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Crustal evolution of carbonatitic melts: Insights from the $CaCO_3$–$MgCO_3$–Na_2CO_3 ternary

PHILIPP M RICHERT AND MAX W SCHMIDT
ETH Zürich

Carbonatites represent the most important host-rocks of REE-(Nb) ore deposits in the continental crust. However, the formation and particularly magmatic differentiation of ascending and crystallizing carbonatitic melts remains poorly understood. This is because intrusive carbonatite rocks are cumulates, about 1/3 of which are dolomite dominated. Yet, in the $CaCO_3$–$MgCO_3$ binary, dolomite is limited to subsolidus conditions at crustal pressures (<0.8 GPa), as dolomite reacts to calcite+periclase+CO_2 at temperatures above the $CaCO_3$–$MgCO_3$ eutectic (~1090 °C)[1]. It is therefore not possible that dolomite-bearing carbonatites crystallize from a simple $CaCO_3$ – $MgCO_3$ (+/- SiO_2) melt. To lower liquidus temperatures and thus allow for dolomitic carbonatites, alkalis and/or H_2O have been proposed as *the* critical components in carbonatite melt evolution [1], both of them potentially suppressing the liquidus surface down to the dolomite stability field.

This study determines the liquidus phase relationships in the $CaCO_3$–$MgCO_3$–Na_2CO_3 ternary at upper crustal conditions (0.2 GPa), as relevant for the intrusion of most carbonatites. Our experiments show that any calcitic or dolomitic carbonatite melt initially evolves towards a calcite-periclase cotectic and would not crystallize dolomite. Co-precipitation of periclase and calcite on the cotectic during cooling fractionates melt compositions towards higher alkalinity. Dolomite replaces periclase on the liquidus only at T <775 °C, at which (peritetic) point the melt has molar fractions of 0.35-0.4 Na_2CO_3 (X_{Na2CO3}). On the Ca-Na-side, nyerereite ($Na_2Ca[CO_3]_2$) + calcite appear on a second cotectic at T < 750 °C and $X_{Na2CO3} = 0.45$. With cooling, such melts evolve towards the calcite-dolomite cotectic. At $X_{Na2CO3} > 0.45$ and T <700 °C calcite is then no longer a liquidus phase, and is replaced by dolomite and nyerereite. The experiments show that a sufficiently alkaline melt is critical to dolomite crystallization. The phase relations and fractionation trends established here indicate that plausible primary carbonatitic melt with 10-20 % Na_2CO_3 could potentially produce dolomitic cumulates, if sufficiently differentiated. The results further suggest that calcite may react out at the dolomite-calcite-nyerereite peritectic during fractionation, and not necessarily remain a primary mineral phases in late-magmatic (dolomitic) carbonatites.

[1]Schmidt, Giuliani & Poli (2024), *J. Petrol.* **65**, egae105.