

Apatite-carbonatite melt sodium partitioning: magmatic Na₂O-contents and the origin and evolution of carbonatite magmas

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Carbonatites are carbonate-rich magmatic rocks that are intensively studied because they host most of the world's rare earth element (REE) deposits, and because they record deep Earth processes involving volatiles. Experimental petrology has been pivotal in constraining carbonatite genesis and inferring their true melt compositions, as carbonatite rocks do not constitute melts [1]. Alkalis play a critical role in carbonatite magmatism by promoting the unmixing of carbonatite melts from CO₂-rich alkaline silicate magmas [1], lowering the melt solidus, enabling and facilitating its evolution [1], and enhancing REE mobility in/around carbonatite systems [2]. Nevertheless, plutonic and fossil volcanic carbonatites exhibit alkali-poor compositions (medians of 0.28 and 0.22 wt.% Na₂O+K₂O, respectively)[1], in clear contrast to the strongly sodic lavas erupted at Oldoinyo Lengai (31-35 wt.% Na₂O)[3], and to the predictions from liquid immiscibility experiments (7-30 wt.% Na₂O+K₂O)[1].

To better constrain Na₂O^{melt}, this study investigates apatite/carbonatite melt sodium partitioning ($D_{\text{Na}}^{\text{apatite/melt}}$) experimentally at sub-volcanic conditions (100-200 MPa, 800-1050°C). Our experiments yield that REE-poor apatite has $D_{\text{Na}}^{\text{apatite/melt}} \sim 0.01$ across the investigated temperature-pressure range, whereas REE incorporation enhances $D_{\text{Na}}^{\text{apatite/melt}}$ via the substitution $\text{Na}^+ + \text{REE}^{3+} = 2\text{Ca}^{2+}$. Application of our partition coefficients to natural plutonic carbonatites yields inferred melt compositions with 5-15 wt.% Na₂O, and 15-30 wt.% for volcanic carbonatites. These results support that intrusive carbonatites are (calcite/dolomite+apatite) cumulates of a mildly sodic melt, in agreement with predictions of liquid immiscibility experiments. Melt compositions calculated for volcanic carbonatites likely reflect a protracted evolution through calcite±apatite fractionation towards strongly sodic compositions (as at Oldoinyo Lengai), alkali-loss occurring then through rapid post-eruptive alteration.

The partition coefficients yield Na-contents at the time of apatite crystallization, yet, often calcite fractionation causing passive P-enrichment is required to saturate these melts in apatite. Thus, we use existing models [4] to model Na₂O contents in the primary melts. Concluding, carbonatite magmatism is mostly mildly sodic, an argument in favor of an origin through immiscibility with alkaline silicate melts.

[1] Schmidt, Giuliani & Poli (2024), *Journal of Petrology* 65, ega105.

[2] Anenburg *et al.* (2020), *Science Advances* 6, eabb6570.

[3] Keller & Zaitsev (2012), *Lithos* 148, 45-53.