The integration modes of structural bound W^{6+} in hematite and goethite

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Hematite (Fe_2O_3; hem) and goethite (FeOOH; goe) are known to incorporate considerable amounts of tungsten (W). Although W concentrations up to 3.8 wt.% in hem and 8.6 wt.% in goe are reported in the literature, an accepted model for a structural incorporation is still open. In this study, we present the first X-ray absorption fine structure (XAFS; W L_3- & L_2-edge) measurements combined with X-ray diffraction, Raman spectroscopy and chemical analyses to determine a general relation of W contents and its structural incorporation in natural and synthetic hem and goe.

In addition to synthetic W-doped samples, we analyzed natural botryoidal hem and goe samples from different host rocks and variable genetic connections to tungsten deposits: (i) Fe-ores from the Schwarzwald Ore District, South Germany, and (ii) W-ores from the Grantcharitza tungsten deposit, Bulgaria.

Extended X-ray absorption fine structure (EXAFS) spectra consistently show similarities of synthetic samples and the W-bearing Fe-ores. The combination of X-ray absorption near edge structure (XANES) and EXAFS shows that W^{6+} resides on the Fe^{3+}-position in both, goe and hem, rather than forming distinct W-rich phases or clusters. Based on our data, we confirm the previously proposed hypothesis that W in hem might be incorporated by an isomorphous exchange of two Fe^{3+} by one W^{6+} which is exclusively coupled to the formation of Fe^{3+}-vacancies next to W^{6+}. The structural incorporation of W^{6+} in goe could be accompanied by deprotonation of O^{2-}-atoms (release of three H^+-atoms) for charge balance. However, since Raman-active Fe-OH vibrations of W-doped goe are scarcely affected, a significant correlation of Fe-O-Fe vibrations indicate that Fe^{3+}-vacancies represent the main mechanism rather than a deprotonation. These results are consistent with chemically observed Fe/W exchange ratios of nearly 2:1 in both, hem and goe.