

EXPERIMENTAL NUCLEATION OF CO-EXISTING MONAZITE AND XENOTIME GRAINS IN CHLORAPATITE USING H₂O-RICH FLUIDS UNDER HIGH PRESSURE AND TEMPERATURE

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The REE geochemistry of metamorphic rocks is directly influenced by the chemistry of apatite, monazite and xenotime. However, the geochemical and crystallochemical relationship between these three phosphate minerals is not well understood (Pan *et al.* 1993). For example, in chlorapatites in a pegmatoid from the Ødegårdens Verk, Bamble Sector, SE Norway (Leiftink *et al.* 1994), numerous monazite and xenotime grains are observed in areas where the chlorapatite was metasomatically altered to a F-poor hydroxyapatite under amphibolite facies conditions. In contrast, regions of unaltered chlorapatite in the same crystal do not contain monazite or xenotime inclusions. This suggests that introduction of OH into the chlorapatite structure induced the formation of these REE phosphates. Two experiments were performed in the piston cylinder. A non-metasomatized sample of the chlorapatite was crushed into 50-200 mm size grains. In the first experiment, chlorapatite (20 mg) and H₂O (5 mg) were placed in a Pt capsule and the capsule welded shut. In the second, a 50/50 molar H₂O/F fluid (6 mg) was used with CaF₂ as the F source. The two capsules were placed in a CaF₂ cell with the NiCr thermocouple located between them and taken up to 900°C and 1 GPa for one week. In the H₂O-chlorapatite experiment, numerous co-existing monazite and xenotime grains volunteered and the chlorapatite was altered to a hydroxyapatite with a minor Cl component. In the H₂O-F-chlorapatite experiment, no monazite or xenotime grains volunteered and the chlorapatite was altered to a fluorapatite with a minor OH and Cl component. These results suggest that, in the H₂O-chlorapatite experiment, the REE in the apatite went into nucleating monazite and xenotime within the body of the apatite crystal structure whereas in the H₂O-F-chlorapatite experiment the REE complexed with the F⁻ and were subsequently leached out of the apatite into the fluid.

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Rb-K EXCHANGE BETWEEN PHLOGOPITE AND LOW H₂O ACTIVITY (K,Rb)Cl BRINES AT HIGH PRESSURE AND TEMPERATURE: IMPLICATIONS FOR THE ROLE OF SUPERCRITICAL KCl BRINES IN THE DEPLETION OF Rb DURING CHARNOKITE GENESIS

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Orthopyroxene-bearing granulite facies terranes (charnockites) are often characterized by extreme depletion in Rb (e.g. Hansen *et al.* 1995) despite abundant high Ti-biotite which should act as a natural sink for Rb. Some workers have speculated that low H₂O activity supercritical (K,Na)Cl-rich brines, originating from mantle derived basaltic underplating, could play a significant role in charnockite formation (Newton *et al.* 1998) as both

a source of heat transport and fluid. If so they could also play a role in the depletion of Rb in these terranes. However, recently some workers (Melzer and Wunder 1999) have demonstrated experimentally that for high H₂O activity (K,Rb)Cl brines, (> 0.9), Rb is strongly partitioned into the phlogopite. Phlogopite synthesis experiments were performed at 800°C and 2 GPa for concentrations of Rb less than 10% relative to K in the presence of a supercritical (K,Rb)Cl brine with an approximate Cl molality of about 100 (Cl/(H₂O+Cl) = 0.7) and an H₂O activity of 0.09 (cf. Aranovich and Newton 1997). The solid run products consisted of phlogopite along with smaller amounts of K-feldspar and very minor quartz. Rb fractionated strongly into the phlogopite, whereas, for the K-feldspar, Rb was distributed almost equally distributed between the feldspar and fluid. The derived exchange coefficients, $K_{D(Rb-K)}^{phl-fluid}$ and $K_{D(Rb-K)}^{fsp-fluid}$ (Henry's law), are 1.88 ± 0.12 and 0.86 ± 0.14 , respectively. Because these charnockites are highly depleted in Rb, our experimental results suggest that the original fluid responsible for the dehydration of these rocks must have already had an extremely low Rb concentration relative to K. They also suggest that the fluid could not have been depleted in Rb during the dehydration process but rather must have been enriched during the breakdown of the amphiboles to pyroxenes with this excess Rb partitioned into the biotite-phlogopites further up the rock column away from the source basaltic underplating.

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SOLID STATE SYNTHESIS AND CRYSTAL CHEMISTRY OF PHOSPHATES IN THE Na₂O-MnO-Fe₂O₃-P₂O₅ SYSTEM: PRELIMINARY RESULTS

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The chemical compositions of alluaudites occurring in Li-rich granitic pegmatites generally range between two ideal endmembers, Na₂Mn(Fe²⁺Fe³⁺)(PO₄)₃ and NaMnFe³⁺₂(PO₄)₃. Moreover, the calculation of the structural formulae of these minerals shows that Mn also shares the A(1) site with Na, or the M(2) positions with Fe (Fransolet *et al.*, 1994). It is the reason why we first envisage the synthesis of phosphates in the Na₂O-MnO-Fe₂O₃-P₂O₅ system.

The phosphates have been synthesized by solid state reaction in air, between 800 and 950°C. The central part of the Na-Mn-Fe³⁺ ternary diagram is occupied by compounds exhibiting the alluaudite structure. These compounds form extensive solid solutions covering 25% of the diagram surface. Other phases have also been identified: NaMn₄(PO₄)₃ (fillowite structure), (Mn,Fe)₃(PO₄)₂ (grafonite structure), FePO₄ (berlinite structure), and Na₃Fe³⁺₂(PO₄)₃ (nasion structure). Interestingly, it must already be pointed out that associations alluaudite + fillowite, and alluaudite + grafonite are known to occur in granitic pegmatites. The unit-cell parameters of 14 alluaudite-like samples have been calculated and compared with the unit-cell parameters of natural alluaudites particularly enriched in