THE OKA CARBONATITE COMPLEX: MAGNETITE COMPOSITIONS AND THE ROLE OF IMMISCIBLE SILICATE LIQUIDS

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A detailed microprobe study has been undertaken to characterize the variations in magnetite compositions between carbonatite assemblages and the associated alkaline igneous rocks of the Oka carbonatite complex. Within the context of an immiscible liquid and/or mechanical unmixing hypothesis for the generation of a carbonatite magma, the data indicate that the probable segregated silicate counterpart to these carbonatites is a melteigite-ijolite of the nephelinite series. These new data are consistent with the experimental work in synthetic "carbonatite"-silicate systems (Koster Van Groos and Wyllie, 1966, 1968). ⁸⁷Sr/⁸⁶Sr ratios, and oxygen and carbon isotope data (Taylor, 1967) also substantiate this "next of kin" relationship.

The carbonatitic magnetites in general are jacobsite-magnetitess. MnO ranges from 1.5 to 13.5 wt%, averaging about 10 wt%. Manganese depletion is generally indicated from crystal core to mantle. Late TiO₂ enrichment (3-8 wt%) accompanies MnO depletion in those magnetites with less than 5 wt% MnO. MgO and Al₂O₃ are virtually constant ranging from 1-4 and 0-3 wt% respectively, (excluding mantle reaction relations, which are generally present). Late MgO-Al₂O₃ depletion may be present, but pleonaste exsolution contributes to this uncertainty. The carbonatite ilmenites are ilmenite-pyrophanite solid solutions ranging from 25-75 mole % pyrophanite. They appear as discrete phases or as exsolution in low MnO (approximately 3%) magnetite. These also exhibit disequilibrium/reaction relationships with the calcite matrix (producing a Mn-siderite). Clean pyrophanite survives only as an exsolved phase or if crystals are wedged between magnetite grains, partially insulated from calcite. The reaction rim texture of the magnetites in the sovite matrix suggests the possibility that they may have been transported in a mobile carbonate liquid upon encountering a silicate-carbonate immiscibility field.

The associated alkaline ultrabasic rocks in their relative order of emplacement are the jacupirangite-okaite series (titanaugite pyroxenitesmelilitites), the melteigite-urtite series of the nephelinites (aegerineaugite + nepheline rocks), and the alnoite-kimberlite diatremes. The magnetites of the jacupirangite-okaite series contain significant MnO (5.5 wt%) on the okaite to Ne-okaite end of the series tapering down toward the jacupirangitic value of 3.5 wt% (refer to figure). TiO₂ ranges from 1.5 to 5.5 wt% with a minimum in Ne-okaite and a maximum in jacupirangite. MgO remains relatively uniform at 3.5 wt% throughout the series, whereas Al_2O_3 reaches a maximum of 3.3 wt% in Ne-okaite and a minimum of 2.5 wt% in jacupirangite.

The magnetite in alnoites are low in MnO (0.5-2.0 wt%), high in TiO_2 (8.5 wt%) and MgO (7.5 wt%), and have intermediate values of Al_2O_3 (2-4 wt%). The magnetites in the Isle Bizard kimberlite have the lowest MnO content of any of the associated rocks (less than 0.25 wt%). TiO_2 is a steady 5.5 wt%, Al_2O_3 less than 1 wt%, and MgO increases from 3.5 to 4.5 wt% from core to mantle (clearly very distant from the type of compositions seen in any of the carbonatites).

The magnetites of the nephelinite series (melteigite-urtite) are only abundant in the intermediate member, ijolite (aegerine-augite/nepheline = 1:1), in which MnO reaches a maximum for the alkaline silicate rocks at 8.5 wt%; TiO₂, Al₂O₃, and MgO average 4.5, 2.2, and 2.8 wt% respectively. These

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values are an extremely close approximation to those of magnetites in the aegerine pyroxene-bearing carbonatite (MnO-7.5 wt%, TiO₂-3.5-4.0 wt%, Al₂O₃ less than 1 wt%, MgO-1.5 wt%). The extreme compositional similarity in magnetite suggests a comagmatic relationship. Although it is widely recognized that magnetite is compositionally responsive to minor environmental changes, the close similarity is unexpected because: (1) the response of component activities anticipated to accompany any form of segregation process should be much greater than that observed; and (2) equilibrium across an immiscible surface may be expected if surface to volume ratios are small, a situation which is clearly not the case at Oka. Further support for immiscibility is provided by oxidation trends in sovite and in ijolite magnetites and these trends are consistent with an increase in CO_2 activity and a concommitant decrease in $\frac{a}{SiO_2}$.

Experimental data in the plane NaAlSi $_{3}O_8$ -Na $_2CO_3$ -H $_2O$ through the quinary system Na $_2O$ -Al $_2O_3$ -SiO $_2$ -CO $_2$ -H $_2O$ (Koster Van Groos and Wyllie, 1968) indicate that fluid immiscibility relations, which are synthetically analogous to co-existing nepheline or ijolite magmas, carbonatite melts, and fenitizing solutions, vary relative to the proportions and partial pressures of CO $_2$ and H $_2O$ as well as P_{total}. Our data indicate that an ijolitic magma is the closest approximation to an equilibrium situation with respect to carbonatitic magnetite stability.

It is emphasized, that considering the extreme range of \underline{a}_{Si02} indicated in sovite mineralogy, that carbonate-silicate immiscibility is not independent of fractional crystallization and should not be considered as a singular event, but more probably as part of an ongoing periodic decarbonationcarbonation process (eg. as alkalis become locally concentrated in response to fractional crystallization).

The following points emphasize the apparent non-singularity of carbonatitic segregation as a process, and contrast the Oka complex with other carbonatitic segregation environments:

-Magnesian carbonatite segregation and subsequent small scale diapiric structures have been observed in the Benfontein kimberlite sills near Kimberley, S. Africa (Dawson and Hawthorne, 1973). Segregation bubbles were shown to need not result from immiscibility in the classical sense, but from density and viscosity contrast, within a rapidly cooling sill.

-Natrocarbonatite lava has been observed by Dawson (1962) in eruption at Oldoinyo Lengai in Tanzania.

-The Oka Carbonatite Complex (Quebec, Canada), has eroded to ring-dike and cone sheet level. The carbonatite is typically neither highly magnesian nor highly sodic. The carbonatite igneous textures vary from phaneritic to porphyritic, and silicates, oxides and immiscible sulfides are present in a calcitic matrix of highly variable matrix to phenocryst ratio, which is typically >0.8. These rocks are also strongly flow-foliated, consistent with the overall ring-dike structure and mode of emplacement.

In summary, although no new model for carbonatite genesis is proposed in this paper, additional support is offered for deep-seated "kimberlitic" devolitilization as a source of CO_2 which is apparently largely responsible for higher level fractionation and immiscibility/segregation processes in upper mantle-low crustal continental rocks. This paper does not establish a detailed genealogy of alkalic-carbonatitic associations, but does identify the carbonate-silicate assemblage which most closely approximates an equilibrium situation. This assemblage is ijolite and aegerine carbonatite. A final and noteworthy comment is that carbonatitic opaque mineral oxides are charac-

terized by high MnO contents, a feature which is also apparent in numerous late stage kimberlitic constituents where high CO_2 activity is apparent.

<u>References</u>: Dawson (1962). Nature, <u>195</u>, 1075; Dawson and Hawthorne (1973). J. Geol. Soc. Lon. <u>129</u>, 61; Taylor et al., (1967). Geochim. et Cosmochim. Acta <u>31</u>, 407; Koster Van Groos and Wyllie (1966). Am. Jour. Sci. <u>264</u>, 234; Koster Van Groos and Wyllie (1968). Am. Jour. Sci. <u>266</u>, 932.



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