

THE ROLE OF FLUORINE IN THE CRYSTALLIZATION OF NIOBIUM AND PHOSPHORUS ORES IN CARBONATITES.

Bruce C. Jago and John Gittins.

Department of Geology, Earth Sciences Centre, University of Toronto, Toronto, Ontario, M5S 3B1, Canada.

Phase equilibria studies have helped to deduce compositional controls on Nb and P mineralization and paths of fractional crystallization that might be experienced by natural carbonate melts. High niobium solubilities (5 - 10 wt. % Nb_2O_5) in simple, water - saturated calcium carbonate melts (Watkinson 1970) conflict with the generally low Nb_2O_5 contents (< 0.5 wt. %) of most carbonatites, with the exception of hydrothermally enriched zones in bodies such as Araxa (Mariano 1989). To evaluate this disparity and determine the effect of alkalinity and F content on perovskite and pyrochlore (Pyr) crystallization, experiments were conducted (1 kbar, 550 - 945° C.) in anhydrous, F - bearing Na - Ca carbonate melts [CaCO_3 - Na_2CO_3 - F (Cc - Nc - F), Jago 1991] with a natural pyrochlore (< 2.1 wt. % F) from Oka (Perrault 1968). The effect of alkalinity and F content on the crystallization history of apatite was determined in the same F - bearing join (1 kbar, 550 - 930° C.) with a natural fluor - apatite (av. 25 anal., 2.8 wt. % F), Jago 1991).

Pyrochlore Crystallization in the Quaternary Cc - Nc - F - Pyr

Figure 1 is a generalized pseudoternary section through the carbonate - rich portion of the quaternary Cc - Nc - Pyr - F (Jago 1991). The plane of the section is dominated by the phase field for pyrochlore owing to the low solubility of pyrochlore (< 0.75 wt. % or < 0.45 wt. % Nb_2O_5 equiv.) at all binary, ternary and quaternary invariant points which is in agreement with Nb contents of natural systems. A perovskite group mineral occurs as an intermediate compound on the carbonate - pyrochlore binary at Nc64 Pyr36 owing to the reaction of pyrochlore with carbonate melt. The perovskite - pyrochlore binary projects into the F - bearing ternary and terminates at a peritectic point with 1 wt. % F ($T > 930^\circ\text{C}$.) at the intersection of the phase fields for carbonate, pyrochlore and perovskite. Under conditions of fractional crystallization, perovskite reacts with the F - bearing melt to form pyrochlore; cotectic crystallization of carbonate and pyrochlore proceeds down temperature to higher F contents and eventual intersection of the phase field for a fluoride mineral at approximately 7 - 8 wt. % F and 590° C. Crystallization of this three phase assemblage enriches the melt in alkalis but proceeds at essentially constant F content to a quaternary eutectic. The location of the peritectic at low F contents and high temperatures explains the general paucity of perovskite + pyrochlore - bearing assemblages in carbonatites, which almost universally experience fractional crystallization, and, the occurrence of pyrochlore reaction rims on perovskite (Oka, Nickel and McAdam 1963; Russian, Kapustin 1980). Alkali - rich hydrothermal fluids must have been F - poor to form lueshite from pyrochlore at Lueshe (Safiannikoff 1959) in Zaire.

Apatite Crystallization in the Quaternary Cc - Nc - F - Apatite

The combined effect of alkalis and fluorine on apatite solubility was examined to extend the range of previous studies to compositions that are relevant to the crystallization of apatite from anhydrous, halogen and alkali - bearing carbonate melts up to extreme compositions of the Oldoinyo Lengai type.

Apatite solubility in Nc - bearing compositions in the ternary Cc - Nc - Ap decreases markedly from 25 wt. % on the Cc - Ap binary to about 4 wt. % on the nyerereite (Ny) - Ap (800° C.) binary. A single ternary eutectic is located on the Cc - rich side of Ny - Ap

at Cc51 Nc 45.5 Ap 3.5 at 787° C. The Nc - rich side of the ternary is dominated by the phase fields for apatite and Na - Ca carbonate - phosphate compounds which results in very restricted phase fields for Ncss and Ny. A ternary eutectic (Nc78 Cc21 Apl, 700° C.) and ternary peritectic (Nc 40.5 Cc 36.5 Ap3.0, 795° C.) were located on the Nc - rich side of Ny - Ap but phase relations on Nc - Ap were not constrained.

Eutectic temperatures are depressed by approximately 200° C. and apatite solubility by about one half with the addition of 8 wt. % F to ternary compositions. This also establishes the fluorite stability field and extends the compositional range over which alkali - bearing, Cc - rich melts (Nc:Cc < 1) may fractionate to Nc - rich compositions (Nc:Cc > 1) and bypass the thermal barrier imposed by nyerereite in Cc - Nc. Two pseudoternary sections (Figures 2 and 3) illustrate contrasting crystallization schemes in the Cc - rich portion of the quaternary which are a function of apatite solubility and dictated by the form of the apatite liquidus (ie. convex with T max; gentle negative slope with increasing F content). For melts with bulk Nc:Cc ratios greater than about 1.5 (Figure 2), apatite solubility in F - bearing carbonate melts is insufficient to deplete the melt in F during the course of apatite precipitation. As a result, fractional crystallization invariably proceeds toward the fluorite - apatite cotectic from the carbonate (A--->) or apatite (B--->) stability fields, and melts with low initial F contents can experience two periods of carbonate precipitation. For melts with bulk Nc:Cc ratios less than about 1.5 (Figure 3), apatite precipitation may or may not be sufficient to deplete the melt in F, and the crystallization scheme is largely controlled by the initial F content of the system. For melts with high F contents (> 7 - 8 wt. %), crystal fractionation of apatite (C--->) enriches the melt in F, and crystallization proceeds toward the fluorite - apatite cotectic prior to intersecting the calcite stability field. For melts with less than approximately 7 - 8 wt. % F, apatite precipitation can deplete the melt in F and fluorite precipitation is possible only after cotectic crystallization of apatite and calcite sufficiently enriches the melt in F. Ternary and quaternary phase relations support a trend of alkali - enrichment during magmatic evolution in anhydrous, F - bearing melts and presents viable crystallization paths that can account for fluorite - bearing, calcite - apatite and calcite - bearing, fluorite - apatite vein assemblages.

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Figure 1

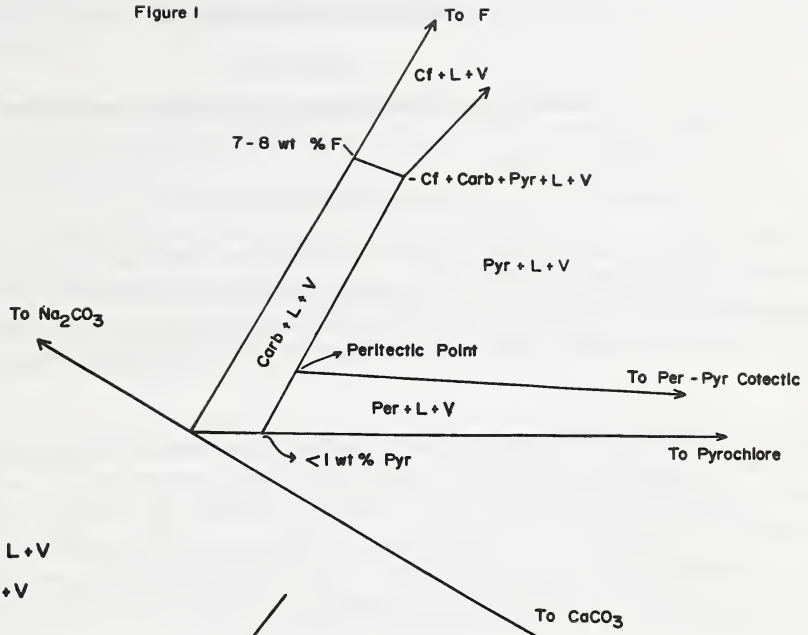


Figure 2

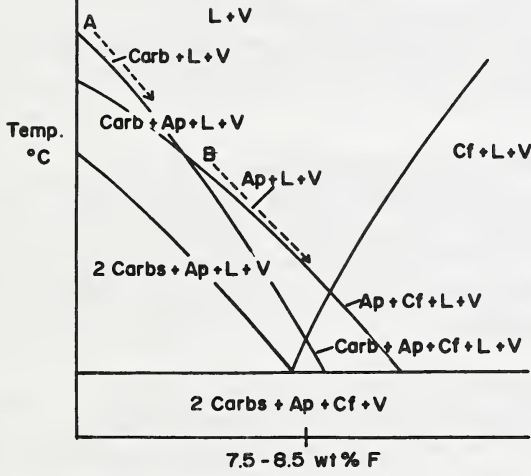


Figure 3

