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## Phase relations of aluminous silica to 120 GPa and lowermost mantle dynamics

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Basalts have 3-10 times higher concentrations of Al, Ti, Ca and Na and more than 5 times lower concentration of Mg than peridotite. The resulting lower mantle basaltic mineralogy has no ferropericlase and low proportion of Mg-perovskite and post-perovskite with high Fe/Mg-ratio. Oversaturation of silica and alumina produces separate silica-dominated phases and Al-rich phases (NAL and Ca-ferrite phases). At pressures of 60-100 GPa common basalts crystallize 15-20% CaCl2-structured silica, 15-25% Ca-ferrite, 35-40% Mg-perovskite and 20-30% Ca-perovskite. The Fe-rich Mg-perovskite makes basaltic material denser than peridotite throughout the lower mantle below 720 km depth, with important implications for mantle dynamics. Partial separation of subducted basaltic crust from depleted lithosphere may occur within the strongly heterogeneous D" zone.

The silica-dominated phases have considerable solubility of alumina [1]. At 3500-4000~K the transition from the CaCl2-phase to seifertite (a-PbO<sub>2</sub>-structure) of pure SiO<sub>2</sub> occurs at 130-140~GPa, with a dp/dT-slope of about 10~MPa/K [2]. The transition pressure is reduced with Al-saturation. We investigated silica with 4 and 6 wt% alumina to 120~GPa, using LH-DAC at the Extreme Conditions Beamline (P02.2) at PETRA-III, DESY. Powdered glass mixed with 10-15~wt% Pt-powder was compressed and heated in NaCl pressure media in Re-gaskets.

To delineate the phase transition, the samples were compressed incrementally with intermittent laser heating. Slow reaction rates required 20-40 min heating at 3500-4000 K for each heating step. The XRD data and pressure estimates were acquired repeatedly during heating and after quenching to room temperature. The first crystallization of seifertite at 3500-4000 K was recorded at about 118 and 108 GPa in samples with 4 and 6 wt% AlO1.5, respectively. The CaCl2-structured silica phase crystallized along with seifertite, consistent with a binary phase loop trending towards lower pressure with increasing Al-content. Due to the presence of the Al-rich Ca-ferrite phase (near the MgAl2O4-NaAlSiO4-join) in natural basaltic compositions, the Al-solubility limits for the silica-dominated phases in basaltic lithologies may be similar to those in the binary system SiO<sub>2</sub>-AlO1.5.

Phase transitions in response to increasing pressure are generally associated with densification. Because of the strong partitioning of light and voluminous AlO1.5 into seifertite, however, the densification effect is more than offset by the lighter alumina component. The unit cell data of ref. [1] indicate a volume increase of about 3.8% associated with the transition. The associated density reduction would be strongly dependent on the substitution mechanism. O-vacancy and cation (3Si4+  $\rightarrow$  4Al3+) substitutions yield density reductions of 5.4% and 1.9%, respectively [1]. The large density reduction accompanying the seifertite transition may limit the role of gravitational accretion of evolved MORB to the LLSVPs. Segregation of Fe-rich picritic, komatilitic or peridotitic rocks with no separate silica phase may be more likely. Deep-mantle cumulates and solidified melts of peridotitic to komatilitic composition were mostly produced in the Hadean and early Archean, indicating that the antipodal and near-equatorial LLSVPs, stabilized by Earth's rotation, could also represent ancient structures.

References: [1] Hirose et al. 2005, EPSL; [2] Murakami et al. 2003, GRL