PHOSPHORUS EQUILIBRIA AMONG MAFIC SILICATE PHASES

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Phosphorus incorporation in major rock-forming silicate minerals has the following implications: (1) Reactions between phosphorus-hosting major silicates and accessory phosphates, which are also major trace element carriers, may control the stability of the latter and thus may affect the amount of phosphorus and other trace elements released to the coexisting melt or fluid phase. (2) Less of a phosphate mineral is needed to account for the bulk phosphorus of planetary mantles. (3) During partial melting of mantle mineral assemblages or equilibrium fractional crystallization of basaltic magmas, and in the absence or prior to saturation with a phosphate mineral, silicate melts may become enriched in phosphorus, especially in the geochemically important low melt fraction regime. Although the small differences in the ionic radii of $^{14}$P$^{3+}$, $^{14}$Si$^{4+}$, and $^{14}$Al$^{3+}$ makes phosphorus incorporation into crystalline silicates perhaps unsurprising, isostructural silicate and phosphate crystalline solids do not readily form solutions, e.g., (Fe, Mg)$_2$SiO$_4$ vs. LiMgPO$_4$, SiO$_2$ vs. AlPO$_4$. Nonetheless, there are reports of, poorly characterized silico-phosphate phases in angrites, 2-4 wt% P$_2$O$_5$ in olivine and pyroxene grains in pallasites and reduced terrestrial basalts which are little understood but potentially useful, and up to 17 wt% P$_2$O$_5$ in olivine from ancient slags. However, such enrichments are rare and only underscore the likelihood of phosphorus incorporation in silicate minerals. The mechanisms that allow phosphorus to enter major rock-forming silicate minerals (e.g., Oliv, Px, Gt) remain little understood and the relevant data base is limited. Nonetheless, old and new high-pressure (5-10 GPa) experimental data suggest that P$_2$O$_5$ wt% decreases from silica-poor to silica-rich compositions or from orthosilicate to chain silicate structures (garnet > olivine > orthopyroxene) which implies that phosphorus incorporation in silicates is perhaps more structure- than site-specific. The data also indicate that D$^{\text{LiQ-P2O5}}$ decreases in the same order, but D$^{\text{Ox-LiQ-P2O5}}$ and D$^{\text{Opx-LiQ-P2O5}}$ are likely constant, respectively equal to 0.08(3) and 0.007(4), in contrast, D$^{\text{Gt-LiQ-P2O5}}$ increases from 0.15(3) to 0.36(10) as garnet becomes majoritic, thus silica-enriched, and may also depend on liquid composition (SiO$_2$, P$_2$O$_5$, and Na$_2$O wt%).

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