# An EXAFS study of the adsorption of $Au^{3+}$ from aqueous chloride solutions to goethite (α-FeOOH)

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The solubility, and therefore the transport, of Au in sedimentary basins has traditionally been attributed to $Cl^-$ in oxidising environments (Cloke and Kelly, 1964). However recent work has highlighted two important points. Firstly the predominant Au species in most natural waters is $AuOH(H_2O)^0$ and secondly where $Cl^-$ is present in sufficient quantities (approximately 0.01 M) the $AuCl_4^-$ complex is formed, but is only stable at low pH. At progressively higher pHs the $Cl^-$ ligands in the complex are successively replaced by O(H) (Farges *et al.*,1993 and references therein). X-ray absorption near edge structure spectroscopy (XANES) analysis has suggested a square planar geometry for the $AuX_4^-$ (X = O(H) or Cl) complexes (Farges *et al.*, 1993).

Adsorption to mineral surfaces is very important in controlling the mobility of trace metals in natural waters and understanding the processes involved are vital for modelling and prediction of their behaviour in natural environments. The three main processes that control the dissolved concentration of any trace metal in natural waters are (1) the solubility of the minerals containing the metal, (2) the kinetics of mass transfer and (3) sorption onto particulate matter (Schoonen *et al.*, 1992).

In the case of Au, the solubility of Au bearing minerals is not thought be a significant control since these minerals are rarely present in aqueous systems (Shenberger and Barnes, 1989). Also, experimental studies have shown that natural waters are undersaturated with respect to Au ($mgL^{-1}$ in experimental studies compared to $ngL^{-1}$ in natural waters)(Vlassopoulos and Wood, 1990). Schoonen *et al.* (1992) suggests adsorption is the most significant in controlling Au transport. If the dissolution of Au bearing minerals is kinetically controlled then fluid flow rate and water/rock ration would control the concentration of Au in solution. Low Au concentrations would be expected in systems where fluid flow rate and water/rock ratio are high (e.g. rivers) and concentrations close to saturation would be expected for systems where fluid flow rate and water/rock ratio are low (e.g. stagnant ground water). The fact that Au concentration in fluids in the latter system are significantly below equilibrium values suggests that the dissolution of Au is extremely slow, or is inhibited by adsorption to minerals present. Adsorption is a more likely mechanism since experimental work has shown that at 25°C aqueous solution can reach equilibrium with respect to native Au in 200 days (Vlassopoulos and Wood, 1990).

Sorption may also be important in aqueous systems where Au concentration reach ore grade levels (1 to 10 μg $g^{-1}$). In many Au deposits as well as being found as the native metal some of the Au is hosted by other minerals such as quartz, various sulphides and goethite (α-FeOOH) (Cabri *et al.*, 1989). The origin of this invisible Au is not well known but it is possibly a result of adsorption of

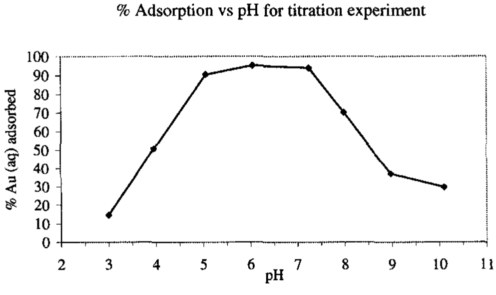

FIG. 1. Showing unexpected decrease in adsorption at low pH.

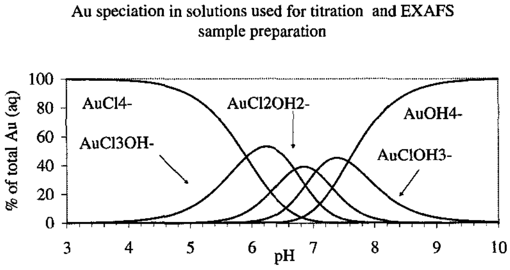

FIG. 2. Showing progressive hydrolysis of the $AuCl_4^-$ complex as pH is increased.

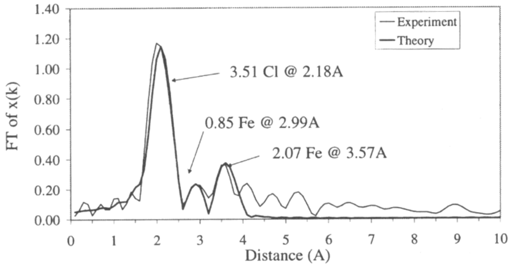

FIG. 3. RDF for sample D2 (pH = 4).

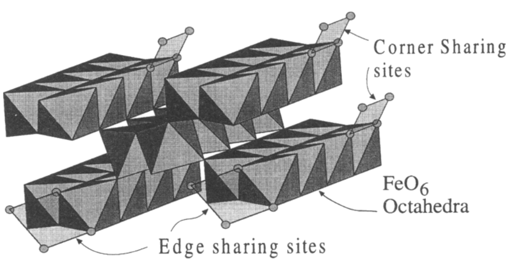

FIG. 4. Proposed structure for AuCl$_4^-$ surface complex on goethite.

aqueous Au to the host minerals during growth (Cabri *et al.*, 1989). Experimental work on the adsorption of Au to goethite has also shown that this mineral is an effective scavenger of Au from solution containing concentrations of Au similar to those found in nature (Schoonen *et al.*, 1992).

## Results

In this work adsorption reactions occurring in the Au$^{3+}$-Cl$^-$-OH$^-$-α-FeOOH system were studied using a combination of potentiometric titration and Extended X-ray Absorption Fine Structure spectroscopy (EXAFS). The titration was performed to assess how the change in aqueous speciation with pH affects the amount of Au adsorbed to the surface. The data obtained from EXAFS was used to assess if the Au speciation on the surface mirrors that in solution and to elucidate the structures of these surface complexes. The aqueous speciation calculations (Fig. 1) show that at all pHs the Au complexes are anionic. The titration data (Fig. 2) shows that at low pH there is a small amount of Au adsorbed and as the pH is increased more Au adsorbs in the mid pH range until at a pH close to pHpzc (8.4) the amount adsorbing starts to decrease. The low adsorption at pHs above the pHpzc is not unusual since the surface has a net negative charge. The low adsorption at low pH is unexpected because the surface in this range has a net positive charge. Comparison with the aqueous speciation (Fig. 1) shows that the decrease in adsorption at low pH coincides with the presence of AuCl$_4^-$ in solution. An initial interpretation of these data is that the Cl$^-$ ligands are less reactive to the surface and the complex being formed is monodentate (since one OH$^-$ ligand is required by the complex before significant adsorption occurs) or that the Au speciation in solution is not reflected by the Au speciation on the surface.

EXAFS samples were prepared at pHs 4, 6.8 and 9.5 and examples of the EXAFS data are shown below for sample D2 (pH = 4). The Fourier transformed RDF is shown in Fig. 3 and the proposed structure of the surface complex formed shown in Fig. 4. In all the samples the AuX$_4^-$ complexes bind to the surface via a bidentate inner sphere mechanism where two of the ligands in the AuX$_4^-$ complex replace two O at the surface of the mineral on a combination of single edge sharing and double corner sharing sites. In the samples at pH 4 and pH 9.5 the species on the surface seem to be the same as the species on the surface(AuCl$_4^-$ (Figs. 1 and 4) and AuOH$_4^-$ respectively).

Whether or not the surface species are the same as the solution species in the sample at pH 6.8 is complicated by two factors. Firstly there is more than one AuX$_4^-$ species present and the error in the coordination numbers (±1) does not permit the determination of the distribution of O and Cl$^-$ in the surface complex. Secondly there is the possibility of isomerisation of the dominant complex (AuOH$_2$Cl$_2^-$) present at this pH.

In order to resolve this complexity calculations using Amsterdam Density Functional modelling will be performed to determine which of the possible geometries is the most stable. This approach will complemented by high resolution titrations and surface complexation modelling in order to elucidate the AuX$_4^-$ complexes on the surface.

## References

Cabri, L.J., Chryssoulis, S.L., de Villiers, J.P.R. and Lafamme, J.H.G. (1989) *Canad. Mineral.*, **27**, 353–62.

Cloke, P.L. and Kelly, W.C. (1964) *Econ. Geol.*, **59**, 259–70.

Farges, F., Sharps, J.A. and Brown, G.E. (1993) *Geochim. Cosmochim. Acta*, **57**, 1243–52.

Schenberger, D.M. and Barnes, H.L. (1989) *Geochim. Cosmochim. Acta*, **53**, 269–78.

Schoonen, M.A.A., Fisher, N.S. and Wente, M. (1992) *Geochim. Cosmochim. Acta*, **56**, 1801–4.