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Hydrogen solubility and speciation in natural, gem-quality chromian diopside

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ABSTRACT

A new technique for performing long duration (up to 300 hours) high-pressure annealing experiments under water-saturated conditions has been developed. This technique has been used to investigate water-solubility and speciation in natural, gem-quality chromian diopside. Capsule design for the technique is a variant of the double-capsule technique, and relies on the use of a semi-permeable Pt membrane, which permits free hydrogen diffusion into samples, but protects samples from reacting with buffer mixtures. The investigation of a natural single crystal of chromian diopside revealed a very unusual annealing behavior: water contents increase sharply after a short annealing period and then decrease slowly to some metastable equilibrium value. The main process that takes place during the annealing experiments is hydrogen diffusion coupled with Fe^{3+} reduction. This essentially reverses the main mechanism for hydrogen loss from mantle samples during exhumation, and the technique therefore provides sample-specific information on original water contents. Absorption bands at 3646 and 3434 cm^{-1} in IR spectra from annealed samples suggest two main mechanisms for hydrogen incorporation in the diopside sample: (1) incorporation of hydrogen onto the O2 site, with vibration of the OH dipole in the direction of a nearby O3 site (along the edge of an M2 site), and (2) incorporation of hydrogen onto the O2 site with vibration of the OH dipole toward a nearby O1 site (along a shared M1–M2 edge) or O2 site (along the edge of an M1 site). The ratio of peak heights between the absorption bands at 3646 and 3434 cm^{-1} is independent of water fugacity but dependent on oxygen fugacity, and appears to provide a measure of the redox state "frozen" into the sample. This ratio could be used to determine whether pyroxenes from upper-mantle xenoliths had experienced concurrent hydrogen-loss and oxidation during exhumation.