

## Structural incorporation of W<sup>6+</sup> into hematite and goethite: A combined study of natural and synthetic iron oxides developed from precursor ferrihydrite and the preservation of ancient fluid compositions in hematite

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### ABSTRACT

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and goethite ( $\alpha$ -FeOOH) can incorporate considerable amounts of tungsten (W). Although W concentrations up to several wt% in hematite and goethite have been reported in the literature, none of the proposed models for a structural incorporation has been generally accepted yet. Here, the first combination of X-ray absorption fine structure (XAFS) measurements with X-ray diffraction (XRD), Raman spectroscopy (RS), electron microprobe (EMPA) and total reflection X-ray fluorescence (TXRF) provides a general relation between W content and its structural incorporation into hematite and goethite.

Botryoidal specimens of goethite and hematite, obtained from the Schwarzwald ore district, Black Forest, SW Germany, and from the Grantcharitza W deposit, Bulgaria, display W concentrations of up to 5.5 and 2.15 mol% W for goethite and hematite, respectively. In addition to these natural specimens, goethite and hematite were synthesized in the presence of W and incorporate up to 7 and 1.3 mol% W, respectively.

X-ray diffraction analysis does not indicate the presence of separate W-phases, supporting the structural incorporation of W into the hematite and goethite. Refined unit-cell parameters indicate no changes with increasing W concentration in hematites but a rising structural disorder within the structure of the synthetic goethites. Raman spectroscopy, however, shows an increasing structural disorder for both synthetics, indicating an increase of Fe vacancies in both hematite and goethite. A deprotonation mechanism for the goethite structure is unlikely according to the Raman results.

XAS near-edge spectra indicate a strong distortion of the WO<sub>6</sub> octahedra in both hematite and goethite. Extended XAFS spectra of the natural and synthetic goethites and hematites show striking similarities and suggest that W<sup>6+</sup> resides in all samples on the Fe<sup>3+</sup> position, again without developing separate W phases.

Calculations of the Fe-loss related to W incorporation reach mean values of ~2.9 and ~2.8 for goethite and hematite, respectively. The formation of two Fe<sup>3+</sup> vacancies in close proximity to the newly incorporated W<sup>6+</sup> in addition to a protonation of the structures achieves charge balance within the hematite and goethite structure.

Hematite and goethite record the presence of W in fluids even in the absence of visible W minerals. After W adsorption to ferrihydrite (the hematite and goethite precursor phase) and after its transformation to either hematite or goethite, only hematite with up to 0.4 wt% W is clearly able to continuously monitor a changing W signature as a record of the fluid history within its oscillatory growth zones. In contrast, goethite is probably not a good monitor of a primary W fluid history. Their combination, however, could be particularly useful, as hematite records the W concentrations in a fluid during ferrihydrite precipitation, while goethite records W concentrations during later ferrihydrite maturation. Botryoidal Fe-ores have never been considered for W recovery but could play an important role to fight a potential supply risk of W as a high-technology metal.

**Keywords:** Tungsten, iron oxides, iron hydroxides, substitution, hydrothermal, crystallography, spectroscopy, XAFS

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