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The evolution of carbonatite melts in the upper crust: crystallization of $CaCO_3$–$MgCO_3$–Na_2CO_3 liquids

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Carbonatites are the most important source- and host-rocks of REE-(Nb) ore deposits, however, the crystallization and magmatic differentiation of ascending carbonatitic melts remains poorly understood. Magmatic carbonatites predominantly occur as carbonate-cumulates, ~41 % of which are dolomite-bearing. While stable at lithospheric mantle pressures, at crustal pressures <0.8 GPa dolomite is limited by the dolomite decarbonation reaction (dolomite→calcite+periclase+CO_2) to temperatures below the $CaCO_3$–$MgCO_3$–eutectic (~1090 °C)[1], i.e. dolomite cannot be magmatic in the $CaCO_3$–$MgCO_3$–system at mid to upper crustal pressures.

Alkalis are critical components in carbonatite melt evolution, as they suppress the liquidus of carbonatitic melts, thereby contributing to the low eruption temperatures (<600 °C) documented for carbonatites[2]. The addition of alkalis to $CaCO_3$–$MgCO_3$ also suppresses the carbonatite liquidus to temperatures of dolomite stability. This experimental study determines the liquidus phase relationships in the $CaCO_3$–$MgCO_3$–Na_2CO_3–system at upper crustal conditions (0.2 GPa, 1100-575 °C) to constrain the magmatic evolution of carbonatites, and in particular the formation of dolomite-carbonatites.

At 0.2 GPa, the $CaCO_3$–$MgCO_3$–Na_2CO_3–system is dominated by large calcite and periclase fields, with a calcite-periclase cotectic extending from the $CaCO_3$-$MgCO_3$ side of the ternary. Dolomite becomes stable on the liquidus at ≤780 °C, when melt compositions have become quite alkaline with X_{Na2CO3}≥0.35 (Na_2CO_3/($CaCO_3$+$MgCO_3$+Na_2CO_3)[molar]). The dolomite-calcite cotectic is initially peritectic (780-730 °C) with dolomite replacing calcite, but then co-crystalizes both minerals at ≤730 °C. From the $CaCO_3$-$NaCO_3$ side, a calcite-nyerereite cotectic joins the calcite-dolomite cotectic in a calcite-dolomite-nyerereite peritectic point at 625 °C and X_{Na2CO3}=0.49. Here, calcite reacts out of the system. The dolomite liquidus field is further bound by a dolomite-magnesite and dolomite-nyerereite cotectic. Ultimately, eitelite ($Na_2Mg[CO_3]_2$) replaces dolomite at X_{Na2CO3}≥0.54. The eitelite-nyererite-Na_2CO_3ss-eutectic at ~575 °C defines the minimum of the system.

Fractional crystallization trends on the $CaCO_3$–$MgCO_3$–Na_2CO_3 liquidus show that dolomite-carbonatites may crystalize from carbonatite melts (I) that are immiscible to high-Mg alkaline melts or (II) from carbonatites derived from kimberlite fractionation; while (III) mantle-derived melts start with an improbable ~20% periclase crystallization, coupled with extensive CO_2-degassing, before producing first a calcite-periclase carbonatite and then dolomite carbonatites.

[1]Schmidt et al. (2024), *J. Petrol.* **65**, egae105.
[2]Weidendorfer et al. (2017) *Geology* **45**, 507–510.