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The incorporation of hydroxyl into zircon

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Abstract

We investigated the incorporation of hydrogen into zircon at 1650 and 1550 °C, and pressures of 2.5 and 1.5 GPa under water-saturated conditions in a piston-cylinder apparatus. Concentrations were determined by polarized Fourier transform infrared spectroscopy using the zircon absorption coefficient $\varepsilon_i = 36\,241$ cm^{-2} per mol H_2O/L and range from ~90 to 200 ppm H_2O by weight. Crystals grown in the presence of Ti^{4+} or Th^{4+} do not differ significantly in their H_2O content. We also synthesized zircons with various concentrations of Lu_2O_3 and Al_2O_3 to characterize changes in band positions and hydrogen concentrations related to coupled substitutions in zircon. Trivalent cations correlate in a nearly 1:1 molar fashion with hydrogen highlighting a potentially important coupled substitution in high water activity environments. Bands from undoped and doped zircons in the OH stretching region of the infrared spectrum show broad agreement when compared to spectra from natural samples. Heating experiments at 1 atm and 1000 °C produce a decrease in the integrated area; while some bands disappeared entirely, others are particularly stable with little decrease in integrated area after 128 h at 1000 °C. Results presented here help eliminate uncertainties that arose from Fourier transform infrared studies of natural zircons and provide further clarification for the origin of band positions in natural samples. In addition to the water activity of the crystallizing medium, the H_2O content of natural grains will likely be significantly influenced by trivalent cation concentrations. In crustal zircons especially, trivalent atomic contents generally exceed those of phosphorus, meaning that hydrogen may be particularly important for trivalent cation charge compensation. An unanticipated result of this study was the development of a reasonably effective technique that produces relatively homogenous zircons doped with minor impurities. This technique could potentially be utilized in studies aimed at developing zircon standards, because it yields crystals that appear to be more homogenous than those produced by the flux method, and are generally free of inclusions.

Keywords: Nominally anhydrous minerals, zircon, water, coupled substitution, FTIR, zircon synthesis