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Fe^{2+}/Fe^{3+} intervalence charge transfer and enhanced *d-d* absorption in mixed-valence iron minerals at elevated temperatures

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Abstract

The absorption of light by Fe/Ti and Fe/Fe intervalence charge transfer (IVCT) bands has previously been found in aluminum oxide and Al_2SiO_5 aluminosilicate minerals to decrease markedly at elevated temperatures. 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 temperatures than they are under ambient conditions has potentially significant implications for the modeling of mantle geophysical processes such as radiative conductivity.

A broad experimental survey of the optical absorption spectra at elevated temperatures of various mixed-valence iron minerals has been conducted. The minerals considered here are cordierite, chloritoid, lazulite, dumortierite, jeremejevite, beryl, osumilite, biotite (mica), pargasite (amphibole), and aegirine (pyroxene). All samples transiently lose significant Fe/Fe IVCT feature intensity at elevated temperatures. In beryl, osumilite, biotite, pargasite, and aegirine, spin-allowed Fe^{2+} *d-d* features also decrease in integral intensity at higher temperatures; in all but beryl, the intensity loss is significant. This trend is consistent with *d-d* band enhancement via Fe^{2+}/Fe^{3+} exchange coupling, which has not previously been identified in the majority of these minerals. It is contrasted against the behavior of ordinary spin-allowed Fe^{2+} *d-d* bands in non-IVCT minerals forsterite (olivine) and elbaite (tourmaline). 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.

Keywords: High-temperature spectroscopy, optical absorption spectroscopy, intervalence charge transfer, enhanced absorption, mixed-valence iron, cordierite, chloritoid, lazulite, dumortierite, jeremejevite, beryl, osumilite, biotite, pargasite, aegirine