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A microprobe investigation of the olivines in a suite of olivine melilitites from Namaqualand, South Africa (previously described by Moore, 1973) reveals a complex and unusual pattern of chemical variation. Fig. 1 illustrates Mg/(Mg + Fe²⁺) - Ni relations defined by olivines from three thin sections cut from one rock specimen (Dik-9, 12,6% MgO). Petrographic and chemical criteria make it possible to distinguish three distinct olivine sub-populations in this and other samples studied:

(a) The first suite consists of the dominant (95% of all olivines) population of euhedral (and sometimes skeletal) olivines that will be termed "hoppers" as they bear a striking resemblance to the growth forms described by Donaldson (1976), with sharply defined crystal edges and corners in contrast to the rounding that would be expected from resorption processes. Some of the olivines enclose groundmass minerals that have apparently crystallized from trapped liquids, which would seem most likely to have been included during rapid crystal growth. Hopper morphology is best developed in the Mg-poor volcanics, possibly reflecting compositional control on growth forms. The interiors of the hoppers define a compositional trend of decreasing Mg/Fe with decreasing Ni, while the olivine margins are characterized by a narrow (100um) rind that shows continued Ni depletion, but strong reversed zoning with respect to Mg/Fe together with marked Ca-enrichment. The margin compositions correspond to those of late-crystallizing olivine microphenocrysts, and apparently reflect equilibration of the hopper margin in response to late-stage changes in the magma composition or conditions of crystallization. Although the hoppers dominate the phenocryst population in all samples studied, major and trace element variations in bulk-rock compositions cannot be explained by crystal fractionation of hopper type olivines. (Moore, Ph.D. thesis (in preparation).

(b) The second suite consists of ragged anhedra with undulose extinction and compositions (Fo₀₁, 0.40%NiO), that fall within the range found for presumed mantle olivines. Such individuals are only common in one of the pipes studied, and this pipe is unusual in having numerous ultrabasic inclusions mainly dunites (Fo₀₂, 0.40%NiO), but also rare garnet lherzolites which appear to have equilibrated at 38Kb and 960°C. (Moore, 1973). This second olivine groups is excluded from further discussion since we believe that they are probably of exotic origin.

(c) The third suite consists of rare anhedral or subhedral olivines that are enriched in Fe and Mn (>1%MnO in some individuals) and markedly depleted in Ni relative to the remaining olivines in the same rock specimen. We have given these the name of high iron, low nickel (HIIN) olivines. Marginal zonation analogous to that displayed by the hoppers results in HIIN edges being enriched in Mg and Ni relative to the cores. (Note that the hoppers have margins relatively enriched in Mg but <u>depleted</u> in Ni.) Representatives of the HIIN suite can be distinguished petrographically by their relatively large size, absence of marked undulose extinction and by the presence of fluid inclusions about their margins and in trains (presumably representing annealed fractures) that traverse the olivine interiors. Data from a range of specimens indicates that Mg/(Mg + Fe²⁺) of the HIIN olivines varies sympathetically with that of the bulk rock, which, together with the subhedral outline of some of the HIIN olivines would indicate that they are true phenocrysts and not accidental inclusions.

Since we believe that both HILN and hopper olivines are phenocrysts from the same magma we must suggest appropriate processes to explain their radically different compositions.

On the basis of their morphology and restricted occurrence we have made the assumption that the HILN olivines crystallized before the hopper olivines, and thus that they crystallized from a magma which did not have unusually low Mg or Ni content (in view of the hopper compositions). It is also unlikely that the HILN composition results from low Ni⁺⁺ distribution coefficients since the high temperatures (Leeman, 1974) or high MgO contents (Hart, 1976) necessary to achieve this would result in the crystallization of a more magnesian olivine. We therefore suggest that the peculiar compositional characteristics of the HILN olivines reflect crystallization at low oxygen activities, significantly below the Ni/NiO buffer but above the Fe/FeO buffer. Crystallization of these olivines at low fO₂ would result in high Fe²⁺/Fe³⁺, Mn²⁺/Mn³⁺ and Ni^O/Ni²⁺ ratios in the magma thus producing high Fe and Mn combined with low Ni in the olivines crystallizing in equilibrium with such a liquid.

The crystallization of hopper olivines could take place at higher fO_2 (above Ni/NiO) giving rise to substantially higher Mg/Fe ratios and higher Ni contents in the olivines crystallizing under these conditions. The Mg and Ni enriched rims surrounding the HILN olivines may reflect partial re-equilibration under the new fO_2 conditions, or may be overgrowths under these conditions.

The trend of decreasing Mg/Fe ratio and decreasing Ni content in the cores of the hopper olivines is seen as a response to falling temperature and the progressive removal of Ni by Raleigh-type crystallization. The reversed-zoned hopper margins may reflect extensive crystallization of Fe-Ti oxide phases or extreme late-stage oxidation of the magma.

Having suggested major changes in f_{02} during the crystallization of the olivine melilitite magma, let us now consider a possible explanation for this crystallization path. Recent experimental studies, for instance Brey and Green (1977) have stressed the importance of C_{02} in the generation of olivine melilitites. It therefore seems plausible that a gas buffer involving C_{02} may have initially maintained the olivine melilitite magma at low oxygen fugacities close to or on the carbon saturation surface. Equations summarized by Heubner (1971) indicate that the carbon - gas buffer will be below the wustite - magnetite buffer, and thus well below the Ni/NiO buffer at high pressures and temperatures (10 - 50Kb, 1000 - 1300°C). Under such conditions, a_{NiO} in the liquid will be held at low values and metallic Ni will be formed, while Fe³⁺/Fe²⁺ and hence Mg/Fe²⁺ ratios will be relatively low. These conditions of low oxygen activity are considered responsible for the compositional characteristics of the HILN olivines. Ilmenite is a rare phase in the olivine melilitites and may similarly have crystallized from such a strongly reduced magma.

Reduction in pressure and loss of volatiles during magma ascent would be expected to lead to a dramatic increase in oxygen activities and hence in Ni^{2+}/Ni^{0} , Fe^{3+}/Fe^{2+} and Mg/Fe²⁺ ratios in the melt. Furthermore, liquidus temperatures would increase, and we suggest that the result would be the rapid crystallization of the relatively Mg and Ni enriched hopper olivines and HILN rims. The marginal fluid inclusions in the HILN olivines may reflect the onset of volatile loss.

Various authors (e.g. Taljaard, 1936; Yoder, 1975) have implied a close genetic relationship between olivine melilitites and kimberlites, and it is therefore possible that kimberlite mineralogy may reflect the effects of exterior oxygen fugacity control. Low fO_2 in kimberlite magmas would strongly affect Cr^{2+}/Cr^{3+} ratios which could account for the crystallization of phases such as chromium-rich ilmenite. In addition, Haggerty (1975) has described some reversed-zoned ilmenites with complex reaction rims which he ascribed to changing fO_2 conditions, and Gurney, Jakob and Dawson (this volume) describe discrete megacrysts from the Monastery Kimberlite, some of which may well prove to be the equivalents of our HILN olivines.



Fig 1 (a) Plot of all olivine analyses from sample DiK-9. Inverted triangles: HILN olivines; Solid dots: Hopper interiors; Open circles: edges and microphenocrysts. Remaining symbols are traverses across three olivines with unusual compositional zonation.

Fig 1 (b) Diagrammatic representation of the fields for HILN, hopper and groundmass olivines. Dotted lines connect points from traverses across olivines with unusual zonation towards hopper centres and edge compositions.

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