

The genesis of natrocarbonatites: Constraints from experimental petrology and trace element partition coefficients

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Despite the widespread studies on natrocarbonatites from Oldoinyo Lengai, their petrogenesis remains controversial. The two most common hypotheses which are used to explain their origin are: (1) closed system crystal fractionation of a primary mantle-derived sodic, dolomitic carbonatite magma (Sweeney *et al.*, 1995); or (2) products of liquid immiscibility at crustal pressures from a wollastonite nephelinite magma (Kjarsgaard *et al.*, 1995). An important observation relevant to the natrocarbonatite petrogenesis problem is recognition that both silicate-free and silicate-bearing natrocarbonatites are present at Oldoinyo Lengai (Petibon *et al.*, 1998). Here we present the trace element data obtained on experimental charges using mixtures of natural wollastonite nephelinite HOL14 and silicate-bearing natrocarbonatite OL5. Experiments were performed at 20, 40 and 100 MPa and 550–900°C.

Run products typically consist of silicate glass and/or quenched carbonate liquid plus crystals (mainly nepheline, clinopyroxene, wollastonite, melanite garnet, melilite, nyerereite and gregoryite), with a co-existing fluid phase. Minor crystal phases observed include combeite, perovskite, titanite, apatite, vishnevite, sodalite, alkali feldspar, spinel and pyrrhotite. The trace element compositions for V, Rb, Sr, Y, Ba, rare earth elements (*REE*), and high field strength elements (HFSE) of quenched liquids and solid phases were determined by laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS).

Two liquid trace element partition coefficients were determined for silicate and carbonate liquid pairs for experiments at $P = 20, 40, \text{ and } 100 \text{ MPa}$ and $T = 750\text{--}900^\circ\text{C}$. For all P-T-X conditions, Ba, Sr and V partition into the carbonate liquid; whereas heavy *REE* (*HREE*) and HFSE partition into the silicate liquid. Depending on P-T-X conditions, Rb, Y, light *REE* (*LREE*) and medium *REE* (*MREE*) partition into either the carbonate or the silicate liquid. Partition coefficients between silicate and carbonate

liquids ($D_{\text{LS/LC}}$) tend to decrease with increasing pressure. No effect of temperature was measured on $D_{\text{LS/LC}}$ for HFSE, but $D_{\text{LS/LC}}$ tend to decrease with decreasing temperature for low field strength elements (LFSE). The effect of decreasing temperature on the $D_{\text{LS/LC}}$ values for the *REE* is to cause an overall decrease and a fractionation of the *LREE* and *HREE*. The effect of the latter is such that the slope of the *REE* $D_{\text{LS/LC}}$ pattern steepens ($\text{Yb/La} - 3.0_{(900^\circ\text{C})}$ to $12_{(800^\circ\text{C})}$). The effect of composition on two liquid partition coefficients was examined at 100 MPa, 900°C. With increasing carbonate content in the starting composition, $D_{\text{LS/LC}}$ values decrease and the *REE* $D_{\text{LS/LC}}$ pattern steepens. Two important observations from this study are that: (1) *LREE* and *LREE* have $D_{\text{LS/LC}} < 1$ only for 100 MPa experiments; and (2) liquid immiscibility fractionates some usually coherent element pairs ($K_{\text{D}} \text{ Nb-Ta} < 1$, $K_{\text{D}} \text{ Th-U} > 1$). However, no element decoupling was measured for Zr-Hf. The observation that liquid immiscibility decouples Nb-Ta and Th-U pairs could be used to assess models of natrocarbonatite genesis.

Trace element partitioning between crystals and silicate or carbonate liquids was also studied. *MREE*, *HREE* and HFSE strongly partition into garnet. *LREE* partition into apatite and *HREE* partition into wollastonite. Most elements are incompatible in clinopyroxene, nepheline and carbonate crystals.

Experimentally determined partition coefficients are used to explain the trace element signature of natural lavas from Oldoinyo Lengai. Partition coefficients between wollastonite nephelinite HOL14 and silicate-bearing natrocarbonatite OL5 are less than 1 for *LREE*, *MREE*, Ba and Sr, but are greater than 1 for *HREE*, HFSE, Y and V. The observation that *LREE* partition into natrocarbonatite strongly suggests that immiscibility took place at $P \sim 100 \text{ MPa}$. The trace element partitioning between natural lava pairs is comparable to that exhibited by two-liquid pairs from experiments at 100 MPa, 800°C, for a starting composition containing 80

wt.% wollastonite nephelinite and 20 wt.% silicate-bearing natrocarbonatite. The $D_{LS/LC}$ REE patterns of natural lava pairs are steeper than those observed in experiments. However, the natural lavas are interpreted to have undergone liquid immiscibility at 700–750°C (Kjarsgaard *et al.*, 1995); hence the steeper D-pattern is consistent with the effect of temperature on element partitioning.

To test the convective fractionation model of Petibon *et al.* (1998), whereby silicate-bearing natrocarbonatite (e.g. OL5) differentiates to silicate-free natrocarbonatite (e.g. CML5), the trace element signatures of these two natrocarbonatite types were examined. Ba, Sr and Rb are more enriched in the silicate-free natrocarbonatite, whereas Y, REE, Zr and Nb are enriched in the silicate-bearing natrocarbonatite. Experiments on OL5 at 20 MPa have indicated a large stability field for melanite garnet and apatite. Fractionation of melanite garnet and apatite (at $T < 650^\circ\text{C}$) can explain the lower concentrations of REE and HFSE in silicate-free natrocarbonatite as compared to parental silicate-

bearing natrocarbonatite.

In summary, the trace element data are compatible with an origin of parental silicate-bearing natrocarbonatites by liquid immiscibility from a wollastonite nephelinite at $P \sim 100$ MPa and $T = 700\text{--}750^\circ\text{C}$. Parental silicate-bearing natrocarbonatite magmas differentiate via convective fractionation in shallow magma chambers (at ~ 20 MPa) to form silicate-free natrocarbonatites.

References

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