

Geochemical cycle of volatiles during plate convergence: Experimental constraints and thermodynamic models

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Convergent plate boundaries are major sites of planetary differentiation, crustal growth, and mass transfer. Plate convergence drives an annual global flux of $2.6 \cdot 10^9$ t H₂O to the Earth's interior, and it is subsequently released by devolatilization reactions. I will review our recent experimental studies and thermodynamic models that highlight fluid dynamics and fluid-mediated mass transfer in the Earth's crust and upper mantle. Fate of juvenile and subducted volatiles is directly related to their solubilities in nominally anhydrous mantle minerals. The high solubility of H₂O in wadsleyite (Mg₂SiO₄), ~3.3 wt.%, influences the pressure and pressure interval of the olivine to wadsleyite phase transformation that is the cause of the 410-km seismic discontinuity. Using multianvil apparatus experiments in the Mg₂SiO₄-H₂O system we demonstrate that the wadsleyite stability field expands to lower pressures by up to 1 GPa. When these results are combined with phase relations in the Mg₂SiO₄-Fe₂SiO₄ system, the significant effects on the pressure and pressure interval of this phase transformation are only expected in colder mantle regions (< 1400 °C) and for H₂O concentrations that are substantially greater than 0.2 wt. %, whereas areas of the mantle with the 410-km discontinuity broader than 20 km indicate temperatures as low as 1200°C and water concentrations close to the level where olivine would become H₂O saturated (~0.5 wt. %). The efficiency of transfer of aqueous solutes in the upper mantle strongly depends on the availability of complexing agents, e.g., halogens. We have investigated the incorporation of chlorine and fluorine in forsterite, enstatite and pyrope, and determined halogen partition coefficients between these minerals and aqueous fluids by piston-cylinder experiments and molecular dynamics. The chlorine solubility in mantle minerals is very

low, 0.2-0.9 ppm, whereas the fluorine solubility is 16-31 ppm in enstatite, 24-52 ppm in pyrope, and 246-267 ppm in forsterite. The fluid-mineral partition coefficients are 10^1 - 10^3 for fluorine and 10^3 - 10^6 for chlorine. Since the latter values are approximately three orders of magnitude higher than those for hydroxyl partitioning, fluid flow from subducting slab through the mantle wedge will lead to more efficient sequestration of H₂O into the nominally anhydrous minerals. In turn, an aqueous fluid will experience gradual increase in its salinity. Mass balance calculations reveal that rock-fluid ratios of $\sim 10^3$, consistent with pervasive wedge metasomatism, are required to produce the characteristic Cl/H₂O signature of primitive arc magmas or fluid inclusions in eclogites. In order to further our understanding of aqueous mass transfer in the upper mantle and lower crust, we have developed a new equation of state for aqueous solutes applicable to 1100°C and 20 kbar. Experimental solubilities for quartz, corundum, rutile, calcite, apatite, fluorite and portlandite in aqueous fluids are now accurately reproduced by the model and reveal that for a given mineral the solubility increases by 4-5 orders of magnitude as temperature rises to 1100 °C along typical geotherms. We show that integrated fluid fluxes characteristic of crustal shear zones are capable of precipitating quartz or calcite veins from low- and medium-grade metamorphic conditions, at geothermal gradient of 20°C/km. In contrast, solubilities of apatite or rutile lie below 1000 ppm but this is still important for the trace element budget in metasomatized lithologies. In subduction zones, the required fluid fluxes are one to two orders of magnitude lower and suggest enhanced efficiency of mass transfer and metasomatic alteration during plate convergence than in continental collisional settings.