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## Adsorption of Au ferrihydrites using Au-L<sub>III</sub> edge XAFS spectroscopy

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Samples of Au(III) adsorbed onto ferrihydrites have been prepared from pure ferrihydrites and various gold(III) chloride solutions and characterized by Au-L<sub>III</sub> edge XAFS spectroscopy. On ferrihydrite surfaces, Au is present either as Au(III)Cl<sub>2</sub>O<sub>2</sub><sup>3-</sup> or Au(III)ClO<sub>3</sub><sup>4-</sup>, Au(III)O<sub>4</sub><sup>5-</sup> square planar complexes with Au-O and Au-Cl distances of 2.00(2) and 2.28(2) Å. These results show that the redox state of Au remains unchanged during adsorption in contrast to the short range environment of Au which is strongly sensitive on the pH and the Cl molality of the solution during adsorption.

**Keywords:** gold, iron, adsorption, ferrihydrites, XAFS

### 1. Introduction

Ferrihydrites (FeOOH, or "HFO") are poorly ordered iron hydroxides that have been proposed to play an important role in the geochemistry of trace elements because of their reactivity and large specific surface area (Benedetti & Boulègue, 1990; Davis & Kent, 1990). The interaction of gold hydroxo-chloro complexes with HFO's during coprecipitation experiments has been investigated by the means of Mössbauer spectroscopy (Benedetti & Boulegue, 1990; Davis & Kent, 1990; Greffié *et al.*, 1996) but these studies were unable to assess the exact location of Au in these iron hydroxides. To determine the speciation of gold at the Fe-hydroxide-water interface, we have used x-ray absorption fine structure (XAFS) spectroscopy at the Au-L<sub>III</sub> edge to characterize Au-sorbed on HFO's as a function of pH, and chloride concentration of the solution.

### 2. Experimental

#### 2.1. Synthesis

Pure ferrihydrites ("2-lines", according to x-ray diffraction) were prepared at room temperature in polyethylene bottles by dropwise addition of 1 M KOH to a ferric nitrate solution, up to pH 7-8. The solution was stirred vigorously during the whole titration, centrifuged and washed repeatedly. The study of sorption dependence on time by Machesky (1991) and Greffié (1996) showed that after less than one hour the equilibrium is reached. Two gold stock solutions (both 2.8 10<sup>-3</sup> mol.L<sup>-1</sup> Au) with 1.2 M and 0.056 M Cl<sup>-</sup>, respectively, were used to perform the adsorption experiments on the pure HFO's at different pH and Cl<sup>-</sup> concentrations (see Table 1). Various mixtures of gold-bearing solutions and freshly

synthesized HFO gels were stirred overnight at a given synthesis pH (adjusted using a KOH-HNO<sub>3</sub> buffer). Each of these mixtures was then centrifuged prior XAFS data collection. The gold concentration of the decanted-, centrifuged solution after equilibrium with HFO has been measured using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES) in order to calculate the gold amount sorbed (Table 1).

#### 2.2 XAFS data collection and analysis

XANES and EXAFS spectra were collected at SSRL (SPEAR ring, Stanford, USA) on wiggler beam line IV-1 at ambient temperature and at the LURE (DCI ring, Orsay) at 10 K on beamline EXAFS2. The SPEAR and DCI rings were operating at 3.0 and 1.8 GeV with electron currents of 70-100 and 200-300 mA, respectively. The spectra were collected using Si-(220) and Si-(111) double crystal monochromators, respectively, detuned approximately 25% to reject high energy harmonics. Incident x-rays and transmitted x-rays were measured using ionization chambers filled with N<sub>2</sub>. Fluorescence yield spectra were measured using a Stern-Heald detector filled with Xe. Ga and Ti filters were used to reject, respectively, the elastic scattering and the Fe-K<sub>α</sub> fluorescence from the samples. Energy calibration was monitored using a Au foil (inflection point of the Au L<sub>III</sub> edge set at 11919 eV). Typically, 6-15 scans were averaged for each sample to minimize signal to noise ratio and to check for photoreduction events. EXAFS spectra were normalized in absorbance using a Victoreen function 300 eV region prior to the Au-L<sub>III</sub> edge and a spline function for the post-edge data (over 1.1 KeV). Energies were converted into k-space, with E<sub>k=0</sub> arbitrarily chosen "half-way" up the absorption step. The k<sup>3</sup>-weighted spectra were Fourier transformed (FT) over the k-range of 3 to 15 Å<sup>-1</sup> using a Kaiser window function with a τ value of π. Phase shift and amplitude functions were extracted from model compounds, Au<sub>2</sub>O<sub>3</sub> and KAuCl<sub>4</sub>.3H<sub>2</sub>O (Farges *et al.*, 1992).

Table 1. Synthesis conditions and EXAFS data reduction parameters for the various ferrihydrites studied.

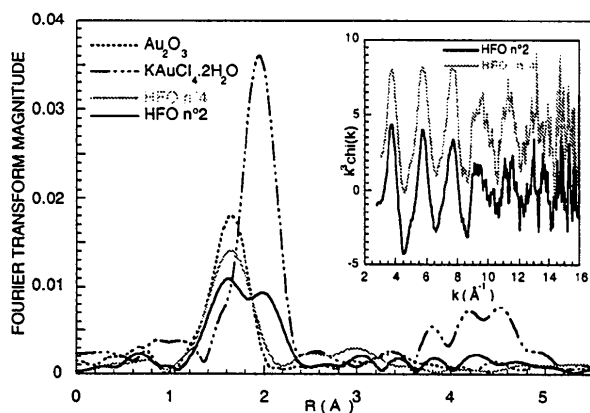
| sample and Cl <sup>-</sup> molality | pH  | [Au] x 10 <sup>-2</sup> mol/m <sup>3</sup> | type/number of 1st neighbors | mean Au-Cl distance (Å) | Δσ <sup>2</sup> x 10 <sup>-3</sup> (Å <sup>2</sup> ) | ΔC <sub>1</sub> x 10 <sup>-4</sup> (Å <sup>3</sup> ) | ΔE <sub>0</sub> (eV) | χ <sup>2</sup> (x10 <sup>-2</sup> ) |      |
|-------------------------------------|-----|--|------------------------------|-------------------------|--|--|----------------------|-------------------------------------|------|
| HFO #1                              | 4.2 | 0.71                                       | O                            | 2.2                     | 2.01   | 0  | 0.12                 | -6.3                                | 0.24 |
| 1.2 M                               |     |  | Cl                           | 2.4                     | 2.28   | 0  | 0                    | +6.0                                |      |
| HFO #2                              | 5.0 | 3.62                                       | O                            | 3.1                     | 1.99   | 0  | 0                    | -0.9                                | 0.27 |
| 1.2 M                               |     |  | Cl                           | 1.1                     | 2.28   | 0  | 0.15                 | +2.0                                |      |
| HFO #3                              | 7.9 | 4.66                                       | O                            | 4.4                     | 1.99   | 3.6  | 0                    | +0.8                                | 0.59 |
| 1.2 M                               |     |  |                              |                         |  |  |                      |                                     |      |
| HFO #4                              | 9.4 | 4.52                                       | O                            | 3.8                     | 1.99   | 0.9  | 0                    | +1.0                                | 0.81 |
| 1.2 M                               |     |  |                              |                         |  |  |                      |                                     |      |
| HFO #5                              | 3.8 | 4.50                                       | O                            | 4.2                     | 1.99   | ~0   | 0                    | +0.0                                | 0.59 |
| 0.056 M                             |     |  |                              |                         |  |  |                      |                                     |      |
| HFO #6                              | 5.1 | 4.76                                       | O                            | 4.4                     | 2.00   | 1.6  | 0                    | -0.8                                | 0.06 |
| 0.056 M                             |     |  |                              |                         |  |  |                      |                                     |      |
| HFO #7                              | 8.3 | 4.33                                       | O                            | 4.3                     | 1.99   | ~0   | 0                    | +0.0                                | 0.36 |
| 0.056 M                             |     |  |                              |                         |  |  |                      |                                     |      |
| HFO #8                              | 9.4 | 3.95                                       | O                            | 4.2                     | 1.99   | ~0   | 0                    | +0.0                                | 0.17 |
| 0.056 M                             |     |  |                              |                         |  |  |                      |                                     |      |
| error                               | 0.1 | 0.02                                       |                              | 0.5                     | 0.01   | 0.5  | 0.05                 | 0.5                                 |      |

Modeling of the EXAFS oscillations using the anharmonic and curved-wave theories (Crozier et al 1988; Rehr et al 1986) gives average structural parameters for the Au environment: identity of the first neighbors (N), a Debye-Waller type factor ( $\Delta\sigma^2$ ), and an anharmonic parameter ( $\Delta C_3$ ). The two last parameters provide a mesure of relative disorder and anharmonicity of the Au-O/Cl pair-correlation.

### 3. Results

#### 3.1 XANES

Edges for Au(0) and Au(I) model compounds are shifted by  $\sim 5$  eV toward lower energies and the Au-L<sub>III</sub> « white line » is much smaller in relative intensity as compared to Au(III)-model compounds, which contain square planar moieties around Au (Farges *et al.*, 1992). The Au-L<sub>III</sub> XANES spectra of the Au:HFO's also show an intense "white line", as in  $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Au}_2\text{O}_3$ . Also, the edges are not shifted from these Au(III)-models compounds, suggesting that gold adsorbed on HFO's is dominantly Au (III), as in the starting Au-solutions (Farges *et al.*, 1992).



**Figure 1**

Fourier transforms of the  $k^3$ -weighted EXAFS spectra,  $\chi(k)$ , (shown in the inset) for 2 selected Au:ferrhydrites (#2 and 4: see Table 1 for experimental details) as compared to two Au(III)-model compounds ( $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Au}_2\text{O}_3$ ). For  $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$ , a feature near 4-5 Å (uncorrected for phase shift) in the FT for  $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$  arises from both a Au (single-scattering) and Au-Cl (multiple-scattering from  $\text{AuCl}_4$  moieties) neighbors.

#### 3.2 EXAFS

The FT's of the  $k^3$ -weighted EXAFS spectra for the samples synthesized under the most acidic conditions (HFO#1, #2) show two components in the main peak of the FT (see Fig. 1 for HFO#2). For HFO#1, the smaller amplitude component occurs at the shortest distance and is due to O-first neighbors (or OH,  $\text{H}_2\text{O}$ ) around Au. The second component is related to Cl ligands at a higher distance from the central Au. In HFO#2,

the two components of the main peak in the FT have the same magnitude (Fig. 1). For the other samples, the FT shows only one component at the shortest distance due to O-first neighbors around Au (for example HFO# 4 in Fig 1). No clear evidence for Fe or Au second neighbors was detected: in the spectra. Results of the least-square fitting of the backtransformed EXAFS spectra for the first shell of neighbors are reported in Table 1. In all solutions, the mean Au-O and Au-Cl distances (when measurable) are about the same, *i.e.*, 2.00(2) and 2.28(2) Å, respectively. These distances are typical of 4-coordinated Au complexes (Farges *et al.*, 1992). However, the number of O/Cl first neighbors around Au depends strongly on pH and the Cl concentration of the original Au-solution. Under the most acidic conditions (together with high Cl concentration), an equal number of O and Cl first neighbors is measured. In contrast, Au(III) sorbed on the other HFO's studied has  $\approx 4$  O first neighbors around the central Au, with no evidence of first-neighbor Cl.

### 4. Conclusions

We have shown that gold adsorbed on ferrihydrites is dominantly trivalent, so no photoreduction occurred during adsorption or data collection. Different local environments of Au(III) have been revealed, depending on pH and Cl concentration, which are similar to the structural environments around Au in the original aqueous solutions. At low pH and high Cl concentration, mixed chloro-hydroxo complexes ( $\text{Au(III)Cl}_2\text{O}_2^{3-}$  or  $\text{Au(III)ClO}_3^{+}$ ) are present around Au. At high pH, or low Cl concentration, the local environment around Au shows only the presence of O ( $\text{OH}$ ,  $\text{H}_2\text{O}$ ) ligands.

The absence of significant EXAFS contributions arising from iron second neighbors around Au in these HFO's would suggest that Au forms outer-sphere complexes. However, the lack of Au-Fe contributions can also be related to disorder effects. The examination of absorption curves as a function of pH may indicate that inner-sphere complexes only at high Cl-concentration (1.2 M).

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