

Adsorption Mechanisms of Trivalent Gold onto Iron Oxy-Hydroxides: From the Molecular Scale to the Model

Benjamin Cancès¹, Marc Benedetti², François Farges^{3,4}, Gordon E. Brown Jr.^{4,5}

¹ *Laboratoire des géomatériaux, Université de Marne-la-Vallée, 77454 Marne la Vallée Cedex 2, France*

² *Lab. de Géochimie des Eaux, UMR CNRS 7047, Univ. Denis Diderot - Paris 7 IPGP, 75005 Paris, France*

³ *USM 201 "Minéralogie-Pétrologie", Muséum National d'Histoire Naturelle, CNRS UMR 7160, Paris, France*

⁴ *Department of Geological & Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA*

⁵ *Stanford Synchrotron Radiation Laboratory, SLAC, MS 69, 2575 Sand Hill Rd., Menlo Park, CA 94025, USA*

Abstract. Gold is a highly valuable metal that can concentrate in iron-rich exogenetic horizons such as laterites. An improved knowledge of the retention mechanisms of gold onto highly reactive soil components such as iron oxy-hydroxides is therefore needed to better understand and predict the geochemical behavior of this element. In this study, we use EXAFS information and titration experiments to provide a realistic thermochemical description of the sorption of trivalent gold onto iron oxy-hydroxides. Analysis of Au L_{III}-edge XAFS spectra shows that aqueous Au(III) adsorbs from chloride solutions onto goethite surfaces as inner-sphere square-planar complexes (Au(III)(OH,Cl)₄), with dominantly OH ligands at pH > 6 and mixed OH/Cl ligands at lower pH values. In combination with these spectroscopic results, Reverse Monte Carlo simulations were used to constraint the possible sorption sites on the surface of goethite. Based on this structural information, we calculated sorption isotherms of Au(III) on Fe oxy-hydroxides surfaces, using the CD-MUSIC (Charge Distribution – Multi Site Complexation) model. The various Au(III)-sorbed species were identified as a function of pH, and the results of these EXAFS+CD-MUSIC models are compared with titration experiments. The overall good agreement between the predicted and measured structural models shows the potential of this combined approach to better model sorption processes of transition elements onto highly reactive solid surfaces such as goethite and ferrihydrite.

Keywords: Gold, adsorption, titration, iron oxides, EXAFS, XANES, RMC, CD-MUSIC.

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INTRODUCTION

In iron-rich tropical soils, gold anomalies lead to micro-mining activities that have a major environmental impact because of the misuse of potentially harmful chemicals (elemental mercury and cyanides). The retention of trace elements in soils depends largely on their interactions with highly reactive soil minerals such as iron oxides. The objective of this study is to better understand the adsorption mechanism(s) of trivalent gold onto iron-(oxy)hydroxides. This improved knowledge is key to modeling and thus predicting the geochemical behavior of this element in iron-rich exogenetic horizons such as laterites. X-ray absorption fine structure (XAFS) spectroscopy is a technique of choice for determining the molecular-scale speciation of trace element interactions at the mineral/water interfaces [1]. However, thermo-chemical simulations are needed to better interpret the XAFS speciation

information. This study consists then of a Au-L_{III} XAFS spectroscopy study combined with surface complexation modeling using CD-MUSIC [2] to provide a description of the adsorption mechanism(s) of Au(III) onto iron (oxy)hydroxides [3] consistent with thermochemical data [2].

EXPERIMENTAL METHODS

Samples of Au(III) sorbed on synthetic goethites (specific surface area = 78 m²/g) were prepared from an aqueous chloride solution under varying conditions of pH (4-9), ionic strength (I = 0.1 M and 0.01 M), and aqueous gold concentrations ([Au]_{aq} = 0.95 mM, 3.45 mM, and 9 mM). These samples were used in the XAFS experiments, and additional details on their synthesis are given elsewhere [3]. For batch uptake experiments, different Au(III) solutions were used with variable pH conditions, controlled with a pH-stat at constant [Au]_{aq} (0.16 mM) for various ionic

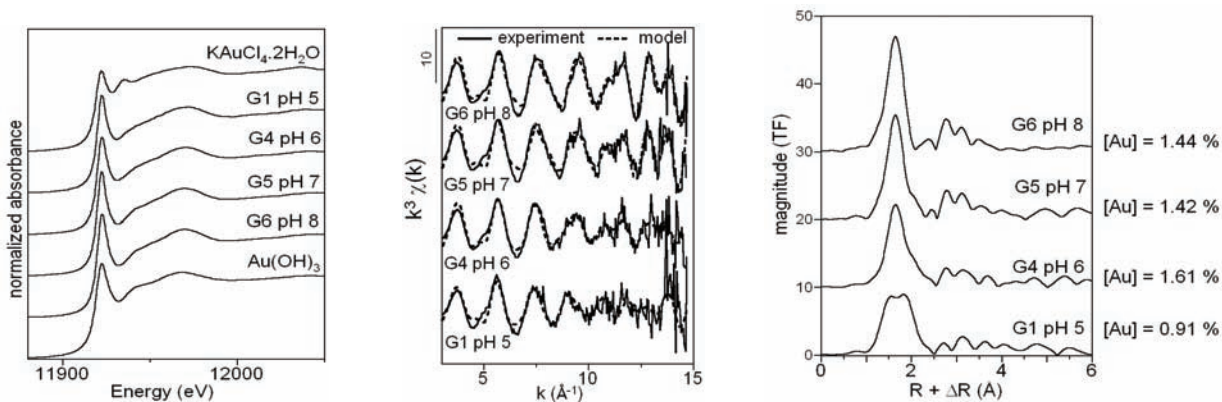


FIGURE 1. Au-L_{III} edge XANES (left), k³-weighted EXAFS spectra (middle) (solid lines: experiment; dotted lines: FEFF7 model) and Fourier Transforms (right) of the EXAFS spectra (shown in the middle figure) for four selected goethites with sorbed Au(III) at [Cl] = 0.1 M and [Au]_{aq} = 0.95 mM at different pH values [3].

strengths (I = 0.1 M and 0.01 M) and chloride concentrations ([Cl] = 0.1 M and 0.01 M). For both sets of samples, the gold concentration in the solid phase is comparable (~ 2000 ppm).

Au-L_{III} edge XAFS spectra (11919 eV) were collected both at SSRL (SPEAR2 beamline 4-3) and at the LURE (DCI beamline EXAFS2). At LURE, we used a double-crystal Si(111) monochromator to collect XAFS spectra at 5-10 K to minimize photo-reduction processes. A single element Ge-solid state detector was used to collect the XAFS data to k = 15 Å⁻¹ in the fluorescence mode. At SSRL, we used a double-crystal Si(220) monochromator to collect XAFS spectra at ambient temperature. A “Lytle” detector (with Ge 3μ filters and filled with Ar) was used to collect the XAFS data to k = 15 Å⁻¹ in fluorescence mode. XAFS spectra were reduced using “xafs” software [4]. We considered photo-reduction, multi-electronic excitations and multiple scattering (within the Au square planar geometry) artefacts [4]. FEFF backscattering amplitudes and phase-shift functions for Au-O, Au-Cl, and Au-Fe pairs were computed using FEFF 7 [5].

The adsorption isotherms from the titration experiments were fit using the CD-MUSIC model [2] integrated within the ECOSAT package [6]. This model was chosen because the XAFS-derived structural information can be used to refine a Au:goethite surface complexation model as a function of pH, chloride concentration, and ionic strength. Thus, molecular-scale information from XAFS spectroscopy can be used to constrain the chemical reactions required to fit macroscopic thermochemical data within CD-MUSIC. In this model, the charge of a specifically sorbed ion (inner-sphere complex) is distributed among the ligands surrounding Au(III) at the mineral/water interface. The adjustable model parameters (Au-binding constants and charge distribution for each surface complex) are computed

by minimizing the difference between the modelled and experimental titration experiments.

TABLE 1. Refined CD-MUSIC model parameters used to describe Au(III) sorption complexes on goethite (110)

surface complex	Log K	charge distribution		
		Z ₀	Z ₁	Z ₂
(≡Fe-OH) ₂ -AuCl ₂	29.6	1.5	-0.5	0
(≡Fe-OH) ₂ -AuClOH	34.5	1.5	-0.5	0
(≡Fe-OH) ₂ -Au(OH) ₂	44.2	1.5	-0.5	0

RESULTS AND DISCUSSION

Examples of Au-L_{III} edge XANES and EXAFS spectra for Au(III) sorbed on goethite are displayed in Figure 1. Analysis of these EXAFS spectra shows that aqueous Au(III) adsorbs from chloride solutions onto goethite surfaces as inner-sphere square-planar complexes (Au(III)(O,Cl)₄) with dominantly O ligands at pH > 6 and mixed O/Cl ligands at lower pH values [3]. Standard EXAFS analysis yielded iron second neighbors around Au at 3.1 and 3.3 Å. These distances correspond to monodentate (single corner sharing) and bidentate (double corner sharing) Au complexes, respectively, on the (110) surface of goethite. The (021) surface is not relevant in this context because it typically represents ~10 % of goethite surfaces (and did not provide a good fit to the titration data). In contrast, Reverse Monte Carlo (RMC) simulations of the same EXAFS spectra indicate the presence of a continuum of Fe next-nearest neighbors around Au [7]. However, RMC models suggest that the bidentate complex is the more plausible complex on the goethite surface. Therefore, only this type of complex (labeled “(≡Fe-OH)₂”) was used for modeling Au(III)/goethite sorption isotherms from the titration experiments.

TABLE 2. Speciation information for Au(III) sorbed on goethite: comparison between CD-MUSIC predictions and results of EXAFS experiments.

pH	CD-MUSIC model		EXAFS
	% surface complexes	Au-Speciation	
4	100 % ($\equiv\text{Fe-OH}$) ₂ -AuCl ₂	2.0 × Cl 2.0 × OH	2.1 × Cl 2.1 × O
5	87 % ($\equiv\text{Fe-OH}$) ₂ -AuCl ₂ 13 % ($\equiv\text{Fe-OH}$) ₂ -Au(OH) ₂	1.7 × Cl 2.3 × OH	1.9 × Cl 2.3 × O
6	6 % ($\equiv\text{Fe-OH}$) ₂ -AuCl ₂ 94 % ($\equiv\text{Fe-OH}$) ₂ -Au(OH) ₂	0.1 × Cl 3.9 × OH	0.1 × Cl 4.1 × O
7	100 % ($\equiv\text{Fe-OH}$) ₂ -Au(OH) ₂	4.0 × OH	4.4 × O
8	100 % ($\equiv\text{Fe-OH}$) ₂ -Au(OH) ₂	4.0 × OH	4 × O
9	100 % ($\equiv\text{Fe-OH}$) ₂ -Au(OH) ₂	4.0 × OH	3.8 × O

Modeling Au(III) Adsorption on Goethite using CD-MUSIC and EXAFS

The fits of the CD-MUSIC model to the Au(III)/goethite sorption isotherms are shown in Figure 2. The refined CD-MUSIC model parameters are reported in Table 1. For these experimental conditions, there is good agreement between the sorption isotherms and the CD-MUSIC model. The various Au(III)-square-planar complexes ($\text{Au(III)(OH)}_{4-n}\text{Cl}_n$; $n = 1-4$) as a function of pH are provided by these fits. They can be compared (see Table 2) with the Au-speciation results obtained from EXAFS analysis (nature and number of first neighbors around Au). The overall agreement is good and confirms that the dominant type of surface complex is Au(III)(OH,Cl)_4 double corner-shared with iron-containing octahedra on the (110) goethite surface.

CONCLUSIONS

EXAFS analysis at the Au-L_{III} edge combined with Reverse Monte Carlo simulations, bond valence constraints, and CD-MUSIC modeling provide a coherent description of Au(III) adsorption onto goethite. Au(III) is dominantly sorbed in a bidentate fashion to iron-containing octahedra on the goethite (110) surface under the experimental conditions of this study. The strong inner-sphere sorption of Au(III) onto goethite can plausibly contribute to “hidden gold” in natural laterites. The approach used in this study (XAFS analysis and thermochemical modeling) can be applied to other iron oxides, such as ferrihydrite (a

complex aperiodic iron-oxy-hydroxide, HFO). A similar combination of EXAFS spectroscopy, sorption isotherm measurements, and CD-MUSIC modeling of the sorption of Au(III) onto HFO has been carried out, and the adsorption isotherm data were fit using parameters for HFO [8]. The results are similar to those for Au(III) sorption on goethite, although there are some notable differences that are currently being investigated.

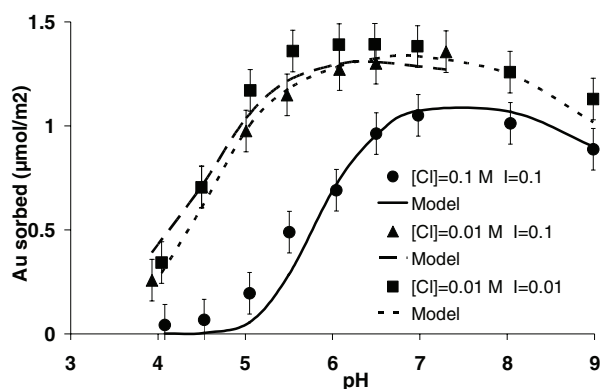


FIGURE 2. CD-MUSIC models (solid lines) of the sorption isotherms (symbols) for Au(III) sorbed on goethite.

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