Adsorption of Gold on Goethite Compared to the Starting Gold(III)-Chloride Solutions by XAFS Spectroscopy

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A better understanding of gold solutions and interactions with synthetic soils is necessary for modelling the gold transport and the deposition phenomena. Adsorption at minerals surfaces could be an important mechanism controlling the solubility of gold in natural environment (Schoonen et al., 1992). The iron oxihydroxides are common phases in tropical soils and they can fix weighted elements like gold (Schoonen et al., 1992; Greffié et al., 1996 ; Karasyova et al., 1998 ; Benedetti and Boulegue, 1990). Several studies of co-precipitation and potentiometric experiments (see Karasyova et al., 1998; Greffié et al., 1996; Machesky et al., 1991) do not give direct structural information on the speciation of Au on these surfaces. Therefore, direct spectroscopic studies are required. The objective of this work has been to provide structural information of sorbed gold on goethites in function of pH (4-9) and chloride (0.1-0.01M) and gold ($3 \cdot 10^{-3}$ - $9 \cdot 10^{-4}$M) concentration. We have characterised our samples of gold solution by ICPAES and our sorption samples by X-ray diffraction, ESEM and both by XAFS at SSRL on beamline 4-3 and at LURE. The gold sorption curve on goethite shows the "retrograde adsorption" for both solutions (0.01M Cl and 3.10^{-3}M Au and 0.1M Cl and 9.10^{-4}M Au) which suggest a inner sphere adsorption mechanism. The adsorption is more intense for low concentrations in chloride this has already been showed by Machesky (1991). During the XAFS experiments, we used either first generation synchrotron source (LURE) or cryostat in second generation synchrotron source (SSRL) in order to minimise the photo-reduction process occurring under the beam. For all solution and sorption samples, only Au(III) was detected, the presence of Au(I) or Au(0) were not observed. The XAFS results show for gold solutions the substitution of chloride ligands by oxygen ligands from acidic pH to basic pH. These results are consistent with the Raman results on gold solutions with low chloride and gold concentration (Murphy et al., 1998). For the solution 0.01M [Cl] and 3.10^{-3}M [Au], gold is present either as $AuCl_4^-$ square planar complex (at pH=2 and 4), as $AuCl_3O^{2-}$ (at pH=5), $AuCl_2O_2^{3-}$ (at pH=6), $AuClO_3^{4-}$ (at pH=7), $AuClO_3^{4-}$ (at pH=8) and/or AuO_4^{5-} with Au-O and Au-Cl distances of 2.00(2)Å and 2.30(2)Å. We have also performed XAFS experiments on decanted centrifuged solution after equilibrium to check that any changes do not occur in solution after sorption. However, the XAFS results on gold sorbed on goethite show a different speciation compared to gold in solution. Indeed, gold sorbed on goethite is present as $AuClO_3^{4-}$ at pH=4 compared to $AuCl_4^-$ in the starting solution; as $AuClO_3^{4-}$ and/or AuO_4^{5-} at pH=5 ($AuCl_3O^{2-}$ in solution), as $AuClO_3^{4-}$ and/or AuO_4^{5-} at pH=6 ($AuCl_2O_2^{3-}$ in solution); as AuO_4^{5-} at pH=7 ($AuClO_3^{4-}$ in solution); as AuO_4^{5-} ($AuClO_3^{4-}$ and/or AuO_4^{5-} in solution). Therefore, adsorption of gold on goethite through Au-Cl-Fe linkage is not

favoured, because we only observed maximum 2 Cl first neighbours around gold (but the starting solution contained 4 chlorides) which is consistent with adsorption curves. This sorption mechanisms can be understood considering Pauling rules which do not allow sorption of square planar Au(III) through Au-Cl-Fe linkages because the sum of the bond valence is higher than the charge of the chloride. For gold sorbed on goethite, we detected two contributions of iron second neighbours near 3.0Å and 3.3Å which correspond respectively to edge linkage and bidenate binuclear linkage on the goethite surface. We can notice that adsorption through a edge linkage is not favour at acidic pH. Another process involved in this region is the multiple scattering of the first neighbours easily observable in gold solutions. Au(III) has a square planar geometry which favour a lot multiple scattering, which interfere with second neighbours, when gold is adsorbed, and make the EXAFS signal difficult to analyse.
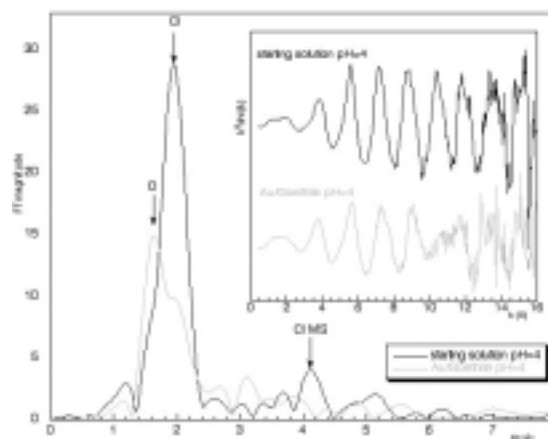

Figure 1: Fourier Transform of the k^3 weighted EXAFS spectra $\chi(k)$, (shown in the inset) for the starting solution (0.01 M Cl and 3.10^{-3}M Au) compared to Au:goethite at pH=4. For the starting solution, a feature near 4 Å (uncorrected for phase sh

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