

## Mineralogy of a natural As-rich hydrous ferric oxide coprecipitate formed by mixing of hydrothermal fluid and seawater: Implications regarding surface complexation and color banding in ferrihydrite deposits

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### ABSTRACT

We characterized the most As-rich natural hydrous ferric oxide (HFO) material ever reported using powder X-ray diffraction (pXRD), transmission electron microscopy (TEM), X-ray fluorescence spectroscopy (XRF), light element analysis using gas chromatography (GC), visible-infrared (vis-IR) diffuse reflectivity, <sup>57</sup>Fe Mössbauer spectroscopy, and superconducting quantum interference device (SQUID) magnetometry. We find that the natural As-HFO material is very similar to synthetic coprecipitated As-HFO materials, but is significantly different from all known natural and synthetic As-free HFO materials and ferrihydrite samples. The pXRD patterns show systematic differences with patterns for 2-line ferrihydrite, that are interpreted as evidence for significant populations of oxygen-coordinated Fe-As pairs. Observations by TEM, combined with energy dispersive spectroscopy (EDS) microanalysis, show agglomerations of nanophase primary particles and no evidence for other Fe- or As-bearing phases. Mössbauer spectroscopy shows octahedrally coordinated Fe<sup>3+</sup>, with a large fraction (~20%) of the octahedral Fe environments that are significantly distorted by the presence of As, compared to the Fe local environments in As-free ferrihydrite and HFO samples. The loss on ignition (LOI) is quantitatively consistent with OH + H<sub>2</sub>O, measured by GC, which, in turn, is consistent with ~1 nm diameter primary particles having all their surface cations (Fe<sup>3+</sup>, As<sup>5+</sup>, Si<sup>4+</sup>, C<sup>4+</sup>) coordinated on the free surface side by OH<sup>-</sup> and OH<sub>2</sub>. The banding into adjacent yellowish and reddish layers that occurs in the As-HFO deposits was studied by performing mineralogical analyses of the separated adjacent layers of two couplets of yellowish and reddish material. The yellowish samples were found not to contain secondary crystalline phases (as did the reddish samples, in small amounts) and to be relatively As-rich, C- and Si-poor. The observed anticorrelations between As and Si and between As and inorganic C suggest that natural HFOs, which usually contain significant molar amounts of Si, may not be as efficient at surface complexing As (and P) as their Si and C-free synthetic counterparts, unless formed by co-precipitation with the As (or P). The yellowish and reddish layers were also clearly resolved by both Mössbauer spectroscopy and magnetometry. Complexation of arsenate onto the HFO core was found to significantly increase the average quadrupole splitting (QS) obtained from Mössbauer spectroscopy by an amount that could not be explained by other chemical differences and that is consistent with an ~1 nm diameter particle size and somewhat smaller HFO core. The Munsell hue YR index (5–10 YR) was found to be strongly correlated to the average QS, thereby establishing that the color differences, corresponding to the measured shifts of the main visible band edge, are due to the local distortions in the <sup>6</sup>Fe<sup>3+</sup> environments that are induced by As complexation, via their influence on the relevant ligand field transitions. SQUID magnetometry allows the following observations. (1) The superparamagnetic to superferromagnetic transitions occur at 25 K and lower in As-HFO, compared to 55 K in synthetic 2-line ferrihydrite, suggesting a smaller magnetic primary particle (or core) size for As-HFO and inter-particle magnetic interaction reduction by surface complexed As, Si, and C. (2) The ratio of supermoment magnitude to magnetic particle size (m<sup>2</sup>/n, where m is the net number of Fe<sup>3+</sup> atomic moments per supermoment and n is the number of Fe<sup>3+</sup> cations per particle or HFO core) decreases with increasing As content in the sequence synthetic-HFO > reddish-As-HFO > yellowish-As-HFO. (3) The magnetic susceptibility magnitudes for As-HFO and synthetic 2-line ferrihydrite differ by a factor of 10 and suggest different supermoment formation mechanisms (m<sup>2</sup>/n < 1 vs. m<sup>2</sup>/n > 1, respectively) related to differences in intra-particle cationic and anionic disorder and magnetic particle size.

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