A common origin of carbonatite magmas

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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-carbonatites. The volcano’s recent major explosive eruptions yielded a mix of nepheline 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. SiO2 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 predominately consist of nyerereite [{Na,K}2Ca(CO3)2] and gregoryite [{Na, Ca, K}2.5CO3] phenocrysts embedded in a heterogeneously quenched matrix of Ba-rich nyerereite, gregoryite, Na-sylvinite, 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(CO3)2 (nyerereite-fairchildite solid solution), while the Na-carbonatites are more alkaline than this composition (Figs. 1 and 2B). The Na-carbonatites may be 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., 1991), melting of Na-evaporites (Milton, 1968) and gregoryite [(Na, Ca x, K)2-xCO3] phenocrysts embedded in a heterogeneous matrix.

In general, fossil carbonatites preserve alkalis at trace concentrations; however, several relatively young intrusive Ca-carbonatites (Gardiner, Greenland; Kerimasi, Tanzania; Oka, Canada) also contain Na-K-Ca-carbonate inclusions indicating the presence of alkalis during carbonatite crystallization (Nielsen et al., 1997; Guzmics et al., 2011; Chen and others, 2013). At Oldoinyo Lengai (an East African Rift carbonatite volcano in Tanzania), melt inclusions in minerals of the erupted carbonate magma point to parental carbonatite compositions with 25–44 wt% Na2O + K2O 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 Na2O + K2O (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 SiO2-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 and others, 1995). In addition, the low...
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,O decreases from 23.3 to 8.6 wt%, and K,O, F, Cl, Ba, and SO3 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,O4 contents as high as 31.9 and 23.3 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 carbonate melt quenches to the commonly observed nyerereite-gregoryite groundmass; at more elevated temperatures (>1100 °C) small resolutate apatite quench crystals (≤50 μm) develop within the carbonate melt (Fig. 2). Abundant vapor void space is present at temperatures exceeding 1100 °C.

Conserving Low SiO2 Contents in Carbonatite Melts at Subvolcanic Conditions

We find that saturation in clinopyroxene, combeite, nepheline, wollastonite, and nyerereite has small effects on the carbonate melt composition regardless of temperature (Table DR2). Reacting the Na-carbonatite with natural augitic clinopyroxene confirms a SiO2 solubility of 0.2–2.9 wt% at 750–1200 °C at subvolcanic pressures, leaving little leeway for dissolving silicates in carbonate 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 SiO2 changes little. This is in line with the observed low SiO2 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).
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 carbonate 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 carbonate melt. Saturating the Na-carbonatite melt in calcite, apatite, clinopyroxene, wollastonite, nepheline, combeite, and nyerereite results in Na2O + K2O 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 carbonate melt is characterized by 6.1–7.0 wt% SiO2, 39.8–44.1 wt% CaO, and Na2O + K2O 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).

Na-carbonatites 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 symplectically intergrown with sylivite (Gittins and Jago, 1998). Experiments in CaCO3-NaCO3-F and CaCO3-NaCO3-CaF2 (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 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 P2O5 contents. This was interpreted to result from fractionation of phosphorous gregoryite (Gittins and Jago, 1998), arguing that low P2O5 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% P2O5, comparable to the erupted Na-carbonatites at <600 °C. Furthermore, P2O5 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 Na2CO3-CaCO3 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% Na2CO3, 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(CO3)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 symplectically intergrown with sylvite (Gittins and Jago, 1998). Experiments in CaCO3-NaCO3-F and CaCO3-NaCO3-CaF2 (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 sōvite with ~8 wt% Na2O + K2O 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 sōvitic parent composition.
The findings of our experiments are strongly corroborated by moderately sodic carbonatite melt inclusions found in nepheline phenocrysts from the nearby Kerimasi volcano (Table 1; Guzmics et al., 2011, 2012). These melts contain on average 19.7 wt% Na$_2$O + K$_2$O, 32.5 wt% CaO, 5.3 wt% P$_2$O$_5$, 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 nephelines. 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 carbonate melt. The formation of euhedral wollastonite and diopside is a result of peritectic reaction of augitic clinopyroxene (Fig. 2) or combeite with the carbonate at temperatures ≤900 °C. Reaction of evolving carbonate melts with silicate crystal mushes is therefore a viable mechanism to generate the observed wollastonite-nephelines and wollastonite cumulates at Oldoinyo Lengai.

Removal of CaO through calcite and apatite fractionation progressively shifts the carbonate 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 liquids 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$_2$O + K$_2$O. 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. Consequently, 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.

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