Thermodynamic controls on water incorporation in San Carlos olivine

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Trace amounts of water stored in olivine as hydroxyl-bearing point defects has a disproportionately large influence on many key physical properties of the upper mantle. The relative stability of these different hydrous defects is controlled by a variety of thermodynamic properties; such as temperature, pressure, fugacities of oxygen and water and activities of silica and co-substituting trace cations (e.g., Ti, Cr^{3+}, Fe^{3+}). All of these properties vary substantially within the upper mantle, yet how they influence the stability of individual hydrous defects and therefore the bulk water storage capacity has not been firmly established. We present the results of a series of 'hydroxylation' experiments, whose premise is to impose a defect population in natural olivine crystals under high temperature conditions, before exploiting the rapid diffusion of hydrogen to decorate the imposed defect population with water at much lower temperatures and 15 kb pressure.

Crystallographically-orientated cubes of San Carlos olivine (Fo_{90}) were annealed at temperatures from 1050-1400 °C at atmospheric pressure, at oxygen fugacities from FMQ-3 to FMQ+2 and in the presence of enstatite or mg-wüstite powders (high and low silica activity respectively). Annealed and un-annealed cubes were then hydroxylated together under water-saturated conditions at 800-900 °C, 15 kb and with similar ranges in oxygen fugacity and silica activity.

Infra-red spectra of hydroxylated olivines reveal the four defect sites characteristic of upper mantle olivine. Differences between the equilibrium defect structure of olivine crystallised from the buffer and the hydroxylated cube indicate succesful preservation of the defects imposed during the high-temperature anneal during hydroxylation. The different silica activity buffers have negligable impact on the hydrous defect structure of the olivine cubes, reflecting the slow diffusivity of silicon vacancies at 800-900ºC. Increasing oxygen fugacity from FMQ-3 to FMQ+2 in the high temperature anneal results in a factor of 4 increase in water content, accomodated by an increase in the availability of Fe^{3+}- and possibly Cr^{3+}-related defect sites. Increasing temperature from 1050 to 1400 °C in the annealing stage at FMQ+2 results in an increase in water by a factor of 2.3.