Fe^{2+}/Fe^{3+} Intervalence Charge Transfer and Enhanced *d-d* Absorption in Mixed Valence Iron Minerals at Elevated Temperatures

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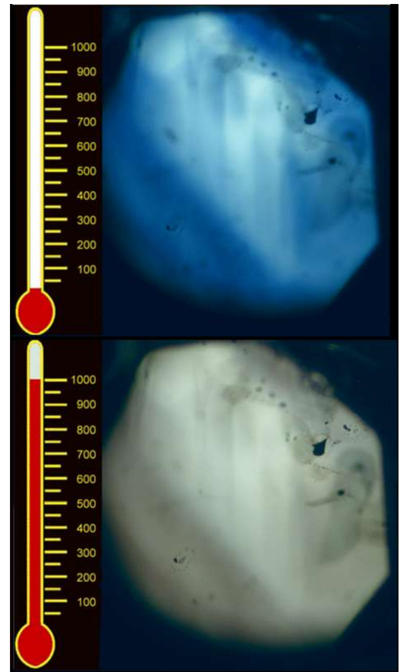

Malacacheta corundum at 23 vs. 1000°C

Extended Abstract: The absorption of light by Fe^{2+}/Ti^{4+} and Fe^{2+}/Fe^{3+} intervalence charge transfer (IVCT) bands has previously been found in aluminum oxide and Al_2SiO_5 aluminosilicate minerals to decrease markedly *in situ* at temperatures up to 1000°C. Given the abundance of iron at depth in the Earth, assessing the generality with which and extent to which IVCT mineral phases become more optically transparent at temperature than they are under ambient conditions has potentially significant implications for the modeling of mantle geophysical processes such as radiative conductivity. Towards that aim, a broad experimental survey has been conducted of the optical absorption spectra at elevated temperatures of mixed valence iron minerals that vary in chemistry, structure and IVCT pair geometric configuration. The minerals considered here are cordierite, chloritoid, lazulite, dumortierite, jeremejevite, beryl, osumilite, biotite (mica), pargasite (amphibole) and aegirine (pyroxene). All samples tested were found to transiently lose significant Fe/Fe IVCT feature intensity at temperature. In beryl, osumilite, biotite, pargasite and aegirine, spin-allowed Fe^{2+} *d-d* features were also found to decrease in integral intensity at temperature. This trend runs counter to the expected behavior of ordinary spin-allowed Fe^{2+} *d-d* bands and is consistent with *d-d* band enhancement via Fe^{2+}/Fe^{3+} exchange coupling. In particular, the observation of coexisting Fe/Fe IVCT and enhanced Fe^{2+} d-d bands in biotite, pargasite and aegirine – all minerals where more extensive electron delocalization occurs across an infinite structural unit of edge-sharing octahedral sites – opens the possibility that similar phenomenology may be found in minerals with higher iron concentrations and/or stoichiometric IVCT, including those phases which abound in the Earth's upper mantle. These results suggest that the depletion of Fe/Fe IVCT and enhanced Fe^{2+} *d-d* band intensity at elevated temperatures may both be important mechanisms by which iron-bearing mineral phases become more optically transparent under conditions at depth.