EXPERIMENTAL STUDIES BEARING ON THE ORIGIN OF THE ALKALIC ROCK-CARBONATITE COMPLEX AND NIOBIUM MINERALIZATION AT OKA, QUEBEC

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ABSTRACT

In the join $NaAlSiO_4$–$CaCO_3$–H_2O at 1000 bars pressure, carbonate-bearing liquid coexists with a sodic aqueous vapour phase and crystalline assemblages of nepheline, melilite, hydroxyhauyne, cancrinite and calcite. Phase assemblages and textures from experiments are strikingly similar to those in rocks of the okaite-carbonatite series and origin by fractional crystallization of carbonated nephelinitic magma is suggested. Fenitization may result from metasomatism by a fluid analogous to the sodic vapour phase of the experiments. Studies in the system CAO–Nb_2O_5–CO_2–H_2O show that about 5% Nb_2O_5 is soluble in "synthetic carbonatite magma" in the absence of vapour. Thus niobium mineralization may be magmatic and not hydrothermal.

INTRODUCTION

The Oka complex, Québec, lies at the western extremity of the Monteregian alkalic-rock province. Its geology has been thoroughly described by Gold (1963, 1966, 1970) and Davidson (1963). The major features of the complex are :

1. The double-ring arrangement of rock types.
2. The concentric intrusions of rocks of the ijolite series characterized by nepheline and pyroxene.
3. The arcuate intrusions of the okaite series characterized by melilite.
4. The carbonate rocks, dominantly calcite-rich.
5. Fenitization of country rocks at the margins of the complex.
6. Economic niobium mineralization.
7. Late-stage alnöitic, kimberlitic and lamprophyric dikes and breccias.

Many of the rocks of the complex exhibit textural features and mineral assemblages which have striking analogs in phase equilibrium experiments. It is possible on the basis of experimental results to test some theories of origin of alkalic — and carbonate-rock complexes in general, and the Oka complex in particular.

HYPOTHESIS OF ORIGIN OF THE OKA ROCKS AND PERTINENT EXPERIMENTS

The limestone assimilation hypothesis

The hypothesis that alkalic magma is generated from subalkalic magma by limestone syntexis was advanced by Daly (1910). Carbonate rocks in alkalic complexes were thought to be remnants of limestone that had not completely reacted with normal subalkalic magma. Daly's hypothesis was adopted by Stanfield (1923) to explain the origin of the melilitic rocks (okaites) at Oka through syntexis of Grenville marble. From a series of experiments which involved the reaction of a variety of igneous rock compositions with carbonates to produce melilite-bearing assemblages, Stanfield (1928) concluded that melilite-bearing igneous rocks are products of limestone syntexis. Other experimental reactions of silicate minerals with carbonates to produce silica-undersaturated assemblages (Schuiling 1964; Philpotts *et al.* 1967) led the respective authors to support the limestone assimilation hypothesis; the latter authors have specifically included the alkalic rocks at Oka.

Watkinson & Wyllie (1964, 1969) and Wyllie & Watkinson (1970) have shown, however, that the limestone assimilation hypothesis is unlikely to be effective from a variety of experimental approaches. The dominant effect of carbonate syntexis is to promote crystallization of the melt reacting with carbonate. The thermal barrier corresponding to feldspar compositions appears to be adequate to prevent desilication of silica-oversaturated feldspathic liquids (Wyllie & Watkinson, 1970) and only minor amounts of silica-undersaturated melt form on reaction of saturated feldspathic melts with calcite (Watkinson & Wyllie 1969). Watkinson & Wyllie (1969) point out that large-scale generation of silica-undersaturated magma is improbable through limestone syntexis, but note that feldspathoidal assemblages may be generated in the subsolidus region.

Hypothesis of genesis of alkalic rock-carbonatite associations

Magmatic carbonatite. Wyllie & Tuttle (1960) showed that calcite could precipitate from melts in the system $CaO–CO_2–H_2O$ through a large pressure region and to temperatures as low as about 600°C. They described liquids in this system as "synthetic carbonatite magmas" and stated that their results confirmed the field evidence from many complexes that the carbonate rocks are not limestone derivatives but are intrusive and magmatic. Wyllie & Boettcher (1969) have extended the study of liquidus temperatures in the system $CaO–CO_2–H_2O$ to 40 kbars pressure.

Further phase equilibrium studies have been carried out in more complex systems with the addition of MgO (Wyllie 1965), CaF_2 (Gittins

& Tuttle 1964), SiO_2 (Wyllie & Haas 1965), P_2O_5 (Biggar 1967) and combinations of these ($CaO–MgO–SiO_2–CO_2–H_2O$; Franz & Wyllie 1967, and $CaO–P_2O_5–CaF_2–CO_2–H_2O$; Biggar 1969). These studies have confirmed that calcite and other petrologically significant phases can precipitate from carbonate-rich melts to low temperatures and that the solubility of these phases in the vapour or gas phase is low. They further showed that the melts are extremely fluid and that crystal settling occurs within a few minutes. Abundant opportunities should therefore exist for the separation of crystal cumulates and residual magma of compositions different from carbonatite magma thus promoting extreme fractional crystallization.

Wyllie, Cox & Biggar (1962) showed that apatite formed stubby prisms when in equilibrium with liquid or vapour in the system $CAO–P_2O_5–CaF_2–CO_2–H_2O$, whereas apatite precipitated from the liquid phase during quenching formed sheaves of acicular, often skeletal prisms. They proposed that acicular apatite in carbonatites might be a useful criterion for the former presence of liquid. Girault (1966) described both habits of apatite from the Oka carbonatite which correspond very closely to those observed in experiments. Girault (1966) also described dendritic calcite from the margin of the Oka carbonatite; dendritic calcite produced in synthetic carbonatite systems is regarded as positive evidence for the former existence of a liquid phase.

In Figure 1 are presented photomicrographs of a specimen of the Oka carbonatite in which the minerals calcite, apatite and phlogopite occur interstitially to large pyroxene and pyrochlore crystals. The aggregates of apatite prisms occur at the bottom of the interstitial areas in Figure 1 and this suggests that these are the result of crystal settling of apatite from carbonatite melt trapped in a matte of pyroxene and pyrochlore. These apatite crystals contain abundant fluid inclusions as have been described by Girault (1966).

The similarity of natural textures from the Oka carbonatite and those obtained in experiments on "synthetic carbonatite magmas" is compelling evidence that the Oka carbonatite was emplaced as magma, an opinion expressed by Girault (1966). The observed extensive crystal settling and banding is consistent with precipitation from a highly fluid magma which would be instrumental in promoting extensive differentiation and fractional crystallization (Wyllie and Biggar, 1966).

Gold (1963) and Davidson (1963) concurred on the magmatic nature of carbonatite at Oka on the basis of field and petrographic evidence.

Primary carbonatite magma and sial syntexis. In an attempt to explain the relationship between carbonatites and associated alkalic rocks it has

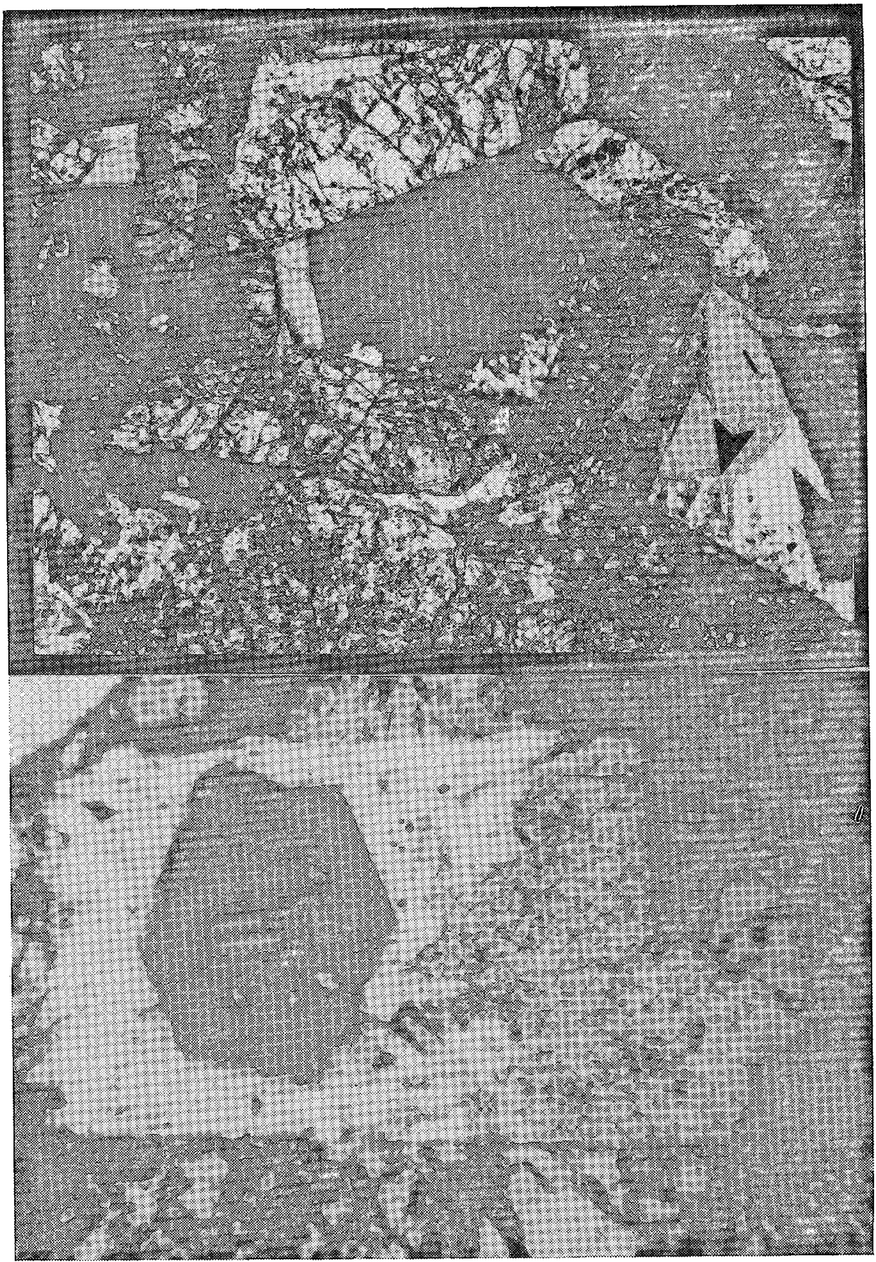

FIG. 1a (top). Pyroxene-pyrochlore carbonatite with coarse calcite and apatite prisms (arrows) in lower portions of interstices. Crossed nicols. Width of photograph is 9.0 mm. 1b (lower). Interstitial assemblage of calcite, apatite and phlogopite framed by pyroxene. Note fluid inclusions in apatite prisms. Plane polarized light. Width of photograph is 2.1 mm.

been suggested that alkalic magmas are generated by the assimilation of sialic country rocks by primary, juvenile carbonatite magma. This hypothesis was conceived by von Eckermann (1948) and Holmes (1950) and later developed by Dawson (1964). Dawson related variations in rocks of alkalic complexes to variations in the chemistry of primary carbonatite especially in the proportions of Na, K, Ca, Mg and Fe, chemical variations in the country rocks, and extent of reaction of these compositions.

These authors consider carbonatite magma to be initially rich in alkali metals but to become enriched in alkaline-earths as alkalies are lost to the country rocks by reaction. The existence of alkalic carbonatite magma was confirmed when sodium-rich carbonatite lava erupted from the Oldoinyo Lengai volcano (Dawson 1962). Koster van Groos & Wyllie (1968) have described experimental studies which demonstrated that sodium carbonate and albitic melts are immiscible. They suggest that immiscibility provides a possible mechanism for the generation of alkalic carbonatites. These magmas would persist as fractions immiscible with silicate magma until the physical conditions favouring immiscibility were removed. Liquid immiscibility persists into calcium-bearing systems (Koster van Groos & Wyllie, 1964) but diminishes in extent.

Although the hypothesis of primary carbonatite and sial syntexis has the merit of simplicity, it suffers from many of the shortcomings of the limestone-assimilation hypothesis. Schuiling (1964) proposed that from a physico-chemical point of view there is no difference between the two theories. Watkinson & Wyllie (1969) and Wyllie & Watkinson (1970) show that experimental arguments similar to those directed against the limestone assimilation hypothesis apply equally to the hypothesis of sial syntexis. They state that it is unlikely that extensive generation of alkalic magma may occur by assimilation of sialic rocks in carbonatite magma.

Carbonatite derived from alkalic magma. Watkinson & Wyllie (1969) showed that in the join $NaAlSi_3O_8$–$CaCO_3$–H_2O at 1 kilobar pressure, liquids precipitating feldspars cannot yield residual liquids which precipitate calcite. The presence of thermal barriers to such liquid trends has been described by Wyllie & Haas (1965), Watkinson & Wyllie (1969) and Wyllie & Watkinson (1970). This suggests that in nature it is therefore unlikely that carbonatite is a late-stage differentiate of feldspathic magma. In the join $NaAlSiO_4$–$CaCO_3$–H_2O (Figure 2) at 1 kilobar pressure, however, liquids are continuous from nepheline-rich to calcite-rich compositions (Watkinson 1965, Watkinson & Wyllie, 1970). These results are consistent with the field observations that carbonatites in general are not intimately associated with feldspathic magmatic rocks but with more silica-undersaturated (nephelinitic) rocks. This is certainly the case in the

Monteregian province, where carbonatite occurs at Oka with nepheline-rich and melilite-rich rocks while more feldspathic alkalic rock associations lack carbonatites.

In addition to the carbonate-rich liquid in the join $NaAlSiO_4$–$CaCO_3$–H_2O (Figure 2), the other phases encountered are vapour, nepheline, melilite, hydroxyhauyne, cancrinite and calcite. The crystalline phase assemblages in the join are strikingly similar to the rocks at Oka, particularly those of the northwestern portion of the complex.

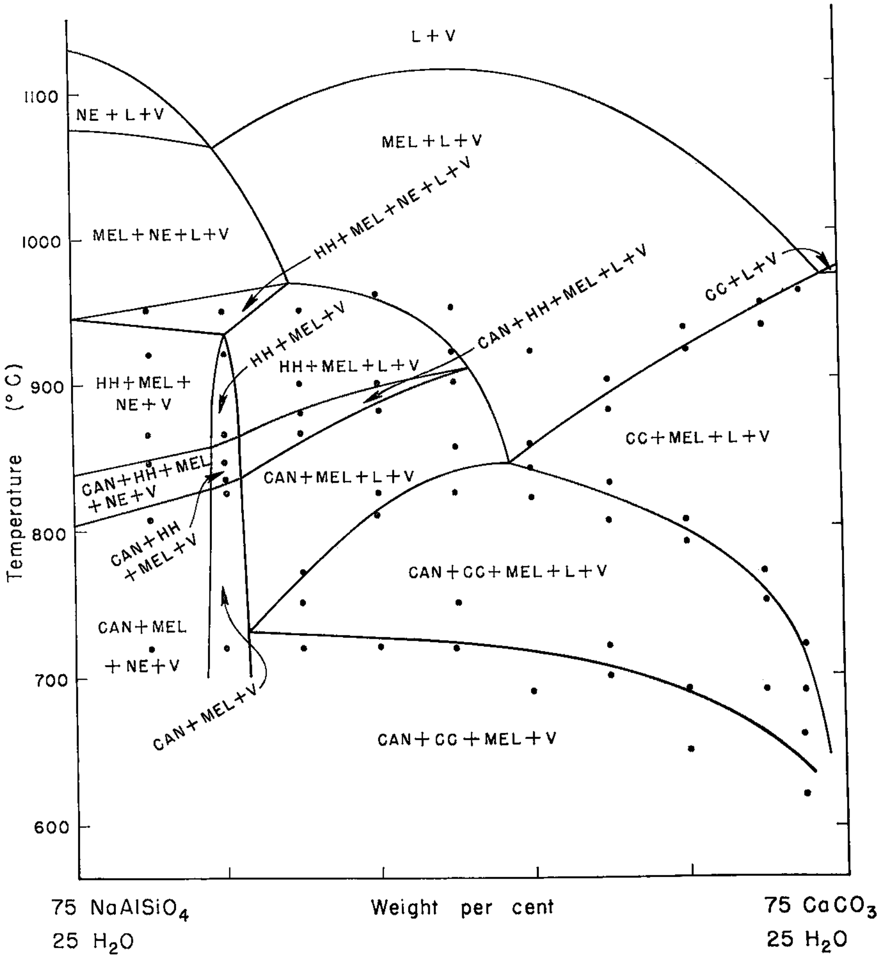

FIG. 2. Phase fields intersected by the join $NaAlSiO_4$–$CaCO_3$–H_2O at 1 kilobar, 25% H_2O. Abbreviations : CAN — cancrinite, CC — calcite, HH — hydroxyhauyne, MEL — melilite, NE — nepheline, L — liquid, V — vapour.

The rocks of the okaite series are characterized by melilite, as are most of the crystalline assemblages in Figure 2. The assemblage melilite+nepheline corresponds to nepheline okaite, and hydroxyhauyne+melilite is analogous to okaite (hauyne+melilite). Cancrinite has been reported from the Oka rocks only as an alteration of nepheline (Rowe, 1955). Its stability with respect to hauyne may be suppressed in the presence of sulphate, and in experimental systems hydroxyhauyne, the high temperature reaction product of cancrinite, may be considered as a substitute for hauyne. The assemblage calcite+cancrinite+melilite may be thought to represent the Oka carbonatites. In experimental assemblages at the lowest solidus temperatures the proportion of calcite is very high.

Not only are the phase assemblages analogous to rocks at Oka, but it is possible to derive the whole suite of appropriate crystalline assemblages by fractional crystallization of one starting composition (Watkinson & Wyllie 1970). Nepheline-rich liquid which contains up to about 20% $CaCO_3$, in equilibrium with vapour, will precipitate the following crystalline phase assemblages : nepheline, melilite+nepheline, hydroxyhauyne+melilite, cancrinite+melilite, calcite+cancrinite+melilite. The temperature ranges of precipitation of these assemblages are given in Table 1, for a starting composition of 90NE:10CC, together with the analogous rock types from Oka.

Equilibrium crystallization of liquid with less than 20% $CaCO_3$ does not produce calcite. Fractional crystallization, however, not only yields calcite in the late stage of crystallization, but also produces a higher proportion of calcite in relation to other phases with increasing degree of fractionation. It has already been pointed out that fractionation is expected to be extensive in the crystallization of carbonatite.

TABLE 1. MAJOR ROCK TYPES OF THE INTRUSION

TABLE 1. Phase assemblages precipitated during fractional crystallization of liquid 90NE : 10CC in equilibrium with vapour at 1 kilobar. The approximate temperature ranges for the precipitation of these phases in the synthetic system are accompanied by the corresponding rock types from Oka.

Crystalline phases	Approximate temperature range, ° C	Analogous rocks from Oka
nepheline	1,104–1,070	ijolite series
melilite + nepheline	1,070– 950	nepheline okaite
hydroxyhauyne + melilite	950- 875	okaite
cancrinite + melilite	875– 800	
calcite + cancrinite + melilite	800– 600	carbonatite

The condensed phases in all the assemblages of the join $NaAlSiO_4$–$CaCO_3$–H_2O (Figure 2) coexist with vapour. This phase is not CO_2–rich as it is in many assemblages on the join $NaAlSi_3O_8$–$CaCO_3$–H_2O (Watkinson & Wyllie 1969) but is rich in H_2O and sodium. Crystals of $NaHCO_3$ result from quenching the vapour especially from carbonate-rich compositions. There is no evidence for continuous solubility of liquid and vapour in these joins; liquid and vapour are miscible, however, in part of the join $NaAlSiO_4$–$Ca(OH)_2$–H_2O and this persists only slightly into carbonate bearing compositions (Watkinson 1965).

Fenitization. The sodic, aqueous vapour phase described above corresponds to fenitizing agents which are ubiquitous at carbonatite complexes, including Oka. Fenites are country rocks altered predominantly by the addition of Na (and K) plus Fe and removal of Si. In some cases, it has been suggested that fenitization has ultimately yielded extensive nepheline-bearing rocks and that these have become mobilized or rheomorphosed. Gold (1970) has suggested that some juvites and rocks of the ijolite series at the margins of the complex are ultrafenites. It appears unlikely, however, that ultrametasomatism could be responsible for the large-scale generation of rocks with igneous structures because of the high temperatures necessary for their rheomorphism. Certainly carbonatite magmas considered to be the progenitors of fenitizing solutions at many complexes would not be sufficiently superheated to promote extensive partial melting of silicate country rocks. It may be that many so-called rheomorphic fenites or ultrafenites are actually early magmatic rocks which have been autometasomatized concurrently with fenitization of the country rocks. This would result in rocks of igneous structure and texture, overprinted by metasomatism.

Although all the experimental assemblages coexist with vapour it is not implied that a free vapour phase existed during the generation of *all* the Oka rocks. Vapour-absent "simplified carbonatite magmas" persist to temperatures only tens of degrees higher than the vapour-saturated equivalents. That a vapour phase was generated during some stage of crystallization of the Oka complex, however, is suggested by the development of pegmatitic facies of some carbonatites and alkalic rocks, deuteric development of hydrous minerals, presence of fluid inclusions (Girault, 1966) and fenitization.

The ijolite series. The rocks of the ijolite series at Oka are characterized by nepheline and pyroxene and include jacupirangites, melteigites, ijolites and urtites. The urtites often contain garnet (melanite) and wollastonite. Melilite is lacking in this series and thus experiments on the join $NaAlSiO_4$–$CaCO_3$–H_2O are not strictly pertinent to their origin. In the join $NaAlSiO_4$–$Ca(OH)_2$–$CaCO_3$–H_2O melilite was found to be unstable below 625°C at 1 kilobar; melilite breaks down in the presence of liquid and vapour to form gehlenite hydrate or hydrogarnet (Watkinson 1965). In other investigations of the experimental breakdown of various melilite compositions garnets, wollastonite, monticellite, vesuvianite, cancrinite and other phases have been produced (Christie 1962; Edgar 1965). In nature, garnet may take the place of hydrogarnet or gehlenite hydrate. At Oka there are melilite carbonatites and garnet-monticellite carbonatites, and in some cases, rocks which show the formation of garnets from melilite (Figure 3). It appears that melilite may undergo a magmatic reaction analogous to that encountered in the experiments. Gold (1963) has pointed out the chemical similarity of the melilite rocks and some of the garnet- and wollastonite-bearing ijolitic rocks of the southern ring at Oka. Differing conditions of pressure and oxygen fugacity may be responsible for the production of these differing series of the Oka complex.

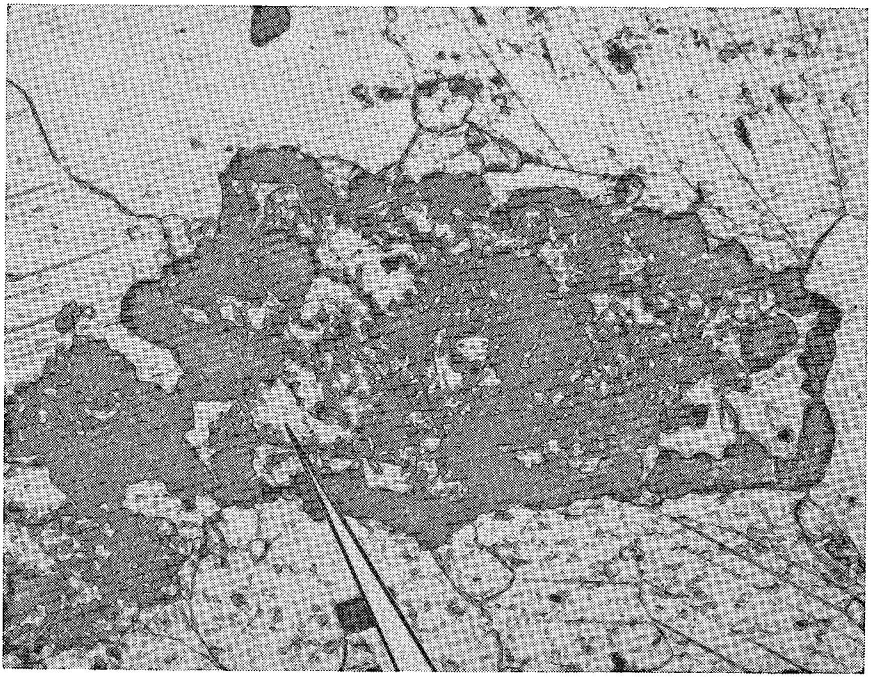

FIG. 3. Melilite (arrow) with rim of garnet, calcite and mica in carbonatite. Width of photograph is 2.6 mm.

THE SYSTEM $CaO–Nb_2O_5–CO_2–H_2O$ AND NIOBIUM MINERALIZATION

Phase relations in the system $CaO–Nb_2O_5–CO_2–H_2O$ have been described by Watkinson (1968). The niobate phases encountered are $Ca_4Nb_2O_9$, analogous to the niobium perovskite mineral latrappite; $CaNb_2O_6$, analogous to fersmite; and $Ca_2Nb_2O_7$. Pyrochlore, the common Nb mineral at carbonatite complexes, has the general formula $A_2B_2X_7$; the end member $NaCaNb_2O_6$ is related to $Ca_2Nb_2O_7$ by Na + F for Ca+O substitution. The latter phase is the most commonly encountered niobate in the experiments at 1 kilobar, 600–950°C. It precipitates from synthetic carbonatite with calcite through a large temperature interval to the eutectic temperature of 635 ± 5°C. About 5% Nb_2O_5 is soluble in the eutectic melt.

In the system $CaO–Nb_2O_5–H_2O$, the perovskite-type phase, $Ca_4Nb_2O_9$, rather than $Ca_2Nb_2O_7$, is stable on the liquidus. The univariant reaction

$$Ca_2Nb_2O_7 + Ca(OH)_2 = Ca_4Nb_2O_9 + V$$

was intersected at 700°C and 1 kilobar. Reaction rims of pyrochlore on niobium perovskite have been reported by Nickel (1962) at Oka, suggesting a similar reaction in the carbonatites.

Experiments in the presence of excess vapour in part of the system $CaO–Nb_2O_5–CO_2–H_2O$ gives results similar to those in vapour-absent conditions although temperatures are about 10°C lower. There is no evidence for the precipitation of niobates from the vapour phase. The large solubility of niobium in simplified carbonatite, the similarity of experimental and natural reaction relations of niobates, and the extensive coprecipitation of the perovskite and $A_2B_2X_7$ phases with calcite in both natural and experimental situations suggest that the small but ubiquitous amounts of niobium minerals in the rocks at Oka and other carbonatites may be magmatic and not hydrothermal. Niobium mineralization is certainly not a common feature in fenitized country rocks at carbonatite complexes (Deans 1966); fenitization has been generally acknowledged to be a hydrothermal process.

CONCLUSIONS

The mineral assemblages and textures of the Oka rocks and the corresponding phase assemblages and textures encountered in experimental studies on carbonate-bearing systems suggest that this alkalic rock-carbonatite complex formed as a result of magmatic processes. These processes have been accompanied and probably in part overprinted by some degree of alkali-iron metasomatism (fenitization). The succession of nepheline and melilite-bearing rocks and the carbonatites can be convincingly interpreted as the products of fractional crystallization of carbonated nephelinitic magma by analogy with phase relations on the join $NaAlSiO_4$–$CaCO_3$–H_2O (Figure 2). The niobium minerals may also be products of magmatic crystallization rather than hydrothermal mineralization as is suggested by analogy with relations in the system CaO–Nb_2O_5–CO_2–H_2O.

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