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Adsorption of Au(I, III) complexes on Fe, Mn oxides and humic acid

Yong Ran[a,*], Jiamo Fu[a], A.W. Rate[b], R.J. Gilkes[b]

[a]*State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou Wushan, 510640, People's Republic of China*
[b]*Soil Science and Plant Nutrition, The University of Western Australia, Perth 6009, Australia*

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Abstract

The adsorption of $AuCl_4^-$, $AuCl_2^-$ and $Au(S_2O_3)_2^{3-}$ at low Au concentrations relevant to most supergene waters on geothite, birnessite and soil humic acid was investigated at pH 4, pH 2–11.6, in 0.01 and 0.1 M $NaNO_3$ solutions. At pH 4 and two electrolyte strengths, the adsorption isotherms for the two Au chloride complexes are well described by the Freundlich equation. The Freundlich parameter $1/n$ reflects the heterogeneity of the birnessite surface and the nonlinearity of Au adsorption isotherm. The adsorption of $Au(S_2O_3)_2^{3-}$ is significantly greater than that of $AuCl_4^-$ on birnessite, but the adsorption of $Au(S_2O_3)_2^{3-}$ is significantly smaller for geothite and humic acid. The adsorption of $AuCl_4^-$ on birnessite and geothite is depressed by increasing electrolyte strength. As birnessite could only adsorb gold anions specifically and goethite could adsorb gold anions by anionic exchange and specific adsorption, the adsorption on goethite is more sensitive to the electrolyte strength. Under these experimental conditions, the Au surface coverage on birnessite is 0.68–0.85% for $AuCl_4^-$ and 1.06–1.10% for $Au(S_2O_3)_2^{3-}$, and for goethite is approximately 2.33–6.02% for $AuCl_4^-$ and 0.6–1.05% for $Au(S_2O_3)_2^{3-}$. For the pH ranges from 2 to 11.6 and with 0.1 M $NaNO_3$ as the background electrolyte, Au adsorption decreases with increasing solution pH, which is consistent with the adsorption regularity for anion adsorption on a variable charge surface. For the three surfaces, true solid–liquid distribution coefficients for the Au complexes at these low concentrations that are relevant to most supergene water are significantly negatively correlated with solution pH with the correlation coefficient ranging from -0.941 to -0.996. According to the Kurbatov plot and surface hydroxyl density, the conditional equilibrium constants ($\log K_{part}$) can be estimated. For the three surfaces, values of $\log K_{part}$ for adsorption of $AuCl_4^-$ are in the order: birnessite > goethite>humic acid; but for adsorption of $AuCl_2^-$ are goethite>birnessite>humic acid. The effect of the dissolved humic acid on data could be corrected by using a three-phase partition model that accounts for the complexation of the solute by dissolved organic matter in the liquid phase. For low pH ($pH < 3$) solutions, the sorption of $AuCl_4^-$ on humic acid may be related to reduction of Au(III) by the humic acid. However, adsorption of $AuCl_4^-$ and $AuCl_2^-$ on humic acid is similar to that for birnessite and geothite for the higher pH solutions. Hence, birnessite, geothite, and humic acid preferentially adsorb chloro and chloro-hydroxo Au complexes produced from hydrolysis of $AuCl_4^-$ and $AuCl_2^-$ hydrolysis. Gold anion surface complexation and Au speciation in solution lead to the decrease in adsorption of Au complexes with increasing solution pH. As birnessite has very strong oxidation and adsorption abilities for monovalent Au complexes such as $Au(S_2O_3)_2^{3-}$, it may play an important role in the deposition and

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[*] Corresponding author.
E-mail address: yran@gij.ac.cn (Y. Ran).

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accumulation of the dissolved gold in the supergene environment. Whether and how Au(III) complexes could be transformed to Au(I) complexes or Au° is controversial and needs further investigation.

Keywords: Variable charge surfaces; Humic acid; Au(I, III) complexes; Hydrolysis; Specific adsorption

1. Introduction

Recent investigation shows that gold may be mobilized, transported and redistributed under the various physical and chemical processes in the supergene environments. The mobilization and transport processes of gold are associated with gold complexes. Various ligands have been hypothesized to be important in mobilizing gold in certain environments. Under most conditions, the prevalent dissolved gold complex has been suggested to be $AuOH{\cdot}H_2O^{\circ}$ (Vlassopoulos and Wood, 1990). Near oxidizing sulfide minerals, complexes such as $Au(HS)_2{}^-$, $AuHS{\cdot}H_2O^{\circ}$ (Renders and Seward, 1989) and $Au(S_2O_3)_2{}^{3-}$ (Plyusnin et al., 1981; Webster, 1986) may aid gold mobility and dispersion. At high Cl^- concentrations that exist in many arid regions, gold may be mobilized as Au(I)– or Au(III)–chloride complexes which are stable under acidic, oxic, and high Cl^- conditions and have been hypothesized as contributing to gold mobility in arid lateritic terrains (Mann, 1984; Gary et al., 1992). Other important forms of transportable gold may include gold complexes with organic matter(Baker, 1978; Wood, 1996) and CN^- (Lakin et al., 1974) and elemental colloidal gold (Ong and Swanson, 1969).

Gold mobility in most thermodynamic models is attributed to the $Au(Cl)_4{}^-$ complex (Krauskopf, 1951; Cloke and Kelly, 1963; Mann, 1984). In such models, the gold and chloride concentrations used are much higher than in many natural supergene waters. In supergene waters, chloride concentrations are commonly in the range 10^{-2} to 10^{-4} mol/l, whereas chloride concentrations used in the models referenced above are in the range of 1 to 0.1 mol/l (Gary et al., 1992; Benedetti and Boulegue, 1991). Moreover, gold concentrations inferred from these models range from 10^{-4} to 10^{-6} mol/l, whereas measured gold concentrations in natural fresh waters are much smaller, being commonly in the range of 10^{-9} to 10^{-10} mol/l (McHugh, 1988).

New thermodynamic data and theoretical calculations for gold hydrolysis demonstrate that in conditions prevailing for most supergene waters the complex that should control the solubility is $AuOH(H_2O)^{\circ}$ rather than $AuCl_4{}^-$ (Vlassopoulos and Wood, 1990; Tossell, 1996). At pH>12, $Au(OH)_2{}^-$ should be the major complex controlling gold solubility, but such higher pH values rarely occur in the environment. Thus, Au(I) should be dominant in natural environments. The pe–pH stability field for $Au(Cl)_2{}^-$ corresponds to acidic oxidizing environments. The maximum solubility of gold as $AuOH(H_2O)^{\circ}$ under natural water conditions appears to be several orders of magnitude higher than measured concentrations for natural waters (Vlassopoulos and Wood, 1990). Benedetti and Boulegue (1991) presented the field water chemistry data for a stream where weathering of auriferous minerals is occurring under supergene conditions in a temperate climate and concluded that gold solubility is controlled by a gold thiosulfate complex.

Organic material has been implicated in gold transport and/or fixation during the formation of laterites (Wilson, 1984; Butt, 1989; Andrade et al., 1991; Colin and Vieillard, 1991; Bowell et al., 1993a; Liu et al., 1994; Machesky et al., 1991, 1992; Zang and Fyfe, 1993). Organic matter has also been found to be associated with gold anomalies in stream sediments and soils (Gregoire, 1985). It is noted that surprisingly few studies have attempted to determine directly the gold content of organic matter extracted from Au-enriched environments, but those that have (e.g., Gregoire, 1985), clearly demonstrate an association between organic matter and gold (Wood, 1996). Vlassopoulos et al. (1990) have demonstrated that complexes between the "soft" Au^+ ion and "hard" O-donor ligands such as carboxylic acids are relatively weak and unlikely to bind gold, primarily because they will have a greater preference for "harder" metal ions such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and Al^{3+}. "Soft" N- and S-donor ligands form much stronger bonds with Au^+. Bowell et al. (1993b) showed that fulvic acid (FA) with a high S content (4.2%) apparently solubilizes more gold than FA with a low S content (0.7%) at a given pH. On the other hand, under some circumstances the major role of organic matter, including humic substances, is to reduce ionic forms of gold to Au° and hence causing its precipitation. Because Au species such as $AuCl_4^-$ are stable only in oxidizing media ($E_o = 1.002$ V), in the absence of a very strong tendency for a particular humic acid (HA) or FA to form stable dissolved complexes with Au^{3+} or Au^+, such species are easily reduced upon entering environments containing HA or FA, for which E_o ranges from $+0.5$ to $+0.7$ V (Szilagyi, 1973; Wilson and Weber, 1979; Skogerboe and Wilson, 1981). However, where gold is transported by complexes with much lower standard reduction potentials, e.g., $Au(OH)(H_2O)^\circ$ ($E_o = 0.506$ V; Vlassopoulos and Wood, 1990), $Au(HS)_2^-$ or $Au(S_2O_3)_2^{3-}$, humic substances may be a much less important factor in causing its reduction and fixation. Where humic substances have a relatively high portion of N- or S-donor binding sites, then strong complex formation may lower the standard reduction potential of the gold species sufficiently to prevent reduction and effect aqueous transport. Finally, it should be noted that even if dissolved gold is reduced by dissolved HA or FA, precipitation may not occur immediately if a finely dispersed colloidal suspension results. The presence of humic substances may in fact stabilize such colloids against coagulation (Ong and Swanson, 1969). Alternatively, humic acid itself might form a colloid and transport gold sorbed onto the surfaces of the colloidal HA particles (Ong and Swanson, 1969).

Adsorption onto mineral surfaces is probably important in determining the extent of gold mobilization, dispersion and deposition. Numerous studies have focused on the adsorption of Au(III)–chloride complexes and thio Au(I) complexes onto oxide mineral surfaces (Krendelev et al., 1987; Nechaev, 1985; Nechaev and Nikolenko, 1987; Fedoseyeva and Strl'tsova, 1987; Fedoseyeva and Zvonareva, 1988; Machesky et al., 1991; Schoonen et al., 1992; Greffie et al., 1996; Ran et al., 1999) and on sulfide mineral surfaces (Jean and Bancroft, 1985; Hyland and Bancroft, 1989; Renders and Seward, 1989; Schoonen et al., 1992) as well as the adsorption of colloidal gold onto iron oxides (Enzweiler and Joekes, 1991). These studies suggest that Au(III)–chloride complexes are adsorbed specifically (inner-sphere coordination) onto hematite and goethite surfaces, while the adsorption of thio Au(I) complexes on iron oxide surfaces is supposed to occur through a nonspecific (outer-sphere) mechanism. Consequently, Au(III) chloride complexes are adsorbed more readily onto goethite than are thio Au(I) complexes. Steric hindrance of the bulky $Au(S_2O_3)_2^{3-}$ might be the reason for the weaker interaction (Mitsyuk et al., 1991). Greffie et al. (1996) suggested that colloidal gold and gold(III) complexes are associated with iron oxides. Colloidal gold particles ranging from 30–60 nm in diameter were embedded in a ferrihydrite matrix. Poorly ordered iron oxides such as ferrihydrite may be highly efficient in trapping gold from solution due to their high surface area.

Adsorption of gold complexes on oxidizable mineral surfaces such as metal sulfides, thioarsenides, and Fe(II)-containing oxides and silicate minerals often involves the reduction of aqueous Au(I) and Au(III) species to elemental gold, which is subsequently sorbed (Lakin et al., 1974; Mironov et al., 1981; Jean and Bancroft, 1985; Hyland and Bancroft, 1989). Gold ions are reduced and adsorbed much more rapidly on pyrite, galena, and pyrrhottite than on quartz or iron oxides (Jean and Bancroft, 1985; Schoonen et al., 1992). The removal of gold colloids from solution is due either to direct uptake by surfaces of the Au colloids or to dissolution and subsequent adsorption (Schoonen et al., 1992). In addition, negatively surface-charged colloidal gold particles could react with positively charged iron oxides by electrostatic interaction (Enzweiler and Joekes, 1991). Although the adsorption of Au complexes on iron oxides and on oxidizable mineral surfaces is quite well understood, no comparison of adsorption of gold among Fe, Mn oxides and humic acid has been made under the same experimental conditions.

A linear free energy relationship (LFER) has been found to exist between the stability constants of Au(I) and Au(III) complexes and those of some transition metal complexes. The stability constants of the common Au(I) and Au(III) inorganic complexes decrease in the following sequence: $CN^- \gg S_2O_3^{2-}$, $NH_3 > OH^- > I^- > SCN^- > OH(H_2O) > Br^- > Cl^- > H_2O$ (Vlassopoulos and Wood, 1990), suggesting that Au(I) and Au(III) ions have relatively high affinities for hydroxyl ions in solutions. A close LFER between cation hydrolysis and adsorption on hydrous ferric oxide has also been observed (Dzombak and Morel, 1990). Machesky et al. (1991) confirmed that the hydrolysis species of gold chloride complexes with < 4 Cl ligands are preferentially adsorbed by goethite and that at a very low surface coverage these species are specifically adsorbed in an inner-sphere, bidentate fashion. Using extended X-ray absorption fine structure spectroscopy (EXAFS), Heasman et al. (1998) verified that the AuX_4^- (X = O(H) or Cl) complexes bind to the surface of goethite via a bidentate inner sphere mechanism. However, Berrodier et al. (1999) used the same technique and found that at low pH and high Cl concentration, mixed chloro-hydroxo complexes ($AuCl_2O_2^{3-}$ or $AuClO_3^{4-}$) are present around Au adsorbed on ferrihydrite, and at high pH or low Cl concentration, the local environment around Au on ferrihydrite shows only the presence of O (OH, H_2O) ligands. The absence of significant EXAFS contributions arising from iron second neighbors around Au on ferrihydrites would suggest that Au forms outer-sphere complexes. Furthermore, the potentiometric titration and surface complexation modeling of $AuCl_4^-$ on hematite conducted by Karasyova et al. (1998) suggest the existence of the following monodentate surface complexes: $FeOHAuCl_3$, $FeOHAuCl_2OH$ and $FeOHAu(OH)_3$. These different results indicate that the nature of Au(III)–chloride speciation remains unclear. The form and coordination of the Au(III)–chloride species present in aqueous solution are controversial, and consequently, free energy data for Au(III)–chloride hydrolysis species are not well constrained (Machesky et al., 1991; Machesky, 2000, personal communication). Since Au(I) thiosulphate is a stronger complex than $AuCl_4^-$, it may be more resistant to hydrolysis and hence less prone to adsorption by goethite. The first hydrolysis constants for Au(I) and Au(III) ions are much larger than those for mercury ion and silver ion, respectively (Vlassopoulos and Wood, 1990; Baes and Mesmer, 1976). So, it is predicted from the observed LFER that Au(I) and Au(III) complexes will be strongly adsorbed by Fe and Mn oxide surfaces. Finally, it should be pointed out that more data from potentiometric titrations and spectroscopic measurements are needed to ascertain the speciation of gold complexes in solutions and surfaces at different pH.

This study deals with the adsorption of Au(III) chloride, Au(I) chloride and thiosulphate complexes on goethite, birnessite and humic acid, and the effects of solution pH and electrolyte strength on adsorption.

2. Materials and methods

Birnessite was synthesized with $KMnO_4$ and concentrated HCl (McKenzie, 1981), then washed with deionized water until the electric conductivity of the filtrate was 1–2 μS/cm, dried at 45 °C and passed through 60 mesh sieve. The specific surface area of birnessite synthesized with this method is about 93 m^2/g (McKenzie, 1981). X-ray powder diffraction analysis, obtained with Cu Kα radiation (Philips XRG 3100 X-ray generator), showed that the sample is a poor ordered material with major, broad diffraction peaks at 0.739, 0.244 and 0.142 nm, as are commonly observed for birnessite. The O/Mn atom ratio of the birnessite measured by the iodide titration method (Balistrieri and Murray, 1982) is 1.92 ± 0.09. MnO_2 and K_2O contents were $68.7 \pm 0.46\%$ and $16.4 \pm 0.33\%$, determined by dissolution of 0.2 g birnessite in 100 ml of 0.1 M ascorbic acid solution, and the Mn and K ions were measured by atomic absorption spectrometry and flame photometry, respectively. The pH of zero point of charge (pH_{zpc}) of birnessite was 1.48 determined by using a batch acid and alkaline titration method and Na adsorption (McKenzie, 1981; Murray, 1974). Murray (1974) used the Na^+ adsorption measurements to extrapolate the titration curves to the PZC. Suspensions of birnessite were spiked with $NaNO_3$ and the pH of the suspensions was adjusted by graduated amount of the standardized 0.1 M HNO_3. After equilibration, the supernatants of the suspensions were separated from the solids by centrifugation, and the solids were washed with 95% alcohol three times and dissolved in 0.1 M ascorbic acid solution for measurement of K and Na. McKenzie (1981) used a batch titration for measurement of the exchange capacity of birnessite at pH 7 in 0.1 M electrolyte solution to locate the PZC. The batch titration was carried out by preparing a series of 0.1-g oxide sample in the appropriate electrolyte solution in 50-ml centrifuge tubes. Graduated amounts of standardized 0.1 M NaOH or 0.1 M HCl were added, giving a final volume of 20 ml. The tubes were stoppered and shaken for 3 h before the pH was measured. The suspensions were prepared in nitrogen-saturated water, and all operations were carried out in an atmosphere of nitrogen to avoid contamination with carbon dioxide (McKenzie, 1981). The exchangeable cation content of birnessite is 2.21 ± 0.06 mmol/g in the 0.1 M $NaNO_3$ solution at pH 7.0 according to the method of McKenzie (1981), except that the adsorbed sodium was determined by dissolving the birnessite in 100 ml of 0.1 M ascorbic acid solution rather than extracting three times with 0.5 M NH_4Cl. This gave a reference point for each electrolyte concentration, from which the net titration curves were converted to surface charge. At pH_{zpc}, the residual K contents of birnessite is 0.659 mmol/g. The total adsorption site density (Ns) measured by the method of Mckenzie (1981) was 2.61 mmol/g or 28.1 $\mu mol/m^2$, which is very close to his experimental and calculated values (Ns = 28 $\mu mol/m^2$ or Ns = 24.8 $\mu mol/m^2$). When Ns is expressed in units of surface adsorption sites per nm^2 (S_T), S_T for birnessite is 16.9 sites/nm^2, which is close to the reported S_T (18 sites/nm^2) (Catts and Langmuir, 1986).

Goethite was prepared according to a procedure of Schwertmann and Cornell (1991), which involved the hydrolysis of a $Fe(NO_3)_3 \cdot 9H_2O$ solution by KOH with subsequent heating of the suspension at 70 °C for 60 h. After synthesis, the goethite was concentrated by centrifugation and then extracted with Tamm's solution three times to remove poorly crystalline iron oxides. The extracted product was then washed repeatedly and dialyzed with deionized water, and freeze-dried. An X-ray diffraction (XRD) pattern was found to be identical to that of a standard goethite reported in the literature (Schwertmann and Cornell, 1991). The procedure yielded a well-crystalline goethite with no apparent crystalline impurities, ferrihydrite or amorphous iron oxide. The pH_{zpc} was 7.8 determined using an acid and alkali titration method (Atkinson et al., 1968). The specific surface area determined by the N_2-BET method is 64 m^2 (Davis and Kent, 1990).

Soil humic acid was extracted according to the procedure recommended by the International Humic Substances Society (IHSS, 1996) from the topsoil of a red soil from Hangzhou, P.R. China. The soil was shaken overnight with 0.1 M NaOH under N_2 with a 10:1 extractant/soil ratio. The alkaline supernatant was separated from the residue by centrifugation, acidified with 6 M HCl to pH 1 and allowed to stand overnight at room temperature. The supernatant was separated from the coagulate (HA) by centrifugation. Suspended clays were removed by dissolving the HA in a minimum volume of 0.1 M KOH + 0.2 M KCl (total of 0.3 M K), centrifuging and decanting, and collecting the HA from the supernatant solution as follows: The solution was acidified to pH 1 and the HA was allowed to precipitate and separated from the supernatant by centrifugation. The HA precipitate was treated with 0.1 M HCl plus 0.3 M HF for 7 days. The purified HA was then dialyzed against deionized water to remove free acid and salt, then freeze-dried. The measured total acidity, carboxylic, phenolic, alcoholic functional groups are 5.82, 3.02, 2.79, 1.52 mmol/g dry weight, respectively, using the $Ba(OH)_2$ and $Ca(OAc)_2$ titration, and acetylation method (Schnitzer and Khan, 1978). The ash content is 5.29%.

The 1.17×10^{-3}M $AuCl_4^-$ stock solution was prepared with analytical grade $HAuCl_4 \cdot 3H_2O$ (Sigma, USA). The 1.05×10^{-3}M $Au(S_2O_3)_2^{3-}$ solution was prepared with 90-ml 1.17×10^{-3} M $AuCl_4^-$ solution and 10-ml 4×10^{-2} M $Na_2S_2O_3$ solution and aged for 24 h (Machesky et al., 1991). The 1.06×10^{-3} M $AuCl_2^-$ solution was prepared with 100-ml 1.17×10^{-3} M $AuCl_4^-$ and 10-ml 2.34×10^{-2} M $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ solution (Mycroft et al., 1995).

A series of 20-mg samples of the adsorbates were weighed into the 100-ml plastic centrifuge tubes and 20 ml of various 5.8×10^{-7} to 2.88×10^{-5} M gold complex solutions containing the 0.1 or 0.01 M $NaNo_3$ electrolyte were added. The solution pH was respectively adjusted to 4.0 for the Au adsorption isotherms and a certain range for the effect of pH on Au adsorption with dilute nitrate acid or dilute sodium hydroxide. It has been reported that the adsorption equilibrium of $AuCl_4^-$ on goethite was reached within 75 min for a pH 4.0, 0.01 M $NaNO_3$ solution (Machesky et al., 1991). Therefore, the samples were shaken for 6 h at room temperature (20 ± 2 °C) and then the suspension pH were determined. The samples were centrifuged for 15 min at 4300 rpm (Beckman, Avanti 30) and filtered through a 0.2-μm Millipore filter. The HA concentration in the supernatant was measured with a Shimadzu UV–VIS 3000 spectrophotometer at a wavelength of 295 nm and a light path length of 0.1 cm. It was shown that light absorbence of the soil HA ranging from 55 to 880 μg/ml was liner. The Au concentrations in the supernatants were measured by flame or graphite furnace ($PdNO_3$ as matrix-adjusted reagent) atomic absorption spectrometry (Perkin-Elmer 5100ZL), with detection limits of 10^{-6} and 10^{-9} M, respectively.

3. Results and discussion

3.1. Dissolution of the soil HA at different pH solutions

The concentration of soluble HA in the Au adsorption supernatants at different pH is illustrated in Fig. 1, which indicates that dissolution of HA increases as solution pH increases. There is a very close relationship between HA concentration and solution pH. At pH 3.0, the dissolved HA content was about 2.8 mg and represents about 14% of the total HA. Hence, HA dissolution should be taken into account in the following interpretation of the Au adsorption experiment.

3.2. Adsorption isotherms of gold complexes

At pH 4.0 and two electrolyte strengths (0.01 M and 0.1 $NaNO_3$), the isotherms for the Au adsorption on goethite, birnessite and humic acid for $Au(S_2O_3)_2^{3-}$ and $AuCl_4^-$ solutions are illustrated in Fig. 2a,b. As shown in Fig. 2a, the adsorption isotherm for $Au(S_2O_3)_2^{3-}$ on birnessite is H-type, demonstrating the very strong affinity of birnessite for $Au(S_2O_3)_2^{3-}$.

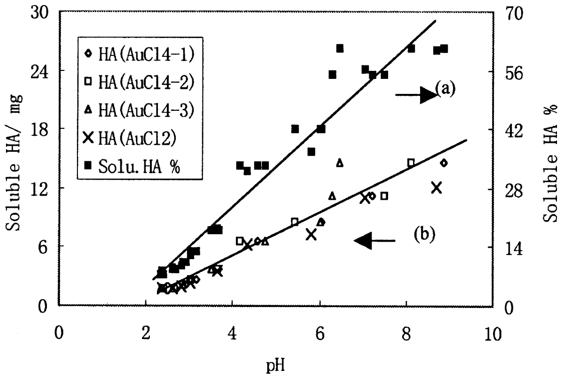

Fig. 1. Relationships between soluble HA expressed as milligram (a) or percent (b) and solution pH; (a) $Y=2.096$, $pH=3.503$, $r=0.97$; (b) $Y=9.659$, $pH=-15.25$, $r=0.98$.

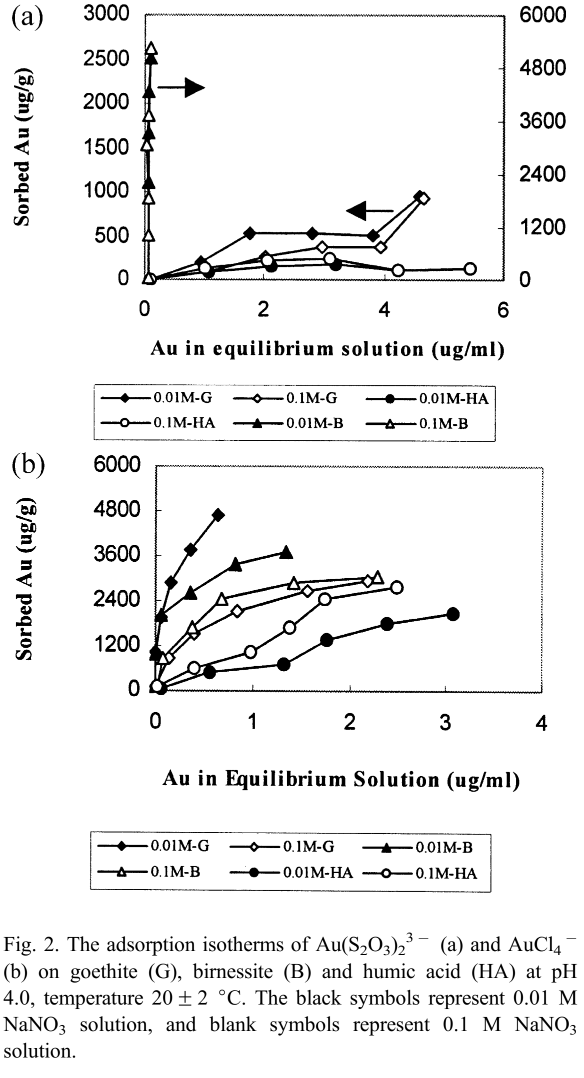

Fig. 2. The adsorption isotherms of $Au(S_2O_3)_2^{3-}$ (a) and $AuCl_4^-$ (b) on goethite (G), birnessite (B) and humic acid (HA) at pH 4.0, temperature 20 ± 2 °C. The black symbols represent 0.01 M $NaNO_3$ solution, and blank symbols represent 0.1 M $NaNO_3$ solution.

The adsorption isotherms are not sensitive to different electrolyte strengths. The adsorption of $Au(S_2O_3)_2^{3-}$ on goethite and humic acid is low. It is obvious from Fig. 2b that the adsorption of $AuCl_4^-$ on goethite is higher than on birnessite and humic acid. Moreover, the adsorption of $AuCl_4^-$ on goethite and birnessite for the 0.1 M $NaNO_3$ solution is lower than that for the 0.01 M $NaNO_3$ solution, as previously reported for the adsorption of $AuCl_4^-$ on goethite by Machesky et al. (1991). Furthermore, the adsorption of $AuCl_4^-$ on goethite is more sensitive to the electrolyte strength than is the case for birnessite. As birnessite (pH_{zpc} 1.48) is negatively charged for the experimental pH range and goethite (pH_{zpc} 7.8) is positively charged for $pH < 7.8$, birnessite could only adsorb gold anions specifically and goethite could adsorb anions by both electrostatic interaction and the specific adsorption. Ionic adsorption of gold anions is sensitive to the electrolyte strength than is the specific adsorption. Hence, adsorption on goethite is affected more strongly by the electrolyte strength than adsorption on birnessite.

Sorption of $AuCl_4^-$ on humic acid (HA) in 0.1 M $NaNO_3$ solution is higher than adsorption in 0.01 M $NaNO_3$ solution, which may be associated with the lower percentage of the HA dissolution in the higher strength electrolyte solution and to reduction of Au(III) by humic acid. As the measured HA concentration varied considerably for each strength of electrolyte solutions, the difference in the soluble HA contents is within the experimental error (Table 1). The large variations in the HA concentrations suggest that our measurement method for the soluble HA is precise. Whether HA is less soluble at high electrolyte strength needs further investigation. On the other hand, reduction of Au(III) by humic acid occurs at $pH < 4$ (see discussion below; Machesky, 1992). Electrostatic repulsion between Au(III)–chloride and humic acid is not conducive to Au(III) reduction. Sodium ion binding to acidic functional groups possibly decreases electrostatic repulsion by acting as a bridge group for the electron process. The higher the electrolyte strength, the lower the electrostatic repulsion between Au(III)–chloride and humic acid, and the higher is Au(III) reduction and fixation (sorption) by humic acid, leading to sorption of $AuCl_4^-$ on humic acid being higher for the higher-strength $NaNO_3$ solution.

The adsorption isotherm is maybe described mathematically by the equations given below.

The Freundlich equation for the adsorption isotherm is:

$$\text{Log } Y = \log K + (1/n)\log C, \tag{1}$$

in which Y is the Au adsorbed (μg/g), C is the Au concentration (μg/ml) in the equilibrium solution, $1/n$ is a constant, and log K is a constant related to the adsorption capacity and the adsorption strength.

The Langmuir equation for the adsorption isotherm is:

$$C/Y = 1/(KQ_m) + C/Q_{\mathrm{m}}, \tag{2}$$

in which Y and C have the same meaning as in Eq. (1) but the unit for Y is mg/g. Q_{m} is the maximum adsorption capacity (mg/g); and K is a constant related to binding energy (ml/μg).

Fig. 3 shows the data fitted to the Freundlich and Langmuir equations. The regression coefficients and adsorption parameters for the equations are listed in Table 2. As indicated by Fig. 3 and the regression coefficients, the Freundlich equation provides a better description of the Au adsorption isotherms. The

Table 1
The soluble HA for isothermal adsorption solutions at pH 4.0 and for two electrolyte strengths

Electrolyte strength	Number	HA concentration (μg/ml)	Soluble HA content (mg)	Soluble HA percent (%)
0.01 M $NaNO_3$	1	178	3.56	17.7
	2	205	4.10	20.6
	3	180	3.60	16.4
	4	210	4.20	20.7
	5	185	3.70	18.0
	6	174	3.48	16.2
Average ± STD		189 ± 15.1	3.77 ± 0.30	18.3 ± 1.97
0.1 M $NaNO_3$	1	180	3.60	17.7
	2	170	3.40	16.6
	3	197	3.94	18.9
	4	166	3.32	16.3
	5	160	3.20	15.5
	6	156	3.12	15.3
Average ± STD		172 ± 15.0	3.43 ± 0.30	16.7 ± 1.37

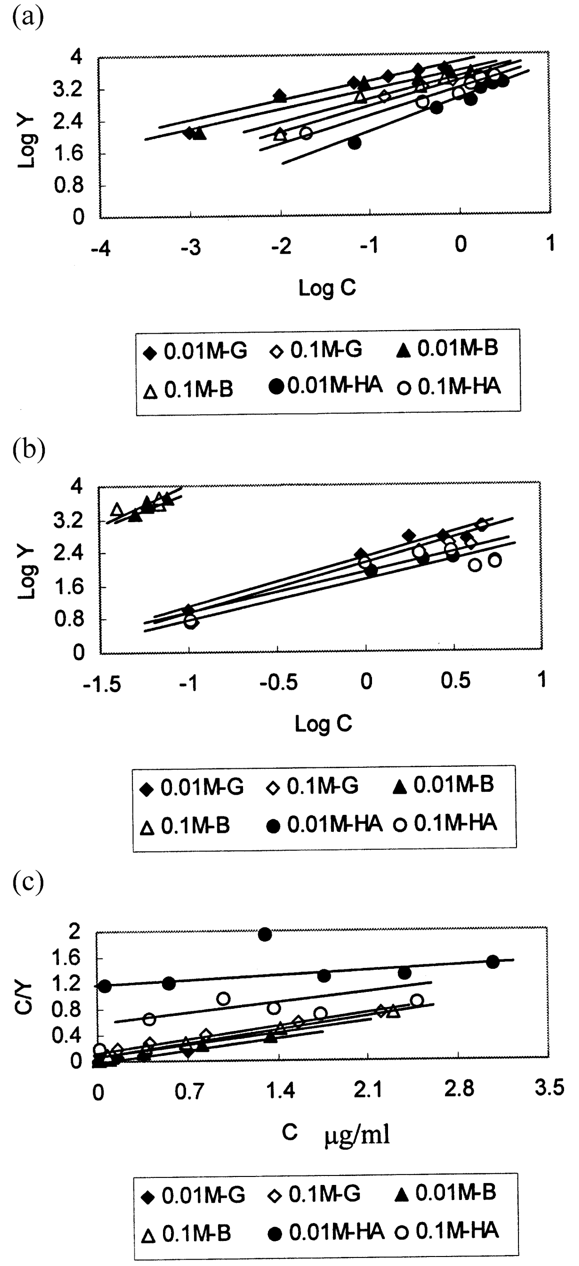

Fig. 3. Freundlich equation fitting for the adsoprtion isotherms of $AuCl_4^-$ (a) and $Au(S_2O_3)_2^{3-}$ (b) on goethite (G), birnessite (B) and humic acid (HA); and Langmuir equation fitting for the adsorption isotherms of $AuCl_4^-$ (c) on goethite, birnessite and humic acid.

Langmuir equation provides an excellent model for the adsorption data of $AuCl_4^-$ on birnessite and a relatively good description of adsorption of $Au(S_2O_3)_2^{3-}$ on humic acid. The parameter $1/n$ in the Freundlich equation is the site energy heterogeneity factor or linearity factor (Weber et al., 1992). As indicated in Table 2, $1/n$ ranges from 0.443 to 2.09 and thus is not equal to 1, showing that there is considerable site energy heterogeneity for birnessite, goethite, and humic acid, and thus nonlinear adsorption behaviour for Au complexes. Adsorbed anions firstly occupy highest-energy sites at low surface coverage. As the high-energy sites become saturated, anions progressively occupy lower-energy sites, resulting in the decrease of the average binding energy on the surface. As indicated by the Freundlich capacity factor log K, Au adsorption on birnessite and goethite is affected by electrolyte strength.

The maximum Au adsorption densities for $AuCl_4^-$ on goethite and birnessite are respectively 25.4, 17.2 μmol/g (0.01 M $NaNO_3$), and 17.4, 19.5 μmol/g (0.1 M $NaNO_3$), and for $Au(S_2O_3)_2^{3-}$ on goethite and birnessite are respectively 4.5, 25.7 μmol/g (0.01 M $NaNO_3$), and 4.5, 26.5 μmol/g (0.1 M $NaNO_3$) for Au concentrations in equilibrium solution ranging from 5.8×10^{-7} to 2.88×10^{-6} M. If expressed in a specific surface area basis, maximum Au adsorption densities on goethite and birnessite are respectively 0.27–0.4 and 0.18–0.21 μmol/m^2 for $AuCl_4^-$, and 0.07 and 0.28 μmol/m^2 respectively for $Au(S_2O_3)_2^{3-}$. Machesky et al. (1991) reported that maximum Au adsorption densities on goethite are 210 μmol/g for $AuCl_4^-$ and 15–35 μmol/g for $Au(S_2O_3)_2^{3-}$ under similar experimental conditions. Although their reported values for adsorption of $AuCl_4^-$ on goethite are much higher than those of this study, the equilibrium Au concentrations ranged from 5×10^{-6} to 204×10^{-6} M in Machesky's experiment and are thus much higher than those used in this study. Under the present experiment condition, the Au surface coverage on birnessite is 0.68–0.85% for $AuCl_4^-$ and 1.06–1.10% for $Au(S_2O_3)_2^{3-}$. If the total adsorption site densities (Ns) of 6.64–11.6 μmol/m^2 for goethite is used (Davis and Kent, 1990), the Au surface coverage on goethite is 2.33–6.02% for $AuCl_4^-$ and 0.60–1.05% for $Au(S_2O_3)_2^{3-}$.

Adsorption isotherms on a heterogeneous surface with sites showing a spectrum of binding energies

Table 2
The fitted parameters for Au adsorption isotherms

Sample	Au solutions	No.	Freundlich			Langmuir		
			r	log *K*(1)	1/*n*	*r*	K(2)	Q_m
Birnessite	$Au(S_2O_3)_2^{3-}$-1	6	0.992 **	6.10	2.09	−0.817	–	–
	$Au(S_2O_3)_2^{3-}$-2	6	0.940 **	5.93	1.85	−0.588	–	–
	$AuCl_4^-$-1	6	0.948 **	3.62	0.449	0.995 **	13.0	3.82
	$AuCl_4^-$-2	6	0.969 **	3.41	0.596	0.996 **	4.10	3.38
Goethite	$Au(S_2O_3)_2^{3-}$-1	6	0.981 **	2.23	1.14	−0.299	–	–
	$Au(S_2O_3)_2^{3-}$-2	6	0.991 **	1.96	1.30	−0.573	–	–
	$AuCl_4^-$-1	6	0.973 **	3.85	0.527	0.989 **	13.0	4.98
	$AuCl_4^-$-2	6	0.990 **	3.34	0.604	0.995 **	2.35	3.42
Humic acid	$Au(S_2O_3)_2^{3-}$-1	6	0.940 **	1.71	0.867	0.894 *	0.923	0.173
	$Au(S_2O_3)_2^{3-}$-2	6	0.868 *	1.80	0.812	0.789	1.23	0.162
	$AuCl_4^-$-1	6	0.992 **	2.86	0.938	0.284	–	–
	$AuCl_4^-$-2	6	0.988 **	3.13	0.671	0.700	–	–

1 and 2 represent the 0.01 and 0.1 M $NaNO_3$ electrolyte solutions, respectively. No. is the number of samples.

* 5% significant level.

** 1% significant level.

typically exhibit slopes of less than 1 for log–log plot of adsorption amount versus concentration of the equilibrium solution. For the adsorption of $Au(S_2O_3)_2^{3-}$ on birnessite, the exponent (1/*n*) higher than 1 may result from the very low Au concentrations in the equilibrium solutions, and the very high sorbent capacity of birnessite. For goethite the high Au concentrations in the equilibrium solution and low adsorption capacity of goethite results in values of 1/*n* larger than 1. The Langmuir equation does not describe the adsorption data for $Au(S_2O_3)_2^{3-}$ on goethite and birnessite as well as for $AuCl_4^-$ on humic acid. If the measurement errors for the Au concentration in equilibrium solution are high, the correlation between *C* and *C*/*Y* of the Langmuir equation will be poor, as shown by the data for $AuCl_4^-$ adsorption on humic acid in Fig. 3c. Besides, the significant dissolution of humic acid and the partial reduction of $AuCl_4^-$ by humic acid at low pH (see discussion below) may contribute to the poor fit of data to the Langmuir equation for the $AuCl_4^-$ adsorption data on humic acid. Further research to overcome the above artifacts and the use of more sensitive analysis methods such as ICP-MS are needed to solve the adsorption deviation.

3.3. Effect of pH on Au adsorption

The stability of the three Au complexes at solution pH ranging from 2 to 11 is quite different. The three 5.8×10^{-6} M Au complex solutions were passed through 0.2-μm filter membrane. The results show that $AuCl_4^-$ and $Au(S_2O_3)_2^{3-}$ are quite stable and do not produce colloidal gold. Berrodier et al. (1999) recently showed that gold adsorbed on ferrihydrite was dominantly trivalent and no photoreduction occurred during adsorption or doing data collection using EXAFS spectroscopy. The Au colloids observed on goethite or in the associated $AuCl_3^-$ solutions by Greffie et al. (1996) and Schoonen et al. (1992) were possibly attributable to oxidation–reduction reactions between Au^{3+} and Fe^{2+} in ferric chloride or a trace of reductive contaminants derived from the ion exchange columns of the water system. However, for the present $AuCl_2^-$ solutions, 35–50% of the Au in solution was retained by 0.2-μm filter (so-called colloidal gold) and the percentage of colloidal gold increased as the solution pH decreased below 5.8. This phenomenon may be related to the disproportionate reaction of $AuCl_2^-$ as the equilibrium constant for the disproportionate reaction of $AuCl_2^-$ producing $AuCl_4^-$ and Au is 5×10^7 (Puddephatt, 1978), favoring the production of colloidal Au. As ferrous sulphate was used for the preparation of the $AuCl_2^-$ solutions and Fe^{3+} was one of the reaction products, this could have resulted in ferric oxide or hydroxide precipitating and incorporating gold, which may also contribute to the colloidal gold. Since the Au(I) hydroxide is more stable than Au(I) chloride in most natural waters (Vlassopoulos and Wood, 1990), the apparent relative stability of $AuCl_2^-$ for high pH solutions may be caused by its hydrolysis.

The effect of the solution pH on Au adsorption by geothite, birnessite and humic acid for Au(5.8×10^{-6} M) complex solutions containing 0.1 M $NaNO_3$ is shown in Fig. 4a,b,c. The adsorption amounts for the $AuCl_2^-$ solution were calculated by deducting the colloidal Au concentration. In the pH ranges from 2 to 11.6, Au adsorption decreases as solution pH increases, which is consistent with anion adsorption on a variable charge surface. Moreover, the observation is also consistent with the same results of Machesky et al. (1991) with $NaNO_3$ as the background electrolyte. For example, Fig. 4 from their paper shows little pH dependence with $NaNO_3$ as the background electrolyte over the pH range of 3.5 to 7. Fig. 4b of the present study also shows little pH dependence to pH 7 for adsorption by goethite and birnessite. The adsorption percentage of $Au(S_2O_3)_2^{3-}$ on birnessite decreases slightly when the solution pH reaches 10. The adsorption percentages of $Au(S_2O_3)_2^{3-}$ on goethite and humic acid are very small. The adsorption of $Au(S_2O_3)_2^{3-}$ on birnessite only decreases for about 10% as the solution pH increases from pH 6.5 to 10, suggesting that nearly all of the gold ions are adsorbed after the ligand of the Au complex is oxidized on birnessite. Therefore, the Au ions are very likely to react with the surface hydroxyls and produce surface Au complexes, i.e., specific adsorption. When the hydroxyls in the solution reach a certain concentration, they compete for the Au ions with the surface hydroxyls and produce the soluble $Au(OH){\cdot}H_2O$ or $Au(OH)_2^-$, whose stability constants are $\log \beta_1 = 20.1$ and $\log \beta_2 = 22$ (Vlassopoulos and Wood, 1990), respectively.

The affinity of the three surfaces for the $AuCl_4^-$ complexes decreases in the sequence: birnessite > goethite>humic acid, and in the sequence: goethite > birnessite>humic acid for $AuCl_2^-$. This affinity difference might be attributed to the large percentage of colloidal Au in the $AuCl_2^-$ solution (Ran et al., 1999) and the adsorption mechanism of anionic exchange on goethite. As the colloidal form of gold

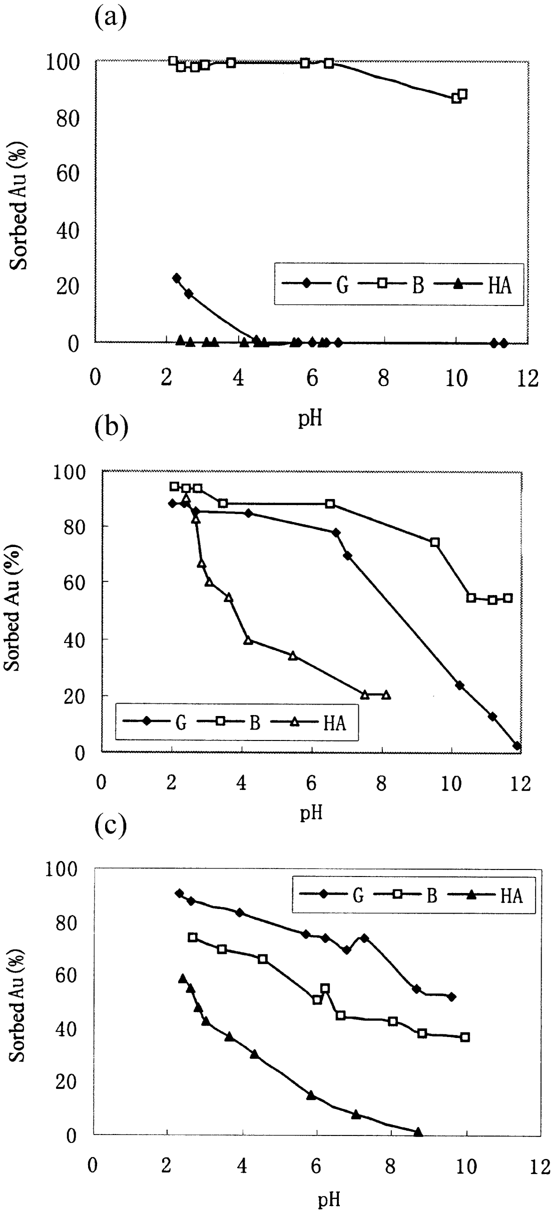

Fig. 4. The adsorption of the Au complexes in 0.1 M $NaNO_3$ solutions containing 5.8×10^{-6} M Au on geothite, birnessite and humic acid at different pH. (a) $Au(S_2O_3)_2^{3-}$, (b) $AuCl_4^-$, (c) $AuCl_2^-$.

is frequently negatively charged, colloidal gold could be adsorbed more strongly than gold anions on the positively charged surface of goethite by anionic exchange, resulting in higher adsorption of $AuCl_2^-$ on the goethite than on birnessite.

The amounts of adsorption of $AuCl_4^-$ and $AuCl_2^-$ decrease less within the range of pH 2–4 than for pH 4–10 for birnessite and goethite (Fig. 4b,c), which is related to the Au speciation in solution, the decrease in positive surface charge density, and/or the increase in negative surface charge density mentioned above. For pH 2–6, 0.01 M $NaNO_3$ solutions containing 2×10^{-4} M $AuCl_4^-$, more than 90% of the Au ions exist as $AuCl_2OH{\cdot}H_2O$ (Machesky et al., 1991). As the solution pH is elevated, the concentrations of $AuCl(OH)_3^-$, $AuCl_2(OH_2)^-$ and $Au(OH)_4^-$ anions increase. When the solution pH is higher than 6, the concentrations of $AuClOH_3^-$ and $AuCl_2OH{\cdot}H_2O$ decrease and $Au(OH)_4^-$ becomes the dominating Au anion. Furthermore, UV/VIS, Raman and EXAFS spectroscopic measurements suggest that Au chloro or chloro-hydroxo complexes in the solutions of 10^{-4}–10^{-1} M gold and 1 M NaCl predominate to more alkaline pH values than are predicted on the basis of calculated equilibrium constants (Peck et al., 1991; Farges et al., 1993; Baes and Mesmer, 1976). Machesky et al. (1991) proposed that the species $AuCl_2OH{\cdot}H_2O$ derived from $AuCl_4^-$ hydrolysis reacts with geothite and produces bidentate, inner-space surface complexes, based on release of 1–2 Cl^- for a Au ion adsorption. However, as the H^+ release/Au^{3+} ratio is smaller than 1, they could not identify the species of the surface Au complex. According to EXAFS, AuX_4^- (X = O(H) or Cl) complexes may form either bidentate inner sphere complexes or outer sphere complexes on iron oxides (Heasman et al., 1998; Berrodier et al., 1999). At high pH or low Cl concentration, the local environment around Au on ferrihydrite shows only the presence of O (OH, H_2O) ligands (Berrodier et al., 1999). However, the potentiometric titration and surface complexation modeling of $AuCl_4^-$ on hematite suggest the existence of the following monondentate surface complexes: $FeOHAu(OH)_3$, $FeOHAuCl_2OH$ and $FeOHAu(OH)_3$ (Karasyova et al., 1998). Whether or not the surface species are the same as the solution species at pH>4 is unclear due to the EXAFS determination errors (Heasman et al., 1998).

It is noted that the above EXAFS spectroscopic investigations of the gold (III) chloride speciation in aqueous solution and adsorbed on iron oxides are based on adsorption using high concentrations of gold (III) chlorides (10^{-3} to 10^{-2} M) and NaCl (1 M). To our knowledge, the single study investigating the adsorption of Au on ferrihydrites at low chloride concentrations (0.056 M Cl^-) by EXAFS showed the existence of very different Au surface species from the solution Au species when the solution pH was higher than 3.8. The local environment around Au on ferrihydrite shows only the presence of O (OH, H_2O) ligands (Berrodier et al., 1999). However, Au chloro and chloro-hydroxo complexes are present in these pH solutions (Peck et al., 1991; Farges et al., 1993). Moreover, as discussed in the Introduction, gold concentrations inferred from the thermodynamic models range from 10^{-4} to 10^{-6} mol/l with chloride concentrations in the range of 10^{-2} to 10^{-4} mol/l in most supergene waters (Gary et al., 1992; Benedetti and Boulegue, 1991). Within the stability field of water, the solubility of Au(I) as hydroxo complexes (ignoring activity coefficients) may theoretically exceed $10^{-5.3}$ M. For concentrations (activities) of $Au(OH)_3(H_2O)^{\circ}$ above $10^{-5.5}$ M, saturation with respect to crystalline $Au(OH)_3$ occurs, which then also controls the activity of Au(I) hydroxide species under very oxidizing conditions (Baes and Mesmer, 1976; Vlassopoulos and Wood, 1990). Under most supergene water conditions, the Au complex, $AuOH(H_2O)^{\circ}$ rather than $AuCl_4^-$, should control the solubility of gold (Vlassopoulos and Wood, 1990; Tossell, 1996). Thus, Au(I) should be dominant in natural environments. Whether and how Au(III) complexes could be transformed to Au(I) complexes or Au° is controversial and needs further investigation (Pan and Wood, 1991; Farges et al., 1993; Tossell, 1996). To improve on the present results, more sensitive spectroscopy and more detailed potentiometric and adsorption data are required to determine Au speciation in solution and on surfaces for the low Au concentrations employed in this study.

3.4. Partition equation for Au adsorption

The effect of the dissolved humic acid (DHA) on adsorption could be corrected by using a partition model that accounts for the complexation of the solute by nonseparable organic matter in the liquid phase. The observed partition coefficient may be defined as (Gschwend and Wu, 1985):

$$K_{\mathrm{p}}^{\mathrm{obsd}} = (P/\text{mass particles}) /((D+N)/\text{volume of water}), \quad (3)$$

where P is the mass of solute adsorbed to separable particles, D is the mass of solute dissolved, and N is the mass of solute adsorbed to DHA. By definition,

$$K_{\mathrm{p}}^{\mathrm{true}} = (P/\text{mass separable particles}) /(D/\text{volume of water}). \quad (4)$$

Combining Eqs. (3) and (4):

$$K_{\mathrm{p}}^{\mathrm{obsd}} = K_{\mathrm{p}}^{\mathrm{true}}/(1+N/D); \quad (5)$$

now defining,

$$K_{\mathrm{DHA}}^{\mathrm{true}} = (N/\text{mass of DHA}) /(D/\text{volume of water}), \quad (6)$$

then,

$$K_{\mathrm{p}}^{\mathrm{true}} = K_{\mathrm{p}}^{\mathrm{obsd}}/(1-K_{\mathrm{p}}^{\mathrm{obsd}} \times (\text{mass of DHA}/\text{volume of water})). \quad (7)$$

Expression (7) allows us to correct for the effect of the dissolved humic on Au adsorption at different solution pH values. From the regression equation shown in Fig. 1, the mass of DHA can be estimated from the solution pH. Assuming $K_{\mathrm{p}}^{\mathrm{true}} = K_{\mathrm{DHA}}^{\mathrm{true}}$, we can correct for the effect of the dissolved humic acid. As the amounts of dissolved (or colloidal) Fe and Mn were very small for the birnessite and goethite adsorption experiments, the $K_{\mathrm{p}}^{\mathrm{obsd}}$ can be considered to be the true values for these Au complexes. The values of true partition as a function of the solution pH are shown in Fig. 5.

In order to allow direct comparison of gold uptake by the three surfaces, it is necessary to consider a general model for the uptake of the gold complexes onto solid surfaces. As discussed above, the speciation of gold complexes in solution and on surfaces is not well understood. It is difficult to develop a simple surface complexation model for this purpose. Therefore, we use a general partitioning equation similar to that of Schoonen et al. (1992) to model adsorptive behaviors of gold ions as a function of pH. Honeyman and Leckie (1986) considered a modified form of the distribution coefficient that describes the adsorption of ion J in terms of the macroscopic observations of proton (or hydroxyl) exchange:

$$\mathrm{SOH} + \mathrm{J} \rightarrow \mathrm{SJ} + \chi\mathrm{H}^{+} \quad (8)$$

$$K_{\mathrm{part}} = \mathrm{SJ}[\mathrm{H}^{+}]^{\chi}/\mathrm{SOH}[\mathrm{J}], \quad (9)$$

in which SJ represents the adsorbed Au ion on the surface in units of mmol/g, [J] is the Au concentration in the equilibrium solution (mmol/ml), $[\mathrm{H}^{+}]$ is the proton (or hydroxyl) concentration in the equilibrium solution (mmol/ml), SOH is the surface hydroxyl concentrations (mmol/g), and χ is the apparent ratio of moles of hydrogen released (or absorbed) per mole of Au ions adsorbed. However, χ does not reveal stoichiometric information about microscopic adsorption reactions at the surface (Honeyman and Leckie, 1986). For adsorption of trace metals, the maximum number of adsorbed species is often much smaller than the total number of surface groups. As a result, (SOH) can be considered constant. The SOH for birnessite is 2.61 mmol/g (NS); for goethite 0.93 mmol/g (Ns = 7 sites/nm^2) (Davis and Kent, 1990); and SOH for humic acid is assumed to be equal to the total acidity (SOH = 5.82 mmol/g dry weight). Eq. (9) can be transformed to:

$$\log K_{\mathrm{p}} = \log(K_{\mathrm{part}}\mathrm{SOH}) + \chi\mathrm{pH}. \quad (10)$$

K_{part} and χ are computed from the intercept and slope of a linear regression of log K_{p} against pH.

The regression lines illustrated in Fig. 5 show very significant negative correlation between log K_{p} and solution pH except for those for $\mathrm{Au(S_2O_3)_2}^{3-}$. The correlation coefficients ranging from -0.941 to

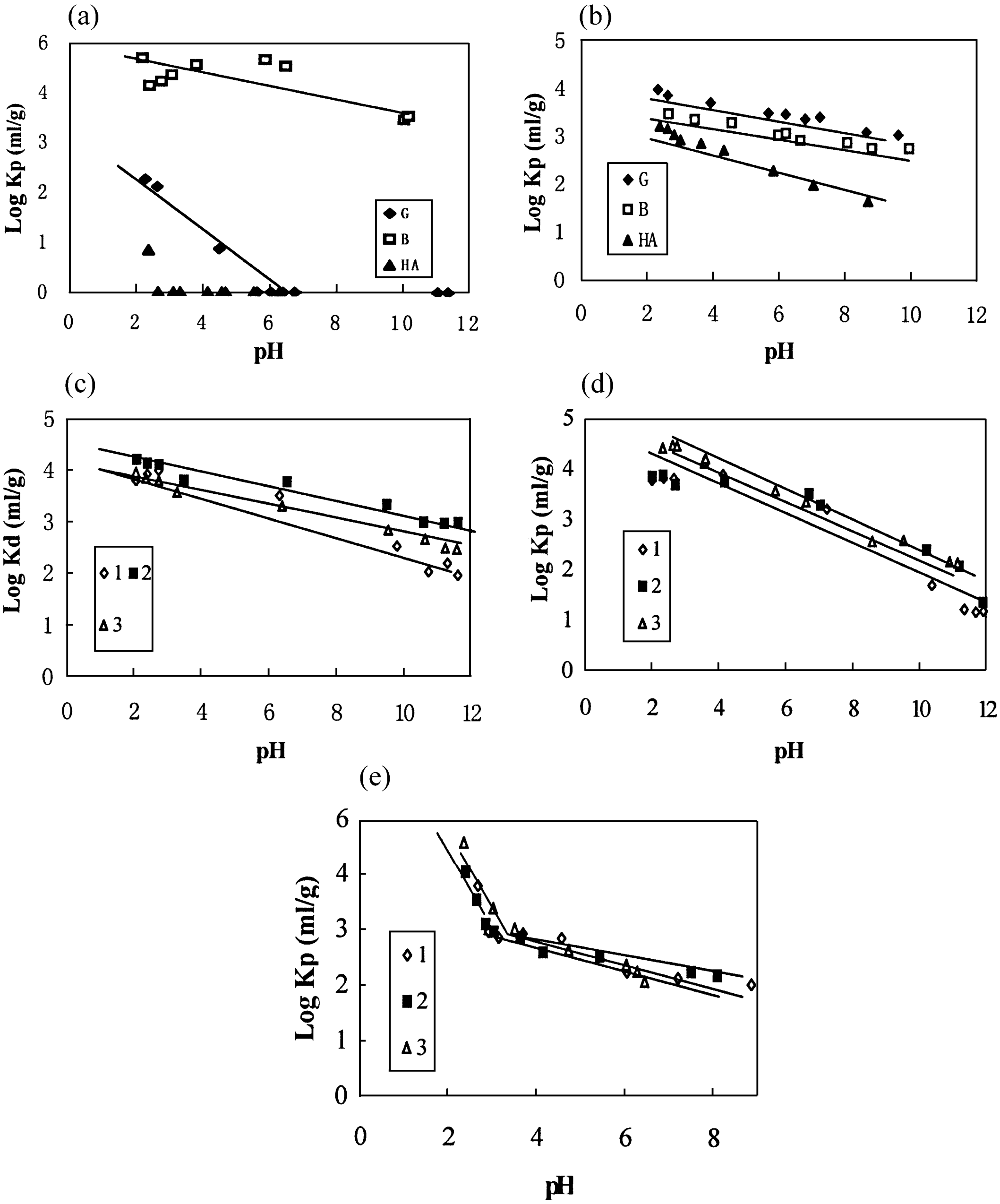

Fig. 5. The true partition coefficients of the Au complexes in the 0.1 M $NaNO_3$ solutions on goethite (G), birnessite (B) and humic acid (HA) at different pH. (a) 5.8×10^{-6} M Au in $Au(S_2O_3)_2^{3-}$ solutions; (b) 5.8×10^{-6} M Au in $AuCl_2^-$ solutions; (c) adsorption of 1–5.8×10^{-7}, 2–5.8×10^{-6}, and 3–2.88×10^{-5} M Au in $AuCl_4^-$ solutions on B; (d) adsorption of 1–5.8×10^{-7}, 2–5.8×10^{-6}, and 3–2.88×10^{-5} M Au in $AuCl_4^-$ solutions on G; (e) adsorption of 1–5.8×10^{-7}, and 2–5.8×10^{-6}, 3–2.88×10^{-5} Au in $AuCl_4^-$ solutions on HA.

Table 3
Log K_{part} and regression coefficients for relationships between log K_p and pH

Sorbent	Au solution	Soluble Au (μg/ml)	n	Coefficient	Intercept (a)	χ	log K_{part}
Birnessite	$AuCl_4^-$	0.113	9	-0.9781^{a}	4.46	-0.204	1.19
	$AuCl_4^-$	1.13	9	-0.9785^{a}	4.42	-0.123	2.28
	$AuCl_4^-$	5.65	9	-0.9941^{a}	4.18	-0.144	1.71
	$AuCl_2^-$	1.13	9	-0.9764^{a}	3.69	-0.102	1.84
	$Au(S_2O_3)_2^{3-}$	1.13	9	-0.7157^{b}	5.25	-0.003	4.79
Goethite	$AuCl_4^-$	0.113	9	-0.9708^{a}	4.66	-0.283	0.730
	$AuCl_4^-$	1.13	9	-0.9407^{a}	4.51	-0.217	1.50
	$AuCl_4^-$	5.65	12	-0.9959^{a}	5.13	-0.271	1.37
	$AuCl_2^-$	1.13	9	-0.9898^{a}	4.21	-0.123	2.52
	$Au(S_2O_3)_2^{3-}$	1.13	9	-0.7540^{b}	2.18	-0.245	-1.22
Humic acid (pH>3)	$AuCl_4^-$	0.113	7	-0.9551^{a}	3.84	-0.192	0.387
	$AuCl_4^-$	1.13	7	-0.9636^{a}	3.78	-0.102	1.59
	$AuCl_4^-$	5.65	5	-0.9840^{a}	4.43	-0.315	-0.745
	$AuCl_2^-$	1.13	9	-0.9963^{a}	3.73	-0.244	-0.451
	$Au(S_2O_3)_2^{3-}$	1.13	9	-0.4841	0.56	-0.112	–

[a] 1% significant level.

[b] 5% significant level.

-0.996 and the conditional equilibrium constant log K_{pat} are listed in Table 3. For the three surfaces and at high electrolyte strength, log K_{part} may be ranked as: birnessite>goethite>humic acid; but for adsorption of $AuCl_2^-$ on goethite the ranking is goethite>birnessite>humic acid. Log K_{part} for the adsorption of $Au(S_2O_3)_2^{3-}$ on birnessite is highest, and that for goethite or humic acid is very small.

The trends of log K_p values for birnessite and goethite for the three Au complex solutions as a function of solution pH are similar to those for their adsorption percentage values discussed above. However, the log K_p curves for humic acid as a function of pH may be divided into two different sections (Fig. 5e). When the solution pH is lower than 3, the log K_p values decrease sharply with increasing pH. Since $AuCl_2OH{\cdot}H_2O$ and $AuCl_4^-$ are the dominating gold ion species in these low pH solutions (Machesky et al., 1992), the high values of log K_p appear to be related to the reduction of the gold ions by humic acid. For solution pH higher than 3, the log K_p values decrease slowly and are nearly constant at the higher pH values, which is similar to the trends for birnessite and goethite. In these higher pH solutions, $AuClOH_3^-$ and $AuCl_2OH{\cdot}H_2O$ decrease and $Au(OH)_4^-$ gradually becomes the dominant Au anion (Machesky et al., 1992). The reduction potentials decrease as Au(III)–chloride becomes more hydrolyzed with increasing solution pH. Because of the presence of these complexes with much lower values of standard reduction potential, humic acid is a less important factor in causing Au(III) reduction and fixation. Furthermore, standard and reference soil, and stream fulvic and humic acids contain 0.42–0.89% sulfur and 89–1420 μmol/g amino acid (IHSS, 1996). Therefore, N-, S-, and OH-donor ligands in the humic acid might complex $AuClOH_3^-$, $AuCl_2OH.H_2O$, $Au(OH)_4^-$, etc. Thus, birnessite, goethite, and humic acid could preferentially adsorb chloro-hydroxo Au complexes produced by hydrolysis of $AuCl_4^-$ and $AuCl_2^-$ hydrolysis.

Based on the neutral and alkaline environment conditions and the significant correlation between gold content and manganese oxide content, Webster and Mann (1984) proposed that gold migrates as $Au(S_2O_3)_2^{3-}$. Gold of low finesses is precipitated by oxidation of $Au(S_2O_3)_2^{3-}$ on birnessite and by reduction of the Au ions at the water table. The concentrations of gold vary from below 1 to about 5 ng/l in most freshwater from unmineralized areas, and can be as much as three orders of magnitude higher in freshwaters from mineralized areas and in mine drainage (McHugh, 1988). It is noted from Fig. 5a that the solid–liquid partition coefficients (log K_p) of gold on birnessite in the $Au(S_2O_3)_2^{3-}$ solutions reach a value of 5. Hence, birnessite might concentrate gold from natural freshwater to the grade of gold deposit. Although the gold contents of birnessite can reach 5000 μg/g (Fig. 2a), the forms of the sorbed gold on birnessite are unclear and need to be further investigated.

4. Conclusion

The adsorption isotherms for the two Au complexes at low Au concentration that is relevant to most supergene waters are well described by the Freundlich equation. The adsorption of $Au(S_2O_3)_2^{3-}$ is significantly greater than that of $AuCl_4^-$ on birnessite at pH 4.0 and for two electrolyte strengths, but the adsorption of $Au(S_2O_3)_2^{3-}$ is significantly much smaller than that of $AuCl_4^-$ on goethite and humic acid. The adsorption of $AuCl_4^-$ on goethite is higher than that on birnessite or on humic acid, and all were affected by the electrolyte strength to some extent. As birnessite could only adsorb gold anions specifically and geothite could adsorb gold anions by both anion exchange and specific adsorption, the adsorption on goethite is affected more strongly by the electrolyte strength than on birnessite. Under these experiment conditions, the Au surface coverage on birnessite was 0.68–0.85% for $AuCl_4^-$ and 1.06–1.10% for $Au(S_2O_3)_2^{3-}$, and that on goethite was approximately 2.33–6.02% for $AuCl_4^-$ and 0.6–1.05% for $Au(S_2O_3)_2^{3-}$. The Freundlich parameter $1/n$ reflected the heterogeneity of birnessite surface and the nonlinearity of the Au adsorption isotherm.

For the pH range from 2 to 11.6 and with 0.1 M $NaNO_3$ as the background electrolyte, Au adsorption decreased as a function of solution pH, which is consistent with anion adsorption regularity on variable charge surfaces. Speciation of gold complexes in solution and on solid surfaces is very complicated and is not yet well understood. Consequently, a partitioning equation was used to model adsorptive behaviors of gold ions as a function of pH. On the basis of the Kurbatov plot and surface hydroxyl density, the conditional equilibrium constants (log K_{part}) was estimated. It is observed that the true solid–liquid distribution coefficients for the Au complexes at the low concentrations that are relevant to most supergene water for the three surfaces are significantly negatively correlated with solution pH, with the correlation coefficients ranging from -0.941 to -0.996 except for those of $Au(S_2O_3)_2^{3-}$. For the three surfaces, log K_{part} for the adsorption of $AuCl_4^-$ is in the order: birnessite>goethite>humic acid; but for the adsorption of $AuCl_2^-$ the order is goethite>birnessite>humic acid. Log K_{part} for the adsorption of $Au(S_2O_3)_2^{3-}$ on birnessite is high, and that for goethite and humic acid is very low. Surface complexation and Au speciation in solution lead to the decrease in adsorption of Au complexes with increasing solution pH. For low pH (<3) solutions, sorption of $AuCl_4^-$ on humic acid may be related reduction of Au(III) by the humic acid. However, at the solution pH higher than 3, adsorption of $AuCl_4^-$ and $AuCl_2^-$ by the humic acid shows similar adsorption behaviors to that for both birnessite and goethite. Hence, it is proposed that birnessite, goethite, and humic acid preferentially adsorb chloro and chloro-hydroxo Au complexes produced by hydrolysis of $AuCl_4^-$ and $AuCl_2^-$. As birnessite has very strong oxidation and adsorption abilities for monovalent Au complexes such as $Au(S_2O_3)_2^{3-}$, it may play an important role in the deposition and accumulation of dissolved gold in the supergene environment.

Whether and how Au(III) complexes could be transformed to Au(I) complexes or Au° is controversial and needs further investigation. To improve on the present results, sensitive spectroscopy such as EXAFS and Raman, and more detailed potentiometric and adsorption data are required to determine Au speciation in solution and on surfaces at the low Au concentrations as employed in this study.

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