

Phosphorus storage in the Earth's mantle

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In spite of its relatively low chondritic abundance (ca. 0.25 wt.% P₂O₅), phosphorus plays an important role in many geochemical processes from the Earth's surface to the deep interior. In the continental crust, where the P₂O₅ concentration amounts to around a weight percent, the phosphorus budget is mainly controlled by apatite, Ca₅(PO₄)₃(OH,F,Cl), and monazite REEPO₄. In the Earth's upper-mantle, the situation is completely different since phosphorus is believed to be present at a concentration level by one to two orders of magnitude lower (McDonough and Sun, 1995). Then, the P-Si replacement in silicate minerals, a crystal-chemical feature which is marginal in the Earth's crust, can potentially become dominant in the mantle. But to what extent? If all phosphorus is sequestered in apatite-type compounds, although minor, they will potentially represent a major sink for REE, U, Ba, Sr, and halogens in the deep Earth. To address phosphorus crystal-chemistry and phosphate stability under mantle conditions, we conducted a series of experiments at ca. 18 GPa and 1873 K in the 2000-ton split-sphere apparatus at GRC (Ehime, University) using 5 mm TEL WC anvils. The starting material was an oxide mixture of pyrolite composition (McDonough and Sun, 1995), to which around 2 wt.% P₂O₅ were added. Ferrous iron in the starting material was reduced at 1373 K in a gas-mixing furnace using a CO₂/H₂/Ar mixture. Gold-palladium or graphite containers were used to isolate the starting material from the surrounding MgO pressure medium (inserted in a LaCrO₃ heater). Temperature was monitored using a W₃Re / W₂₅Re thermocouple and adjusted manually in the course of the run which lasted 6 hours. Ringwoodite (Mg_{0.89}Fe_{0.11})₂SiO₄ along with garnet are the dominant phases in the run product as identified using micro-focussed X-ray diffraction. EDS-SEM characterization of the samples revealed the presence of a Ca-dominant phosphate, (Ca_{2.5}Mg_{0.4}Na_{0.1})(PO₄)₂. From the derived stoichiometry, structural similarity with the dense polymorph of Ca₃(PO₄)₂ (Murayama et al., 1986) can be envisaged. This dense polymorph has also been reported in the shock melt veins of the Suizhou meteorite (Xie et al., 2001). Should we then conclude that this Ca-phosphate will be the main host for phosphorus in the deep mantle? Actually, EDS data show that garnet, in the run product, may incorporate as much as a wt.% P₂O₅. This value is being confirmed using the Electron Microprobe. But readily, it may be concluded that in most part of the mantle, garnet will be the main phosphorus reservoir. In subduction zones, however, where P₂O₅ content of the trench sediments can amount to up to 0.5 wt.% or more (Plank and Langmuir, 1998), calcium phosphate may be a stable phase of the slab provided that the phosphate precursor (apatite) survives dissolution and/or partial melting. Experiment above majorite garnet stability field are in progress and will also be presented.