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SPECIAL COLLECTION: APATITE: A COMMON MINERAL, UNCOMMONLY VERSATILE

# From phosphates to silicates and back: An experimental study on the transport and storage of phosphorus in eclogites during uplift and exhumation

**Jürgen Konzett[1,*]**

[1]Institute of Mineralogy and Petrology, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

## Abstract

High *P-T* experiments have shown that in major rock types such as MORBs, peridotites, and pelitic sediments, increasing *P* (and *T*) leads to a gradual transfer of P from phosphates mostly represented by apatite to silicates with garnet as most important silicate P carrier. This is due to the formation of a $Na_3Al_2(PO_4)_3$ phase component in garnet via $^{[8]}Na^{[4]}P^{[8]}M^{2+}_{-1}{}^{[4]}Si_{-1}$ that is strongly *P*-, and to a lesser extent *T*-dependent and creates garnets with significant P and Na at *P* as low as 2–3 GPa. Based on this experimental evidence, one would expect to routinely find P-Na-rich garnets in UH*P*-rocks with a wide range in composition. With very few exceptions, however, this is not the case. This discrepancy indicates that both P and Na are effectively released from garnet and re-distributed within the garnet matrix during uplift and exhumation. To explore the mechanisms of this P-Na release, P-Na-rich garnet pre-synthesized at 7 GPa and 1200 °C, containing 0.7 wt% $P_2O_5$ and 0.3 wt% $Na_2O$, was exposed to *P-T* conditions of 2 GPa and 800–1000 °C in a simplified, $H_2O$-bearing, model eclogitic bulk composition. The experiments show that at subsolidus temperatures of 850–975 °C, and in the presence of a hydrous fluid, apatite quickly forms from garnet breakdown involving consumption of coexisting quartz and clinopyroxene. The apatites usually appear as rounded to lath-shaped isolated grains scattered in the garnet + clinopyroxene ± orthopyroxene + quartz + rutile matrix. More rarely, single apatite inclusions, or clusters of inclusions, may form in clinopyoxene or garnet. The observed apatite grain size is in the range ≤ ~1 × 1 to 24 × 6 μm with the largest grains occasionally containing clinopyroxene inclusions. Combined garnet breakdown and neo-formation, using pre-existing garnet as a nucleation site, may form zoned garnets with Na-P-depleted and Ti-enriched rims that represent an approach to a garnet composition typical for mid- to shallow crustal *P-T* conditions. Partial melting experiments indicate that eclogites containing P-rich garnet may produce P-rich and apatite-undersaturated melts for moderately $SiO_2$-rich melt compositions. These melts can crystallize abundant apatite during solidification and, thus, would be effective agents for P-extraction during partial melting. Due to their very low apatite saturation concentration, the P-transport and storage capacity of granitic melts would be much more limited. An unexpected finding of this study are the substantial P and Mg contents in kyanite with 0.17–0.20 wt% $P_2O_5$ and 0.20–0.56 wt% MgO, respectively. The combined P-Mg incorporation into kyanite is consistent with the coupled substitution $^{[4]}Si^{4+} + {}^{[6]}Al^{3+} = {}^{[4]}P^{5+} + {}^{[6]}Mg^{2+}$ and with a strong preference of P for orthosilicate structures. The results of this study suggest that some to even all of the apatite now present in eclogites that underwent deep subduction formed by chemical adjustment of the eclogite garnet to decreasing $Na_3Al_2(PO_4)_3$ solubility during uplift and exhumation. This results in the appearance of apatite as a new phase in a hitherto apatite-free assemblage. Rapid transport to the surface and/or a lack of suitable reactants can suppress this re-equilibration and explain the occasionally high P- and Na-contents of eclogitic garnet-inclusions in diamond or garnets from diamondiferous eclogites sampled by kimberlites. Similarly, concurrent decreasing Ti-solubility in garnet may lead to rutile-saturation in eclogites that did not contain this phase under peak-*P* conditions as evidenced by the joint occurrence of (oriented) rutile and apatite inclusions in the eclogitic garnets. For the application of geothermobarometry, this delayed Ti (+P) saturation is important to be kept in mind.

**Keywords:** Phosphorus, garnet, apatite, kyanite, eclogite, exhumation