

**Kimberlites, carbonatites, peridotites
and silicate-carbonate liquid immiscibility explained
in parts of the system $\text{CaO}-(\text{Na}_2\text{O}+\text{K}_2\text{O})-(\text{MgO}+\text{FeO})-(\text{SiO}_2+\text{Al}_2\text{O}_3)-\text{CO}_2$**

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New experimental data between 1.0 and 2.5 GPa in the system $\text{CaO}-\text{MgO}-\text{SiO}_2-\text{CO}_2$ and in selected joins through the more complex system $\text{CaO}-(\text{Na}_2\text{O}+\text{K}_2\text{O})-(\text{MgO}+\text{FeO})-(\text{SiO}_2+\text{Al}_2\text{O}_3)-\text{CO}_2$ have advanced understanding of: (1) the possible relationships among lherzolite and wehrlite, carbonate-rich liquids, and kimberlite and melilitite liquids, and (2) the effect of alkalis in promoting silicate-carbonate liquid immiscibility. A critical end-point on the solidus for peridotite- $\text{H}_2\text{O}-\text{CO}_2$ is a possible explanation for the aqueous and carbonate-rich fluid inclusions reported in diamonds by Schrauder and Navon (1994).

The nature and distribution of carbonate-rich melts in the mantle and in the context of kimberlite genesis has been of recent interest, given evidence for metasomatism by carbonate-rich melts (e.g. Rudnick et al., 1993), and discoveries of carbonate minerals in mantle xenoliths. Several investigators have interpreted rounded carbonate minerals (ocelli or globules) in xenoliths in terms of immiscible silicate and carbonate liquids (e.g. Pyle and Haggerty, 1994). The carbonate-rich mantle melts have also been related to proposed primary calciocarbonatite magmas (e.g. Bailey, 1993), or dolomitic carbonatite magmas (Harmer and Gittins, 1997).

The only way known to bring the compositions of liquids generated from mantle minerals into the low- SiO_2 range of kimberlites and other related igneous rocks is by dissolving CO_2 at high pressures (Eggler, 1974). With the discovery that carbonated lherzolite melts to a dolomitic carbonatite liquid, Wyllie and Huang (1975) provided the conceptual framework relating kimberlite magmas to liquidus paths through the phase fields between model lherzolite, and carbonatite liquids on the silicate-carbonate field boundary. There is a complex array of depth-temperature-composition paths involving magma generation, fluid migration, metasomatism, and explosive termination of rock-magma reactions associated with the evolution of dense vapor (Wyllie and Huang, 1976), and the prospect of silicate-carbonate liquid immiscibility at some stage (Lee and Wyllie, 1997a). These paths may be deduced from the study of exposed rocks, but they must be calibrated by experimental petrology.

The key phase elements illustrating and controlling magmatic processes in the model system $\text{CaO}-\text{MgO}-\text{SiO}_2-\text{CO}_2$ are: (1) the silicate-carbonate liquidus field boundaries between (2) the silicate liquidus and (3) the carbonate (or periclase) liquidus; and (4) the vapor-absent silicate liquidus field boundaries involving peridotite minerals which connect liquids on the silicate-carbonate field boundaries to the CO_2 -free eutectics and peritectics. With addition of alkalis, the carbonate liquidus field extends to alkali carbonates, and additional phase elements are introduced. As represented within the pseudoquaternary system $\text{CaO}-(\text{Na}_2\text{O}+\text{K}_2\text{O})-(\text{MgO}+\text{FeO})-(\text{SiO}_2+\text{Al}_2\text{O}_3)-\text{CO}_2$, these are (5) a liquid miscibility gap which appears within the silicate liquidus field, bounded by a surface (6), which gives the compositions of coexisting silicate- CO_2 and carbonate-rich liquids.

The Silicate-carbonate Liquidus Field Boundary: Carbonatite Liquid Compositions

The near-solidus magmas generated in carbonated (dolomite/magnesite)-peridotite at depths greater than $\sim 70\text{ km}$ (2 GPa) lie on the silicate-carbonate liquidus field boundary. The dolomitic liquid composition ($\sim 70\%$ CaCO_3) determined in the model system for dolomite-lherzolite at ~ 3 GPa was later confirmed by analysis of quenched liquids in experiments with whole rock lherzolite systems (e.g. Wallace and Green, 1988; Thibault et al., 1992; Sweeney, 1994). There are literature claims

that when magnesite replaces subsolidus dolomite with increasing pressure, liquid compositions sweep toward higher Mg, kimberlitic compositions; however, the control of liquid compositions by the liquidus profile for $\text{CaCO}_3\text{-MgCO}_3$ (Irving and Wyllie, 1975) ensures that this change does not occur. Dalton and Presnall (1997) have confirmed that the liquid composition remains dolomitic to at least 7 GPa, even when the subsolidus carbonate has changed to magnesite.

At depths shallower than ~ 70 km, wehrlite is the only peridotite which can be carbonated and thus yield carbonate-rich magmas (Wyllie and Huang, 1976). At this limiting depth, the near-solidus liquid for dolomite-lherzolite and dolomite-wehrlite is the same, about 60% CaCO_3 (CC)-30% MgCO_3 (MC)-10% Silicate. With decreasing pressure from depths of ~ 70 km (2 GPa) to ~ 35 km (1 GPa), the near-solidus liquid coexisting with wehrlite- CO_2 changes to about 70% CC-15% MC-15% Silicate, as located by our new experiments. Dalton and Wood (1993) reported liquids coexisting with model wehrlite at 1.5 GPa approaching 90% CaCO_3 , with low silicate content; we believe that their analyses of quenched liquids differ from the compositions of liquids present during the experiments. We find silicate-carbonate-boundary liquids with silicate contents ranging from about 10% for dolomitic compositions to 15% for more CaCO_3 -rich compositions. We find no evidence for the existence of silicate-derived liquids with 90-99% CaCO_3 , and we conclude that the calcite ocelli described in mantle xenoliths must represent rounded crystals and not quenched liquids (Pyle and Haggerty, 1994; Kogarko et al., 1995; Ionov et al., 1996).

The Silicate-carbonate Liquid Miscibility Gap

This is a "forbidden volume" for magmas. Under normal mantle conditions with primitive (magnesian) compositions, magmatic paths between ~ 70 and 35 km depth are unlikely to intersect the miscibility gap according to experiments by Baker and Wyllie (1990) and Lee and Wyllie (1997b). Increasing K/Na or CO_2 may enlarge the miscibility gap (personal communication, Brooker and Holloway, Kjarsgaard, Ulmer). Experimentally determined phase boundaries indicate that immiscible carbonatite magmas in Mg-free systems contain no more than 80% CaCO_3 , and at least 15% $(\text{Na,K})_2\text{CO}_3$. Calcite ocelli in xenoliths cannot represent immiscible liquids.

The Carbonate Liquidus

The carbonate content of magmas associated with silicate parents is limited by the position of the silicate-carbonate liquidus boundary. The liquidus for primary carbonate is thus another "forbidden volume" for magmas.

The Vapor-absent Silicate Liquidus Field Boundaries

The carbonatite magmas generated from CO_2 -bearing peridotites are the first (lowest-temperature) part of a continuum of small-volume partial melts including melilitites and kimberlites, which follow vapor-absent liquidus paths from the silicate-carbonate field boundary toward the volatile-free model peridotite assemblages. Host rock and pressure control the critical variables (1) Ca/Mg of liquid as $f(T)$, and (2) increase in %liquid as $f(T)$. For the lherzolite assemblage, Huang and Wyllie (1976), Baker and Wyllie (1989) and Moore and Wood (1997) determined that in the 2-3 GPa range, the liquid remains carbonatitic through at least 200°C above the solidus. Dalton and Presnall (1997) reported that at 7 GPa, in contrast, only a small increase in temperature is sufficient to change the liquid composition all the way from carbonatite to kimberlitic. The phase relationships in model systems indicate that there is a large field of carbonatitic liquid coexisting with peridotite assemblages, grading with increasing temperature into more silicate-rich liquids; there is no restricted "carbonatite-liquid stability field" limited by amphibole breakdown.

Estimated positions of the vapor-absent liquidus paths for harzburgite in our diagrams pass through the region of projected kimberlites, with higher Mg/Ca than the "lherzolite" liquidus paths.

Our new results show that the vapor-absent fusion path for wehrlite at 1 GPa has significantly

higher Ca/Mg than that for lherzolite. The compositions of Italian carbonatite-melilitite associations (Stoppa and Woolley, 1997) project into this region, suggesting that their origin might be related to shallow wehrlite mantle. Other melilitites with a range of Ca/Mg occupy the volume between the 1 GPa "wehrlite path" and the "lherzolite path", perhaps related to wehrlite mantle at depths between 70 and 35 km.

Rising carbonate-rich melts

Carbonate-rich melts with compositions on the lherzolite vapor-absent field boundary retaining equilibrium with mantle will react, crystallize and release CO₂ vapor at depths ~70km, precipitating lherzolite with relatively high clinopyroxene/olivine ratio, thus causing a minor transformation of lherzolite toward wehrlite. The release of CO₂ could facilitate explosive eruption of primary dolomitic carbonatite magmas, with intrusive style approximating that of kimberlites. At shallower depths, only wehrlite can coexist with carbonatite magma. If dolomitic carbonatite liquid rising above the ~70km level metasomatizes lherzolite to protective wehrlite, the liquid can continue to rise, with continuous release of CO₂ vapor. From 70 km to 35 km depth (2-1 GPa), the CaCO₃ component of the liquid near the solidus increases from ~67% to ~82% (reduced in real rocks by the FeO associated with the dolomite component), and the silicate component increases. This enrichment in CaCO₃ component is smaller, through a greater depth interval, than that proposed by Dalton and Wood (1993). The CaCO₃ component of the liquid is also reduced according to how high above the solidus the reaction is occurring.

Critical fluids between carbonatite and dense aqueous vapor

The simplest interpretation for the reported inclusions in diamonds with compositions ranging between end-members carbonatite and aqueous, siliceous fluid (Schrauder and Navon, 1994) is that these fluids were sampled in a mantle volume somewhat deeper than the pressure of a second critical endpoint on the solidus for peridotite-H₂O-CO₂ (Wyllie and Ryabchikov, 1997).

Selected References

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