1995).

In general, fossil carbonatites preserve alkalis at trace concentrations; however, several relatively young intrusive Ca-carbonatites (Gardiner, Greenland; Kerimasi, Tanzania; Oka, Canada) also contain
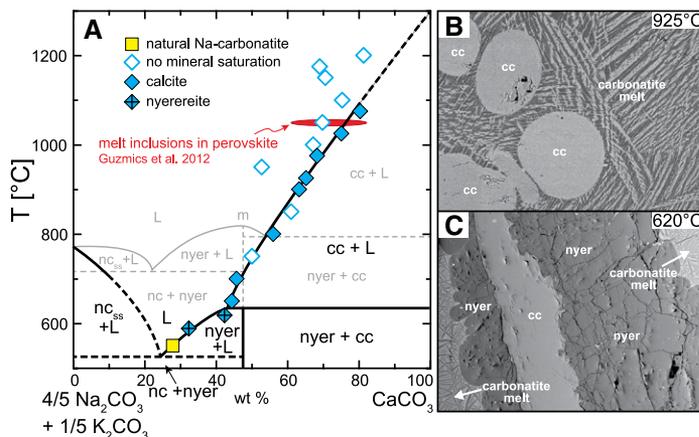

Figure 1. A: $CaCO_3$-$(Na,K)_2CO_3$ pseudobinary at the natural Na/K ratio of ~4. Thermal maximum (m; T is temperature) in the synthetic system (in gray, after Cooper et al., 1975) is suppressed in the natural Oldoinyo Lengai system (in black), where calcite (cc) disappears in favor of nyerereite (nyer) at a peritectic of ~630 °C. Red oval indicates the array of carbonate melt inclusions in perovskite at the preferred homogenization temperature of 1050 °C (Guzmics et al., 2012) (nc—sodium carbonate; ss—solid solution; L—liquid). B: Rounded calcite crystals within carbonatite melt at 925 °C. Calcite quench forms spinifex texture in carbonatite melt. C: Peritectic reaction between calcite and nyerereite. Calcite is entirely mantled by newly formed nyerereite at temperatures ≤620 °C.

Na-K-Ca-carbonate inclusions indicating the presence of alkalis during carbonatite crystallization (Nielsen et al., 1997; Guzmics et al., 2011; Chen et al., 2013). At Oldoinyo Lengai (an East African Rift carbonatite volcano in Tanzania), melt inclusions in minerals of the erupted silicate magmas point to parental carbonatite compositions with 25–44 wt% $Na_2O + K_2O$ and a small but varying silicate component (Mitchell, 2009). Furthermore, perovskite-hosted melt inclusions in nephelinitic rocks at the nearby Kerimasi volcano (Guzmics et al., 2012) are much less alkaline and show increasing $Na_2O + K_2O$ (12–22 wt%) with decreasing CaO (43–33 wt%), indicating calcite fractionation during melt evolution (Guzmics et al., 2011).

Possible calcite fractionation is further supported by liquid immiscibility experiments at 2–5 kbar, 900–1000 °C (Kjarsgaard and Peterson, 1991), that yield SiO_2-bearing Ca-rich carbonatites separating from nephelinites and primary calcite in both conjugate silicate and carbonate melts. Previous liquid immiscibility experiments were based on the assumption that spatially associated natural peralkaline silicate rocks and Na-carbonatites represent conjugate liquid pairs. These experiments demonstrated that, once equilibrated, alkali-rich carbonatite and peralkaline silicate melt pairs have no natural equivalents. Conceptually, this indicates that both melts have evolved independently from time of unmixing to eruption involving significant crystal fractionation, at least within the carbonatite melt (Twyman and Gittins, 1987; Kjarsgaard et al., 1995). In addition, the low
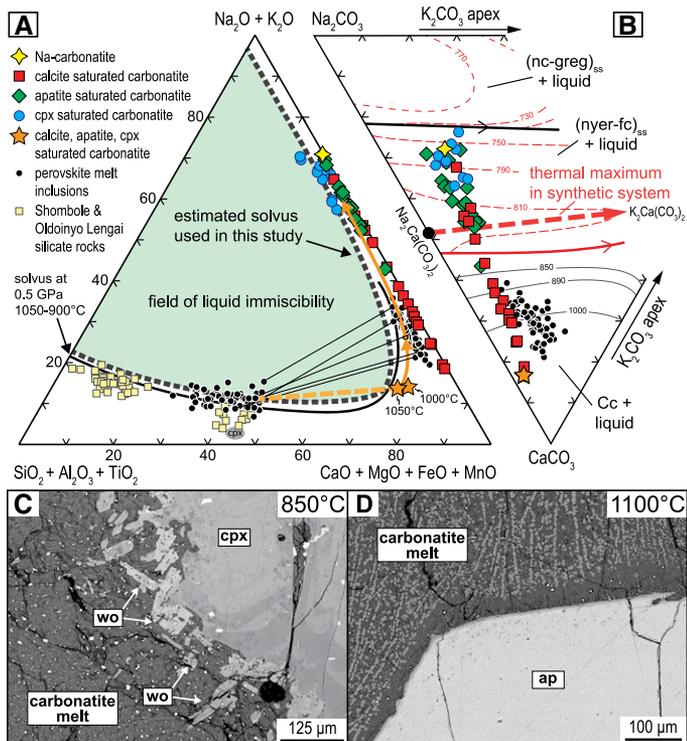
*E-mail: weidendorfer1@ucla.edu

Figure 2. A: Whole-rock compositions of the East African Rift Oldoinyo Lengai and Shombole volcanoes compared to perovskite-hosted melt inclusions (Guzmics et al., 2012) and experimental carbonatite melt compositions (in wt%; projection after Freestone and Hamilton, 1980). Black line represents experimentally determined nephelinite-carbonatite melt miscibility gap at 0.5 GPa (Kjarsgaard and Peterson, 1991); gray dashed line shows the miscibility gap inferred for this study; solid orange line represents the calculated liquid line of descent from a calcic carbonatite melt considering calcite, apatite, and clinopyroxene fractionation; dashed orange line is the suggested tie line between experimentally determined multiphase saturated carbonatite melt and an average conjugate silicate melt corresponding to melt inclusions in perovskite from Guzmics et al. (2012). For references of silicate whole-rock compositions (yellow squares), see the Data Repository (see footnote 1). B: Carbonatite melts plotted into the Na-K-Ca-carbonate ternary. Black liquidus surface elements are valid for both the natural and synthetic system; red elements are valid for the synthetic system after Cooper et al. (1975). Cc—calcite; fc—fairchildite, greg—gregoryite, nc—sodium carbonate, nyer—nyerereite. C: Peritectic reaction between clinopyroxene (cpx) and carbonatite melt forming euhedral wollastonite (wo). D: Apatite-saturated carbonatite melt at 1100 °C showing apatite (ap) quench crystallization.

viscosity of carbonatite melts facilitates crystal settling and deposition during melt evolution; thus, neither the original crystal load nor the primary carbonatite melt composition is expected to surface during eruption.

SATURATION EXPERIMENTS

Using rapid-quench cold-seal high-pressure vessels at temperatures of 590–1200 °C at 1 kbar pressure, we investigate the saturation of Na-carbonatite with minerals (calcite, apatite, clinopyroxene, nepheline, wollastonite, nyerereite, combeite) that are saturated in possible conjugate silicate magmas erupted at Oldoinyo Lengai (for methods, see the GSA Data Repository[1]). The background to this endeavor is straightforward: if the carbonatite has unmixed from a silicate melt that was saturated in a suite of minerals, the carbonatite melt, at this point in equilibrium with

the silicate melt, must also saturate in the same minerals. Such a criterion on identifying conjugate liquid pairs was reported by Church and Jones (1995), who identified gregoryite-bearing silicate melt globules in the A.D. 1993 erupted Na-carbonatites at Oldoinyo Lengai. However, disequilibrium textures, including corroded and resorbed rims of clinopyroxene phenocrysts from the 1966–1967 and 2007–2008 Oldoinyo Lengai explosive eruptions (Mattsson and Reusser, 2010), indicate that Na-carbonatite is not saturated with the phenocryst phases present in the silicate rocks. The purpose of this study is to reconstruct the carbonatite composition that may result from immiscibility with observed silicate melts at Oldoinyo Lengai.

RESULTS

Breaking the Thermal Maximum; Calcite and Apatite Saturation

Calcite and apatite saturation drastically change the melt composition and shift the Na-carbonatite composition with increasing temperature toward the Ca-rich side of the Na-K-Ca carbonate system (Figs. 1 and 2). In particular, calcite saturation increases CaO from 15.9 wt% in the original Na-carbonatite to 22.4 wt% at 650 °C, and then to as much as 44.1 wt% at 1075 °C (Fig. 1). The latter value corresponds to 163% of calcite assimilation with respect to the initial melt mass, or if inverted, 61% calcite fractionation from 1075 °C to the Na-carbonatite eruption temperature of ~550 °C at Oldoinyo Lengai (Fig. 1). Concomitantly, Na_2O decreases from 23.3 to 8.6 wt%, and K_2O, F, Cl, Ba, and SO_3 become proportionally diluted. Calcite is stable down to temperatures of 650 °C and is then replaced by nyerereite at ≤620 °C through a peritectic reaction at ~630 °C (Fig. 1).

Saturation of the Na-carbonatite in apatite leads to CaO and P_2O_5 contents as high as 31.9 and 20.3 wt%, respectively (1200 °C; Fig. DR2 in the Data Repository), while total alkalis decrease from initially 41.5 to 24.5 wt%. At temperatures exceeding 900 °C, apatite displays rounded crystal edges and embayment textures along crystal-melt interfaces. At temperatures of 650–1100 °C the apatite-saturated carbonatite melt quenches to the commonly observed nyerereite-gregoryite groundmass; at more elevated temperatures (>1100 °C) small rosulate apatite quench crystals (≤50 μm) develop within the carbonatite melt (Fig. 2). Abundant vapor void space is present at temperatures exceeding 1100 °C.

Conserving Low SiO_2 Contents in Carbonatite Melts at Subvolcanic Conditions

We find that saturation in clinopyroxene, combeite, nepheline, wollastonite, and nyerereite has small effects on the carbonatite melt composition regardless of temperature (Table DR2). Reacting the Na-carbonatite with natural augitic clinopyroxene confirms a SiO_2 solubility of 0.2–2.9 wt% at 750–1200 °C at subvolcanic pressures, leaving little leeway for dissolving silicates in carbonatite melts. At 750–900 °C, wollastonite is the equilibrium Ca-silicate mineral for this composition. Wollastonite crystallizes euhedrally along clinopyroxene grain margins without mantling them (Fig. 2). At temperatures >900 °C a peralkaline silicate melt forms through peritectic melting of augitic clinopyroxene to almost pure diopside. The peralkaline silicate melt and the Na-carbonatite liquid are immiscible at pressures of 1 kbar. A free vapor phase is present in all clinopyroxene saturation experiments and the amount of bubbles or void space increases with temperature.

Combeite is surrounded by radially growing wollastonite at 650–750 °C; at >800 °C combeite is entirely replaced by wollastonite, leading to a decrease of 1–2 wt% CaO in the melt while SiO_2 changes little. This is in line with the observed low SiO_2 solubility described above; the peritectic reaction from combeite to wollastonite changes melt compositions little. Only minor changes in melt composition were also observed when saturating the Na-carbonatite with nepheline, wollastonite, or nyerereite (see the Data Repository).

---

[1]GSA Data Repository item 2017160, methods and materials, experimental run details, and melt compositions, is available online at http://www.geosociety.org/datarepository/2017/ or on request from editing@geosociety.org.

Primary Carbonatite Melt Composition Determined by Multiphase Saturation

Multiphase saturation experiments were performed at 650–1050 °C, 1 kbar, using a seven-mineral assemblage of calcite, apatite, clinopyroxene, wollastonite, nepheline, combeite, and nyerereite or a three-mineral assemblage of calcite, apatite, and clinopyroxene.

Seven-Mineral Saturation Experiments

At 650 °C the carbonatite melt coexists with calcite, apatite, clinopyroxene, nepheline, nyerereite, and large amounts of subhedral wollastonite, the latter implying complete reaction of combeite to wollastonite. At 700 °C all phases were present except nyerereite and combeite, which were, however, added at a lower quantity. At 750 °C, apatite, wollastonite, combeite, and nyerereite are present, whereas clinopyroxene and calcite were not encountered in the polished cross section of the experimental charge. At 800 °C all added phases coexisted with carbonatite melt. Saturating the Na-carbonatite melt in calcite, apatite, clinopyroxene, wollastonite, nepheline, combeite, and nyerereite results in $Na_2O + K_2O$ decreasing from 41.5 to 37 wt% at 650 °C and to 32.1 wt% at 800 °C.

Three-Mineral Saturation Experiments

Calcite, apatite, and clinopyroxene coexist with moderately alkaline calcic carbonatite melt at 1000 and 1050 °C (Table 1). Calcite contains abundant submicron carbonatite melt inclusions, whereas clinopyroxene is surrounded by radially growing diopside and by an immiscible silicate melt. The multiphase saturated carbonatite melt is characterized by 6.1–7.0 wt% SiO_2, 39.8–44.1 wt% CaO, and $Na_2O + K_2O$ contents of 8.8 and 7.9 wt% at 1000 and 1050 °C, respectively.

DISCUSSION

A 60-year Lasting Controversy about the Primary Melt Composition of Na-Carbonatites

Since the discovery of the East African Rift Na-carbonatites in 1954 (Guest, 1956), their petrogenesis and chemical disparity to fossil alkali-poor carbonatite compositions has remained a central matter of debate (Milton, 1968; Freestone and Hamilton, 1980; Kjarsgaard et al., 1995).

Le Bas (1981) suggested that Na-carbonatites are parental to all other carbonatite varieties, and considered the alkali-poor nature of intrusive carbonatite rocks to result from synmagmatic and postmagmatic fluid-rock interaction. Liquid immiscibility between nephelinitic silicate melt and alkali-bearing carbonatite at 1000–1100 °C was suggested as the most likely carbonatite-generating process at Oldoinyo Lengai. At these temperatures, a nephelinite is close to its liquidus, whereas the Na-carbonatite is 500 °C above its liquidus temperature (Le Bas, 1981; Twyman and Gittins, 1987). Liquid immiscibility experiments involving natural or synthetic Na-carbonatite always result in silicate melts far too rich in alkalis with conjugate carbonate liquids significantly depleted in $Na_2O + K_2O$ when compared to the nephelinites and Na-carbonatite lavas of Oldoinyo Lengai. Consequently, Kjarsgaard et al. (1995) suggested extensive post-immiscibility crystal fractionation to account for the compositional gap between their experimentally produced calcic carbonatite liquid and the naturally observed Na-carbonatites, identifying the overly alkalic silicate melts as a serious problem.

Because Na-carbonatite lavas are mainly composed of nyerereite and gregoryeite phenocrysts, Gittins and Jago (1998) interpreted erupted phenocryst-rich carbonatite lavas to be compositionally close to their parental liquids. During the 1988 eruption, lavas evolved with time to lower P_2O_5 contents. This was interpreted to result from fractionation of phosphorous gregoryite (Gittins and Jago, 1998), arguing that low P_2O_5 concentrations in the Na-carbonatites would prohibit fractionation of phosphate minerals (Gittins and Jago, 1998). Our experiments show that the latter argument does not hold; apatite saturation at 650 °C results in 1 wt% P_2O_5, comparable to the erupted Na-carbonatites at <600 °C. Furthermore, P_2O_5 solubilities of 5.8–13.3 wt% at 900–1100 °C (Fig. DR2) suggest that apatite fractionation could contribute a decrease in CaO of 5–12 wt% in the evolving carbonatite, depending on the temperature at which apatite saturation is achieved.

Na-Carbonatites: Fractionated Derivatives of Moderately Sodic Ca-Carbonatite Melts

Phase relationships in the synthetic Na_2CO_3-$CaCO_3$ system at 1 kbar (Fig. 1) show that nyerereite melts congruently at 817 °C, and hence, two eutectics occur, which lie at 78.5 wt% and 47 wt% Na_2CO_3, 725 and 813 °C (Cooper et al., 1975). Consequently, in the synthetic system, calcite crystallization is restricted to liquids with >53 wt% CaO for a temperature range of 1300–813 °C, and the thermal barrier on the $(Na,K)_2Ca(CO_3)_2$ join prohibits a continuous differentiation from calcic to alkali carbonatites (Cooper et al., 1975).

Na-carbonatites may contain substantial concentrations of halogens, to as much as ~8 wt% fluorine and ~4 wt% chlorine (Twyman and Gittins, 1987), that typically lead to groundmass fluorite symplectitically intergrown with sylvite (Gittins and Jago, 1998). Experiments in $CaCO_3$-$NaCO_3$-F and $CaCO_3$-$NaCO_3$-CaF_2 (Jago and Gittins, 1991, and references therein) reveal that fluorine suppresses the calcite liquidus by 160–290 °C and could potentially suppress the thermal barrier on the nyerereite composition; for this, 8 wt% fluorine is required (Jago and Gittins, 1991). Our experiments show that the naturally observed halogen concentrations of 2.7 wt% F and 4 wt% Cl (Table 1) are sufficient in the complex natural system, which contains further anionic components such as sulfate and phosphate, to suppress congruent melting of nyerereite and the thermal barrier.

Based on computational modeling, Twyman and Gittins (1987) postulated a mildly alkali-bearing olivine sövite with ~8 wt% $Na_2O + K_2O$ to represent the parental composition for Oldoinyo Lengai Na-carbonatites, a composition that is similar to the result of our multiphase saturation experiments at 1000–1050 °C (Table 1). Twyman and Gittins (1987) considered calcite, apatite, biotite, Fe-Ti oxides, amphibole, and dolomite as fractionating phases; a total crystallization of ~84 wt% would be required to reach Na-carbonatites from a sövitic parent composition.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF NATURAL AND EXPERIMENTAL CARBONATITES

| | Na-carb | Carbonatite melt saturation component | | | | | | | | Melt inclusion in prv§ |
| | | calcite | | apatite | | cpx | | multiphase† | | |
T (°C)		620	1075	750	900	750	1200	1000	1050	
SiO_2	0.1	0.1	0.2	0.1	0.2	0.2	2.9	6.1	7.0	1.6
TiO_2	0.0	0.2	0.0	0.3	0.3	0.2	0.1	0.4	0.2	0.4
Al_2O_3	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0
FeO	0.3	0.1	0.0	0.1	0.6	0.4	0.7	1.7	1.4	1.5
MnO	0.4	0.5	0.0	0.4	0.4	0.4	0.1	0.4	0.1	0.3
MgO	0.4	0.5	0.1	0.0	0.0	0.0	1.1	0.5	0.7	2.4
CaO	15.9	21.6	44.1	16.5	20.4	15.8	12.3	44.1	39.8	32.5
SrO	1.5	2.7	1.2	1.3	1.6	1.3	0.7	2.8	1.0	–
BaO	1.4	3.2	0.1	0.6	0.6	0.7	0.6	0.6	0.3	0.3
Na_2O	33.6	23.4	8.6	30.6	28.5	31.0	30.0	7.4	6.6	15.3
K_2O	7.9	6.1	2.2	6.8	5.5	6.4	9.8	1.4	1.3	4.4
P_2O_5	1.0	0.2	0.4	1.9	5.8	1.0	0.9	2.9	3.7	5.3
Cl	4.0	4.5	0.6	2.5	1.4	2.0	5.2	0.4	0.6	0.0
SO_3	3.3	3.1	0.7	2.9	2.8	3.0	7.9	0.4	0.5	0.2
F	2.7	7	0.0	2.2	2.7	1.9	0.9	1.1	0.0	1.0
Total	72.5	73.3	58.2	66.2	70.8	64.3	73.3	70.3	63.3	65.2
CO_2*	27.5	26.7	41.8	33.8	29.2	35.7	26.7	29.7	36.7	34.8

Note: Na-carb—sodium carbonatite; cpx—clinopyroxene; prv—perovskite.
*CO_2 represents difference to 100.
†Multiphase = calcite + apatite + clinopyroxene
§Perovskite hosted melt inclusion from Guzmics et al. (2012)

The findings of our experiments are strongly corroborated by moderately sodic carbonatite melt inclusions found in nephelinite phenocrysts from the nearby Kerimasi volcano (Table 1; Guzmics et al., 2011, 2012). These melts contain on average 19.7 wt% $Na_2O + K_2O$, 32.5 wt% CaO, 5.3 wt% P_2O_5, and only 1.6 wt% SiO_2. Our experimental results indicate that these compositions approximate natural parents to the Na-carbonatites of Oldoinyo Lengai. The melt compositions indicate an unmixing temperature of ~1050 °C, which is in agreement with homogenization temperatures of these melt inclusions (Guzmics et al., 2012). The upper end of Ca concentrations in these melt inclusions also indicates calcite saturation at ~1050 °C (Fig. 1).

Starting from the immiscible carbonate melt composition (Guzmics et al., 2012), our fractionation model yields crystallization of 47.7% calcite, 11.5% apatite, and 1.9% clinopyroxene in order to differentiate the experimental Ca-carbonatite into the natural Na-carbonatite (Fig. 2). Experimental co-saturation in these minerals confirms that the Oldoinyo Lengai Na-carbonatite can be back-fractionated to melts very similar to the calcic Kerimasi carbonatite melt inclusions; the best fit is obtained at 1000–1050 °C (Table 1). Therefore, the unique sodic character of the Na-carbonatites results from fractionation of moderately alkali-rich Ca-carbonatites that unmix from nephelinites. Carbonatite volcanism at Oldoinyo Lengai requires no principally different mechanism from any other carbonatite associated with alkaline silicate magmatism.

The scarcity of the Na-carbonatites in the fossil record may be the combined result of rarely met conditions for prolonged crystal fractionation in carbonatites and the very difficult preservation of such rocks under atmospheric conditions. In fact, the Na-carbonatites at Oldoinyo Lengai alter to Ca-carbonate rocks within days to months (Zaitsev and Keller, 2006), and we suspect that Na-carbonatites formed frequently in the past but had no chance to be preserved over geological times.

CONCLUSIONS

Silicate saturation experiments show low SiO_2 solubilities in Na-carbonatite melts, even at high temperatures. Any major reaction involving silicate minerals should therefore be peritectic and conserve relatively low SiO_2 contents in the carbonatite melt. The formation of euhedral wollastonite and diopside is a result of peritectic reaction of augitic clinopyroxene (Fig. 2) or combeite with the carbonatite at temperatures ≤900 °C. Reaction of evolving carbonatite melts with silicate crystal mushes is therefore a viable mechanism to generate the observed wollastonite-nephelinites and wollastonite cumulates at Oldoinyo Lengai.

Removal of CaO through calcite and apatite fractionation progressively shifts the carbonatite melt composition toward Na-carbonatite. The thermal barrier of the synthetic system is suppressed in the natural system, which instead has a peritectic at ~630 °C where calcite disappears in favor of nyerereite (Fig. 1). Nyerereite is then the liquidus phase of the Na-carbonatites between 630 °C and eruption temperatures of 490–595 °C.

Our experiments show that Na-carbonatites derive from Ca-carbonatites with 8–9 wt% $Na_2O + K_2O$. We postulate that in general, both Ca-carbonatites and Na-carbonatites have similar parent melts, i.e., moderately alkaline Ca-carbonatites. The global Ca-carbonatite array has alkalis at trace concentrations; however, such values cannot represent true liquid compositions. Most of these carbonatites crystallize biotite and/or Na-rich clinopyroxene, yet measured bulk compositions have no alkalis other than those hosted in these two minerals. Consequentially, the former liquid from which sodic and potassic phases crystallized lost its original alkali content during crystallization, implying that Ca-carbonatite liquid compositions are significantly more alkaline than what is preserved in the fossil carbonatite rock record.

REFERENCES CITED

Chen, W., Kamenetsky, V.S., and Simonetti, A., 2013, Evidence for the alkaline nature of parental carbonatite melts at Oka complex in Canada: Nature Communications, v. 4, 2687, doi:10.1038/ncomms3687.

Church, A.A., and Jones, A.P., 1995, Silicate-carbonate immiscibility at Oldoinyo Lengai: Journal of Petrology, v. 36, p. 869–889, doi:10.1093/petrology/36.4.869.

Cooper, A.F., Gittins, J., and Tuttle, O.F., 1975, The system Na_2CO_3-K_2CO_3-$CaCO_3$ at 1 kilobar and its significance in carbonatite petrogenesis: American Journal of Science, v. 275, p. 534–560, doi:10.2475/ajs.275.5.534.

Freestone, I.C., and Hamilton, D.L., 1980, The role of liquid immiscibility in the genesis of carbonatites—An experimental study: Contributions to Mineralogy and Petrology, v. 73, p. 105–117, doi:10.1007/BF00371385.

Gittins, J., and Jago, B.C., 1998, Differentiation of natrocarbonatite magma at Oldoinyo Lengai volcano, Tanzania: Mineralogical Magazine, v. 62, p. 759–768, doi:10.1180/002646198548142.

Guest, N.J., 1956, The volcanic activity of Oldoinyo Lengai, 1954: Geological Survey of Tanganyika Records, v. 4, p. 56–59.

Guzmics, T., Mitchell, R.H., Szabó, C., Berkesi, M., Milke, R., and Abart, R., 2011, Carbonatite melt inclusions in coexisting magnetite, apatite and monticellite in Kerimasi calciocarbonatite, Tanzania: Melt evolution and petrogenesis: Contributions to Mineralogy and Petrology, v. 161, p. 177–196, doi:10.1007/s00410-010-0525-z.

Guzmics, T., Mitchell, R.H., Szabó, C., Berkesi, M., Milke, R., and Ratter, K., 2012, Liquid immiscibility between silicate, carbonate and sulfide melts in melt inclusions hosted in co-precipitated minerals from Kerimasi volcano (Tanzania): Evolution of carbonated nephelinitic magma: Contributions to Mineralogy and Petrology, v. 164, p. 101–122, doi:10.1007/s00410-012-0728-6.

Jago, B.C., and Gittins, J., 1991, The role of fluorine in carbonatite magma evolution: Nature, v. 349, p. 56–58, doi:10.1038/349056a0.

Keller, J., and Hoefs, J., 1995, Stable isotope characteristics of recent natrocarbonatites from Oldoinyo Lengai, in Bell, K., and Keller, J., eds., Carbonatite volcanism, Oldoinyo Lengai and the petrogenesis of natrocarbonatites: Berlin, Springer, p. 113–123, doi:10.1007/978-3-642-79182-6_9.

Kjarsgaard, B., and Peterson, T., 1991, Nephelinite-carbonatite liquid immiscibility at Shombole volcano, East Africa: Petrographic and experimental evidence: Mineralogy and Petrology, v. 43, p. 293–314, doi:10.1007/BF01164532.

Kjarsgaard, B.A., Hamilton, D.L., and Peterson, T.D., 1995, Peralkaline nephelinite/carbonatite liquid immiscibility: Comparison of phase compositions in experiments and natural lavas from Oldoinyo Lengai, in Bell, K., and Keller, J., eds., Carbonatite volcanism, Oldoinyo Lengai and the petrogenesis of natrocarbonatites: Berlin, Springer, p. 163–190, doi:10.1007/978-3-642-79182-6_13.

Le Bas, M.J., 1981, Carbonatite magmas: Mineralogical Magazine, v. 44, p. 133–140, doi:10.1180/minmag.1981.044.334.02.

Mattsson, H.B., and Reusser, E., 2010, Mineralogical and geochemical characterization of ashes from an early phase of the explosive September 2007 eruption of Oldoinyo Lengai (Tanzania): Journal of African Earth Sciences, v. 58, p. 752–763, doi:10.1016/j.jafrearsci.2010.06.005.

Milton, C., 1968, The "natrocarbonatite lava" of Oldoinyo Lengai, Tanzania: Geological Society of America Abstracts with Programs, 1968, p. 202.

Mitchell, R.H., 2009, Peralkaline nephelinite-natrocarbonatite immiscibility and carbonatite assimilation at Oldoinyo Lengai, Tanzania: Contributions to Mineralogy and Petrology, v. 158, p. 589–598, doi:10.1007/s00410-009-0398-1.

Nielsen, T.F.D., Solovova, I.P., and Veksler, I.V., 1997, Parental melts of melilitolite and origin of alkaline carbonatite: Evidence from crystallized melt inclusions, Gardiner complex: Contributions to Mineralogy and Petrology, v. 126, p. 331–344, doi:10.1007/s004100050254.

Twyman, J.D., and Gittins, J., 1987, Alkalic carbonatite magmas: Parental or derivative?, in Fitton, J.G., and Upton, B.G.J., eds., Alkaline igneous rocks: Geological Society of London Special Publication 30, p. 85–94, doi:10.1144/GSL.SP.1987.030.01.06.

Zaitsev, A.N., and Keller, J., 2006, Mineralogical and chemical transformation of Oldoinyo Lengai natrocarbonatites, Tanzania: Lithos, v. 91, p. 191–207, doi:10.1016/j.lithos.2006.03.018.