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The influence of water on the environment of transition metals in silicate glasses

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ABSTRACT

The effect of water (= H_2O + OH) on the environment of Co^{2+} and Ni^{2+} in albite glass was investigated by electronic absorption spectroscopy. The visible spectra of Co^{2+}-doped glasses change only slightly over the range of water concentrations studied. Co^{2+} is in a distorted tetrahedral environment, producing a dark blue color in the glasses. Up to about 5 wt% water, Ni^{2+}-doped glasses are brown and only minor variations in the spectra are seen. At 5.6 wt% water, however, the color of these glasses changes abruptly from brown to light green and a new type of absorption spectrum is observed. Three bands are observed in the visible spectra of the brown glasses. Two bands near 20 500 cm^{-1} can be assigned to Ni^{2+} in a distorted octahedral environment. A third band at 15 500 cm^{-1} could either be due to the distorted octahedral site or to a small amount of tetrahedrally coordinated Ni^{2+}. The spectra of the green glasses with 5.6 and 5.7 wt% H_2O resemble closely spectra of aqueous $NiCl_2$-solution containing the $[Ni(H_2O)_6]^{2+}$ complex. The formation of such a hydration shell around transition metals in hydrous silicate melts should strongly effect partitioning of these elements between silicate melts, minerals, and a metal phase. Consideration of ligand field stabilization energies, suggests that hydrated Ni^{2+} is stabilized in the melt such that mineral-melt and metal-silicate melt partition coefficients decrease by one to two orders of magnitude relative to a dry melt at 1100 °C.