

FINE TUNING OF CARBONATE - SILICATE LIQUID IMMISCIBILITY: CO₂ - RICH ALKALINE COMPLEXES WITH AND WITHOUT CARBONATITES

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Most igneous carbonatites are thought to result from silicate-carbonate liquid immiscibility during the evolution of alkaline fluid-saturated silicate magma. This process is controlled by fluid regime and melt composition. It is instructive therefore to compare carbonatite-bearing and carbonatite-free igneous complexes with similar compositions of silicate rocks. Nielsen et al. (1997) studied melt inclusions in the melilitolites of the carbonatite-bearing Gardiner massif, Greenland and determined the compositions of melts and conditions of carbonatite melt separation. Similar melilite-bearing rocks are known in the Upper Rhinegraben igneous province (Dunworth, Wilson, 1998). This paper presents the results of a study of olivine melilitites from Mahlberg, 100 km north of Keiserstuhl. In contrast to Gardiner, the melilite-bearing rocks of the Mahlberg massif do not associate with carbonatites and the comparison of the two massifs will provide some insight into the conditions of natural carbonate-silicate liquid immiscibility.

The olivine melilitite sample (XKR 37 OM) studied is composed of olivine (Fo₈₉₋₈₂, 0.18 - 0.87 wt % CaO) and clinopyroxene phenocrysts in a fine-grained groundmass. Clinopyroxene also occurs in the groundmass, as crystalline inclusions in olivine phenocrysts, in late miarolitic cavities, and as daughter minerals in melt inclusions.

The holocrystalline groundmass consists of olivine, clinopyroxene, melilite, nepheline, phlogopite, Ti-magnetite and perovskite. There are also miarolitic aggregates up to 5 mm across. They are composed of euhedral clinopyroxene, nepheline, melilite, Ba-rich phlogopite, perovskite and Ti-magnetite crystals cemented by secondary hydrous minerals (wairakite, lawsonite, and others).

Olivine phenocrysts bear numerous melt inclusions containing a variety of daughter crystals including Fe - monticellite (10.4 wt.% FeO), olivine (Fo₈₈₋₈₃, up to 1.2 wt % CaO), clinopyroxene, melilite, Ba-rich phlogopite, nepheline, F-bearing apatite and magnetite (up to 15 wt % TiO₂). The inclusions are partially decrepitated and some of their fluid evidently leaked. Because of this, most of the inclusions were not homogenized during thermometric experiments. The melting temperatures of daughter phases ranged from 1130-1220°C. Some late and secondary melt inclusions were homogenized at 1160-1100°C.

Clinopyroxene crystals in the miarolitic aggregates contain rare silicate melt and fluid inclusions. These inclusions were homogenized at temperatures of 1100-1140°C. The density of the fluid inclusions is lower than 0.01 g/cm³.

The homogenized melt inclusions in olivine phenocrysts have low SiO₂ and high CaO (up to 18 wt. %) and alkali contents. Sodium dominates over potassium in early melts, but K/Na ratio increases with melt evolution and reaches 1.4 in the most evolved compositions. MgO contents are no higher than 9 wt %. The melts are rich in P₂O₅ (up to 1.6 wt %), BaO (up to 0.65 wt %), SrO (up to 0.3 wt %), and F (more than 0.5 wt %). The concentration of Cl was always below the electron microprobe detection limit (0.1 wt %).

In addition to melt inclusions, olivine phenocrysts contain abundant gas ± liquid fluid inclusions. They are dominated by CO₂ (melting temperature from -56.9 to -59.2°C) with a density from 0.30-0.73 g/cm³. Kaersutite was detected on the wall of one primary CO₂ fluid inclusions by Raman spectroscopy. CO₂-rich fluids were also observed in the gas bubbles of melt inclusions. All fluid inclusions are partially decrepitated.

The examination of melt and fluid inclusions suggests a considerable role of CO₂ in the genesis and evolution of magma. The maximum density of CO₂ fluid inclusions (0.73 g/cm³) corresponds to a fluid pressure of 5 kbar at 1220°C (the maximum temperature of daughter mineral resorption in melt inclusions). The maximum pressure of fluid inclusion entrapment was certainly higher, because part of fluid escaped from inclusions. The distribution of the densities of fluid inclusions in olivine suggests at least two stages of phenocryst crystallization differing in fluid regime. During early stages, cores of olivine and clinopyroxene were formed under relatively stable fluid-saturated conditions. This was followed by a rapid decrease of pressure accompanied by extensive degassing and growth of outer phenocryst zones with abundant fluid inclusions of varying density.

Coexisting silicate and carbonate melt inclusions were found in melilite from Gardiner melilitolite (Nielsen et al., 1997), indicative of silicate-carbonate liquid immiscibility and formation of alkali-rich carbonatite magmas similar to that of Oldoinyo Lengai. In contrast, melt inclusions in the Mahlberg melilitite contain no carbonate phases, which is in agreement with the absence of carbonatites in this complex. The silicate melts of the Mahlberg and Gardiner complexes are chemically similar and their differentiation occurred under essentially identical CO₂-saturated P-T conditions. There are however some minor distinctions in melt compositions, which predetermined fundamentally different evolution paths. The melts from Gardiner are in general lower in Al₂O₃ and SiO₂ at given MgO contents than those of Mahlberg. This difference is not very large but it could be critical in determining degassing behavior and carbonate stability.

Experimental investigations of silicate-carbonate liquid immiscibility (e.g. Freestone and Hamilton, 1980; Kjarsgaard and Peterson, 1991) contoured a two-liquid field in the SiO₂+Al₂O₃+TiO₂ - CaO+MgO+FeO - Na₂O+K₂O ternary diagram. On this diagram, the least evolved melts from melilitites of the Gardiner rocks fall within the field of silicate liquid, but their

differentiation (melilite fractionation) moves the melt composition toward the two-liquid boundary. This is consistent with the appearance of carbonatite melts at late stages of melt evolution. In contrast, melts from the Mahlberg melilitites were initially richer in Al (and Si) and plot further from the liquid immiscibility field. Moreover, higher Al content at high Na expanded the nepheline stability field and resulted in early nepheline crystallization (together with olivine) from the melt. The resulting liquid evolution path goes parallel to the liquid immiscibility boundary and even the most evolved melts remain outside the carbonate-silicate field. Thus, the minor differences in melt composition may have a dramatic effect on the behavior of volatile components. In the case of Gardiner, the formation of carbonate melts consumed a significant portion of CO₂ and the crystallization of evolved melts occurred under subvolcanic conditions. In contrast, the accumulation of CO₂ in the Mahlberg melt resulted eventually in rapid degassing and a catastrophic eruption.

References

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