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THE ADSORPTION OF $[Au(HS)_2]^-$ ON KAOLINITE SURFACES: QUANTUM CHEMISTRY CALCULATIONS

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ABSTRACT

Electronic structure and energies of the system of $[Au(HS)_2]^-$ adsorbed on an atomic cluster of kaolinite were calculated using the self-consistent-field discrete-variation (SCF–X_α–DV) method. A hexagonal ring of SiO_4 tetrahedra with three Al octahedra, including 38 atoms, was used to model the flake of kaolinite. Calculations were performed on all possible systems with $[Au(HS)_2]^-$ adsorbed at different sites. The energy calculations show that the systems with lower total energy are those in which $[Au(HS)_2]^-$ is adsorbed on edge surfaces; adsorption of $[Au(HS)_2]^-$ at the edges is thus more stable than adsorption on the basal plane. The bond-order calculations suggest that significant shifts in atomic charge and the overlapping of electron clouds between Au^+ of the $[Au(HS)_2]^-$ and the surface ions of kaolinite would take place in the systems with $[Au(HS)_2]^-$ adsorbed on the edges, especially at the site near Al octahedra. The interaction between $[Au(HS)_2]^-$ ion and kaolinite is expected to be strong. This kind of adsorption can be regarded as the formation of a surface complex.

Keywords: chemisorption, kaolinite, gold, self-consistent-field discrete variational method, covalent bond, electronic population.

SOMMAIRE

Nous avons calculé la structure électronique et les énergies associées pour le cas de l'ion $[Au(HS)_2]^-$ adsorbé sur un groupement d'atomes définissant la kaolinite en utilisant la méthode des variations distinctes dans un champ auto-conforme (SCF–X_α–DV). Nous considérons un anneau hexagonal de tétraèdres SiO_4 associé à trois octaèdres Al, comprenant en tout 38 atomes, pour simuler une particule de kaolinite. Les calculs ont été faits sur tous les systèmes possibles avec l'ion $[Au(HS)_2]^-$ adsorbé aux sites disponibles. Les calculs d'énergie montrent que les systèmes ayant le plus faible niveau d'énergie totale sont ceux dans lesquels l'ion $[Au(HS)_2]^-$ est adsorbé aux surfaces en bordure des feuillets; l'adsorption de $[Au(HS)_2]^-$ en bordure serait donc plus stable que l'adsorption sur le plan des feuillets. Les calculs de l'ordre de liaison font penser que des déplacements importants en charge atomique et le chevauchement des nuages d'électrons entre Au^+ de l'ion $[Au(HS)_2]^-$ et les ions de surface de la kaolinite pourraient bien avoir lieu dans les systèmes dans lesquels l'ion $[Au(HS)_2]^-$ est adsorbé en bordure, spécialement près des sites Al. On s'attend à ce que l'interaction entre l'ion $[Au(HS)_2]^-$ et la kaolinite soit forte. On peut interpréter ce type d'adsorption en termes de la formation d'un complexe de surface.

(Traduit par la Rédaction)

Mots-clés: chemisorption, kaolinite, or, méthode de variation distincte en champ auto-conforme, liaison covalente, population d'électrons.

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INTRODUCTION

In most deposits where the gold is submicrometric, it is closely associated with clay minerals, such as kaolinite and illite. Experiments and observations show that clay minerals have the capacity of adsorbing Au-bearing complex ions (Boyle 1979). Data for the solubility of gold indicate that it is somewhat soluble in near-neutral to slightly alkaline solutions, and much less soluble in strongly acidic or alkaline solutions; it forms extremely stable hydrosulfido-complexes over a wide range of temperature. The dominant complexes in near-neutral to slightly alkaline solutions are $[Au(HS)_2]^-$, $AuHS^0$, and $[Au_2S_2]^{2-}$, especially the first (Renders & Seward 1989, Shenberger & Barnes 1989, Benning & Seward 1996). These complexes provide the dominant mechanism of transport of gold in hydrothermal ore-forming fluids. In order to understand the formation of this kind of deposit, it is necessary to establish the interaction between clay minerals and Au-bearing complex ions that govern the mechanisms of accumulation of gold during the depositional process. This is our purpose in this article.

BACKGROUND INFORMATION

The adsorption of ions on clay-mineral surfaces has been the subject of much attention for several years. Interactions at solid–liquid interfaces are considered to be important in governing the transport of a number of trace and major elements in natural systems. Many investigations of cation and anion adsorption on kaolinite surfaces have been undertaken, and most of these ions are of environmental interest, such as divalent cobalt, divalent cadmium and organic acids (Pennell *et al.* 1991, Angove *et al.* 1998, Ward & Brady 1998). However, adsorption of Au-bearing complex ions onto clay-mineral surfaces has barely been studied; moreover, whether the complex ion is present in chemical combination with clay minerals or whether it occurs as a result of electrostatic interaction remains controversial. None of the studies provides convincing evidence to conform to the inferences. Using the SCF–X_α–DV method of quantum chemistry calculation, we have calculated the models of adsorption of an Au-bearing complex ion $[Au(HS)_2]^-$ onto kaolinite surfaces; some useful data were obtained about the manner of adsorption in the present study, which provides a scientific basis for understanding the close association of Au and clay minerals and hence the mechanism for deposition of submicrometric gold.

THEORETICAL APPROACH

Method of calculation

The self-consistent-field discrete-variation method, proposed by Ellis & Painter in 1970, has been commonly used to solve problems at the level of atoms and molecules. It describes the energy level of electrons and the charge density of atoms in a solid system, which makes it possible to explore the properties of the system on the basis of the semiquantitative data on chemical bonds from model calculations.

The basic point of SCF–X_α–DV method is the Schrödinger equation. With the approximation of one electron orbital, the Schrödinger equation is converted into the Hartree–Fock equation, which can be applied to the system of atoms, molecules, and electrons. Then a statistical approximation is undertaken to the exchange potential in the Hartree–Fock equation

$$V_{X\alpha} = -3\alpha \left[{}^{3}\!/_{8}\, \alpha \times \rho\,(\gamma) \right]^{1/3} \tag{1}$$

where $V_{X\alpha}$ is Slater's exchange-correlation operator, α is the exchange potential constant (usually from ½ to 1), and $\rho\,(\gamma)$ is the charge density. With the above approximations, the X_α equation is obtained.

A number of discrete sampling points in a three-dimensional grid could be used, however; depending on the degree of research interest, the number can be chosen to give the desired accuracy. Variation is made in the parameter of the trial function to obtain the minima for the points. The various Coulomb and exchange integrals are numerically approximated by weighted summation of the sampling points. The matrix elements of secular equations, therefore, can be obtained, and then the energy levels of the molecular orbitals and wave functions are derived.

The strength of a covalent bond, reflecting the distribution of the electron cloud between the two atoms, can be described by Mulliken's overlapping populations, or orders of covalent bonds. The overlapping population of electrons between atoms A and B can be expressed as

$$P(A-B) = \sum_{n} \sum_{i,j} C_{in}^{A}\, C_{nj}^{B} \int \Psi_i \Psi_j \, dv \tag{2}$$

where Ψ_i and Ψ_j are the wave-functions of i^{th} and j^{th} orbitals of atoms A and B, respectively, and C^{A}_{in} and C^{B}_{nj} are coefficients showing magnitudes of linear combinations of atomic orbitals; the summation of n is extended over all the occupied molecular orbitals.

With respect to an atom in the system, the bond order of atom A is written

$$P\,(A) = 0.5\, \Sigma\, P\,(A - B_j) \tag{3}$$

Here, the summation of *j* is extended over the other atoms except atom *A*. Thus, the value *P*(*A*) represents the strength of the covalent bond involving atom *A*.

Generally, the strength of chemical bond comprises components of both a covalent bond and an ionic bond. The ionic bond depends dominantly on net charge of an ion, which is expressed as the difference between its atomic number and its electronic population calculated for the system.

Cluster chosen and adsorption models

Kaolinite is one of the most widespread phyllosilicates of the Earth's crust. The (001) basal surfaces of kaolinite are considered to position the electronegative oxygen atoms above the surface (Gerson 1997), and edges are composed of exposed silica and alumina sheets (Williams & Williams 1978). Its general structure is well known and understood (Brindley & Robinson 1946). The basic layer can be regarded as consisting of a sheet of SiO_4 tetrahedra and a sheet of Al octahedra in which the Al is octahedrally coordinated by O and OH; it has a unit-cell thickness of 0.713 nm. In the basic layer, six SiO_4 tetrahedra link together by sharing oxygen ions, which therefore forms the framework. In such a ring of tetrahedra, the various tetrahedra are subtly rotated asymmetrically, not identically, with only a small deviation from a hexagonal arrangement. As a first approximation, Brindley & Robinson (1946) placed the tetrahedra rather symmetrically. Thus, considering the surface atoms and structural periodicity of kaolinite, a symmetrical cluster of atoms, with a hexagonal ring of tetrahedra and with three Al octahedra, were chosen in the present study for SCF–X_α–DV calculation. Hyde (1993) has investigated the warping of the aluminosilicate layer based on a modulated structure of kaolinite and imogolite. He found curved hyperbolic kaolinite layers containing six rings of tetrahedra and the associated octahedra, which attests to the fact that this atomic cluster represents well a flake of a kaolinite crystal. As shown in Figure 1, the cluster was projected onto the basal plane (001); positional parameters of the atoms were derived from Brindley & Robinson (1946) and expressed in the coordinate system shown in Table 1. The SiO_4 tetrahedra have three oxygen ions in the basal plane, the apical oxygen atom is 0.219 nm from that plane, and the silicon is at the center of the tetrahedra, 0.050 nm above the plane. In the Al (hydr)oxide octahedra $[AlO_2(OH)_4]$, the Al is located 0.327 nm from the basal plane, two oxygen ions are at 0.219 nm from the basal plane, each coordinates to both Al and Si, oxygen ions in three of the four OH are at 0.437 nm above the basal plane. The other OH is 0.219 nm from the basal plane, and its projection onto it is at the center of the hexagonal ring. In the atomic cluster, there are three equivalent octahedra, two of

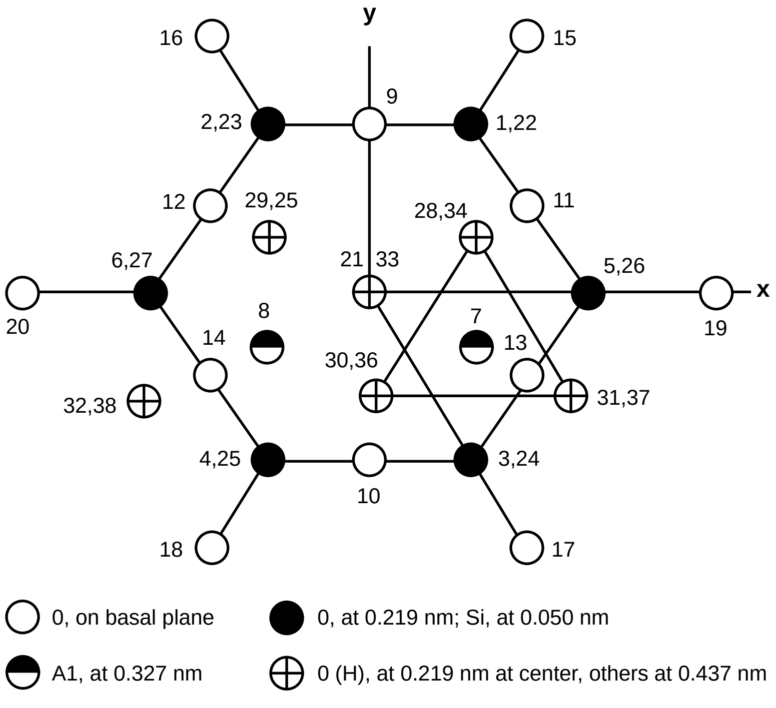

FIG. 1. Projection of atoms in kaolinite in the *XZ* plane. The numbers indicate the position of the atoms.

TABLE 1. POSITIONAL PARAMETERS OF THE ATOMS IN THE CLUSTER IN KAOLINITE, FOR PURPOSES OF CALCULATION

Atom		x	y	z	Atom		x	y	z
Si	1	2.8081	1.1338	4.8638	O	20	-8.4244	0.0000	0.0000
Si	2	-2.8081	1.1338	4.8638	O	21	0.0000	4.1483	0.0000
Si	3	2.8081	1.1338	-4.8638	O	22	2.8081	4.1483	4.8638
Si	4	-2.8081	1.1338	-4.8638	O	23	-2.8081	4.1483	4.8638
Si	5	5.1613	1.1338	0.0000	O	24	2.8081	4.1483	-4.8638
Si	6	-5.1613	1.1338	0.0000	O	25	-2.8081	4.1483	-4.8638
Al	7	2.8081	6.1791	-1.6213	O	26	5.6163	4.1483	0.0000
Al	8	-2.8081	6.1791	-1.6213	O	27	-5.6163	4.1483	0.0000
O	9	0.0000	0.0000	4.8638	O	28	2.8081	8.2577	1.6213
O	10	0.0000	0.0000	-4.8638	O	29	-2.8081	8.2577	1.6213
O	11	4.2122	0.0000	2.4319	O	30	0.0000	8.2577	-3.2425
O	12	-4.2122	0.0000	2.4319	O	31	5.6163	8.2577	-3.2425
O	13	4.2122	0.0000	-2.4319	O	32	-5.6163	8.2577	-3.2425
O	14	-4.2122	0.0000	-2.4319	H	33	0.0000	6.0611	0.0000
O	15	4.2122	0.0000	7.2957	H	34	2.8081	10.1805	1.6213
O	16	-4.2122	0.0000	7.2957	H	35	-2.8081	10.1805	1.6213
O	17	4.2122	0.0000	-7.2957	H	36	0.0000	10.1805	-3.2425
O	18	-4.2122	0.0000	-7.2957	H	37	5.6163	10.1805	-3.2425
O	19	8.4244	0.0000	0.0000	H	38	-5.6163	10.1805	-3.2425

TABLE 2. POSITIONS OF MONOVALENT GOLD OF $[Au(HS)_2]^-$ IN EACH MODEL AND SOME CALCULATED RESULTS

No.	Au^+ site	No. of O atoms in contact with Au^+	total energy (eV)	P(Au)	Q(Au)	P(S)	Q(S)
1			-1169.53				
2	Under	11,13,19; 12,14,20	-1817.68	0.632	0.5874	0.903	-0.2486
3	Under	11; 12	-1817.64	0.735	0.5502	1.097	-0.2435
4	Under	13; 14	-1817.70	0.687	0.5492	1.093	-0.2428
5	Above	28,30,31; 29,30,32	-1815.70	0.548	0.4753	0.911	-0.2426
6	Edge	19; 20	-1817.42	0.773	0.5657	1.099	-0.2403
7	Edge	13; 14	-1818.74	1.207	0.6308	0.829	-0.1812
8	Edge	11; 12	-1818.66	1.250	0.6045	0.825	-0.1883
9	Edge	13,17; 14,18	-1818.48	0.962	0.6713	0.881	-0.1823
10	Edge	11,15; 12,16	-1818.31	0.967	0.6699	0.872	-0.1817

which are occupied by Al and the other is vacant. This atomic cluster can be written as $[Si_6Al_2O_{24}H_6]$, including 38 atoms, and is named model 1.

In surface-complexation models, the functional groups on the sorbent surfaces are treated as analogs of complexing ligands in solution (Davis & Leckie 1978, Hayes & Leckie 1987). When dealing with oxides and oxyhydroxides, adsorption of aqueous metal complexes generally involves coordination of the adsorbate nucleus to oxygen-donor ligands. Jean & Bancroft (1985) used X-ray photo-electron spectroscopy (XPS) to obtain information on the type of chemical bonds formed on the surface of a number of different sulfides that had reacted with solutions containing $[AuCl_4]^-$, $[Au(CN)_2Br_2]^-$, and $[Au(CN)_2]^-$. Their results show that the adsorption of Au-bearing complex ions is due to coordination of the gold ion to a surface sulfur-donor ligand. As kaolinite contains octahedrally coordinated Al and tetrahedrally coordinated Si, which are exposed at clay surfaces, the donor ligands are likely oxygen, and adsorption of $[Au(HS)_2]^-$ by coordination of the Au^+ ion to an oxygen-donor ligand is the most plausible surface-reaction model for our calculations.

The calculation models are considered dominantly with the sites of adsorption of $[Au(HS)_2]^-$ on the kaolinite surface, at edges and above or under the basal plane. In a model, two $[Au(HS)_2]^-$ ions are placed in the system according to mirror symmetry to simplify the calculation. As shown in model 2, one of the $[Au(HS)_2]^-$ is placed just under the basal plane, its projection onto it overlaps with atom 5, contacting atoms O(11), O(13), and O(19); another $[Au(HS)_2]^-$ ion is located under the basal plane, and its projection coincides with atom 6, contacting atoms O(12), O(14), and O(20). Finally, nine models are selected for calculation by further consideration of the difference in contacting atoms (numbers 2–10 in Table 2).

The shortest distance between Au and the surface O of kaolinite is based on the covalent radii of Au and O. A "frozen core" approach was employed in our calculations. The frozen orbits are O *1s*, Al *1s2s2p*, Si *1s2s2p*, S *1s2s2p*, and Au *1s to 5d*, respectively, whereas the unfrozen orbits are O *2s2p*, Si *3s3p*, Al *3s3p*, S *3s3p*, and Au *6s6p*, respectively.

RESULTS AND DISCUSSION

Stability of the models

The total energy of a chemical system reflects its stability; especially for systems composed of the same atoms, relative stability can be readily evaluated. The total energy of the models mentioned above is presented in Table 2. Of all the models, model 6 has the largest total energy, which indicates that it is a most unstable system, with Au in contact with O(19) or O(20); on the whole, models 7 to 10 have smaller values of total energy compared to models 2 to 5, which suggests that the models of $[Au(HS)_2]^-$ adsorption onto the edge surface of kaolinite are more stable than $[Au(HS)_2]^-$ adsorption onto the basal plane.

The order of covalent bond of the Au^+ ion, P(Au), and its net charge, Q(Au), are shown in Table 2. Models 7 to 10 have larger values of P(Au) relative to models 2 to 6. It can therefore be inferred that covalent bonds involving Au in models 7 to 10 are stronger than those in models 2 to 6. On the other hand, the Q(Au) values of models 7 to 10 are also larger than those of models 2 to 6, which is indicative of their stronger ionic bond. In covalent bonds involving the Au^+ ion, the smaller the Q(Au) value, the larger the density of the electron cloud around the Au^+ ion, and hence the larger is the electron cloud density for bond-forming overlaps, so that the covalent bond is stronger. Thus, the larger Q(Au) values and P(Au) values suggest that the chemical bonds, both covalent and ionic bonds, between Au^+ ion of $[Au(HS)_2]^-$ and the oxygen-donor ligands of kaolinite surfaces in models 7 to 10, are significantly stronger than those in models 2 to 6. On the contrary, the order of covalent bond between sulfur and Au^+ ion, P(S), and the net charge of sulfur, Q(S), show that both P(S) and Q(S) values in models 7 to 10 are smaller than those in models 2 to 6, which indicate that in models 7 to 10 the chemical bond between Au^+ ion and the sulfur ion in the complex $[Au(HS)_2]^-$ is weaker than that in models 2 to 6, which would promote the formation of stronger chemical bonds between the complex $[Au(HS)_2]^-$ and the kaolinite surfaces. As a result, adsorption of $[Au(HS)_2]^-$ onto the edge surfaces is more stable than those that adsorb onto the basal plane.

Interaction between $[Au(HS_2)]^-$ *and kaolinite*

The intimate association of clay minerals and submicrometric Au has been recognized since the Carlin gold deposit was found in the seventies. Foster (1970) pointed out that most of the Carlin gold is related to clay minerals, kaolinite and "hydromica". In the oxidized zone, clay minerals play an important role in the accumulation of Au during the mineralization process (Boyle 1979). Recently, investigations using transmission electron microscopy (TEM) show that there is submicrometric gold adsorbed on the edges of clay minerals, kaolinite and illite (Ye *et al.* 1994, Hong & Ye 1998, Hong *et al.* 1999).

It is well known that kaolinite has a heterogeneous surface-charge; the basal surface is believed to carry a constant negative charge attributed to the isomorphous substitution of Al^{3+} for Si^{4+}. The charge on the edges is due to the protonation – deprotonation of surface hydroxyl groups. It depends on the solution pH (Zhou & Gunter 1992). Zhang *et al.* (1987) pointed out that at the edges, especially at the concave margin of broken crystals of kaolinite, the charge is positive, and hence kaolinite can adsorb a complex Au ion with a negative charge. Qian *et al.* (1986) showed that submicrometric Au particles are associated with clay minerals; they inferred that gold particles, with $(OH)^-$, were electrostatically adsorbed onto the edges of kaolinite crystals. However, they claimed that the interaction of adsorption between Au and kaolinite is similar to that of interstitial atoms in a compound.

As mentioned above, the system should be more stable with $[Au(HS)_2]^-$ on the edges of kaolinite, particularly in models 7 and 8. The calculated results show that in model 1, Q(O13) and Q(O11) are –0.7591 and –0.7069, respectively, whereas in models 7 and 8, Q(O13) and Q(O11) become –0.7826 and –0.7732, respectively; the values of net charge on the oxygen atoms in both models increase significantly. In addition, the Q(Au) value of model 8 is smaller than that of model 7. On the contrary, the Q(Si) value of model 8 is larger than that of model 7, which indicates that some of the Si charge involves a redistribution and balancing of charge in the system. In this scheme, charge distribution in model 7 would an favor to increase the stability of the system, as the electronegativity of Si is larger relative to Au. In view of the Au–O interaction, Q(Au) of model 7 is larger than in model 8, and P(Au), on the contrary, is smaller, which implies that the covalent Au–O bond in model 7 is weaker than that in model 8. On the other hand, the Q(13) value in model 7 is larger than that in model 8, which is indicative of its stronger ionic Au–O bond relative to model 8. Thus, the ionic Au–O bond may be responsible for the difference in stability between model 7 and 8. We conclude that there should be a chemical link between $[Au(HS)_2]^-$ and kaolinite as the ion is adsorbed onto its edges, and that $[Au(HS)_2]^-$ at the sites near Al octahedra (model 7) is more stable than that near vacant octahedra (model 8). This result agrees well with the experimental data on the surface chemistry of kaolinite by Ward & Brady (1998). Their experiments show that the interaction between oxalate and the kaolinite surfaces occurs primarily at exposed Al sites. Nechayev & Nikolenko (1986) performed the experiments on adsorption of Au^{3+} chloride complexes onto oxides. They pointed out that during chemisorption, the electronic structure of the surface will change, and there will be overlap between the wave functions for the electrons of the adsorbate and adsorbent, and hence the bond is of covalent type.

In fact, the adsorption of heavy metals onto kaolinite has been investigated in some detail (Angove *et al.* 1998). The results show that adsorption involves complexation of adsorbing ions with aluminol, and perhaps silanol, groups that reside predominantly at the crystal edges. Rosliyakov (1990) proposed that gold is adsorbed on the crystal surface of clay minerals. However, there is adequately strong adsorption bond between gold and clay minerals, and hence it approximates a kind of chemical adsorption. Boyle (1979) pointed out that in clay minerals, most of the gold is combined as gold – clay mineral complexes. The results from quantum chemistry calculation in the present study agree well with these earlier conjectures and with experimental data.

CONCLUSIONS

Based on data from a quantum chemistry calculation using the SCF–X_α–DV method, the adsorption of $[Au(HS)_2]^-$ onto the edge surfaces of kaolinite is more stable than adsportion of $[Au(HS)_2]^-$ onto the basal plane. The results indicate that the edge surfaces of kaolinite crystal are more likely to adsorb $[Au(HS)_2]^-$ relative to its basal plane, especially at sites near Al octahedra on edges.

Chemical bonds between the Au of $[Au(HS)_2]^-$ and the surfaces of kaolinite are expected to form while $[Au(HS)_2]^-$ is adsorbed onto the edges; this kind of adsorption can be regarded, in nature, as the formation of surface complexes, taking into account the shifting of atomic charge and the overlapping of the electron cloud between Au and the surface oxygen of kaolinite.

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REFERENCES

ANGOVE, M.J., JOHNSON, B.B. & WELLS, J.D. (1998): The influence of temperature on the adsorption of cadmium (II) and cobalt (II) on kaolinite. *J. Colloid Interface Sci.* **204**, 93-103.

BENNING, L.G. & SEWARD, T.M. (1996): Hydrosulfide complexing of Au (I) in hydrothermal solutions from 150-400°C and 500–1500 bar. *Geochim. Cosmochim. Acta* **60**, 1849-1871.

BOYLE, R.W. (1979): The geochemistry of gold and its deposits. *Geol. Surv. Can., Bull.* **280**.

BRINDLEY, G.W. & ROBINSON, K. (1946): The structure of kaolinite. *Mineral. Mag.* **31**, 781-786.

DAVIS, J.A. & LECKIE, J.O. (1978): Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. *Environ. Sci. Technol.* **12**, 1309-1315.

ELLIS, D.E. & PAINTER, G.S. (1970): Discrete variational method for the energy-bond problem with general crystal potential. *Phys. Rev. B* **2**, 2887-2898.

FOSTER, R.L. (1970): Gold deposits at Slate Creek, northern Nye County, Nevada. *Econ. Geol.* **66**, 965-966.

GERSON, A.R. (1997): The surface modification of kaolinite using water vapour plasma. *In* Computational Chemistry and Chemical Engineering (G. Cisneros, J.A. Cogordan, C.M. Wang & M. Castro, eds.). World Scientific Press, River Edge, New Jersey (227-235).

HAYES, K.F. & LECKIE, J.O. (1987): Modeling ionic strength effects on cation adsorption at hydrous oxide/ solution interfaces. *J. Colloid Interface Sci.* **115**, 564-572.

HONG HANLIE, WANG QINYAN, CHANG JIANPING, LIU SHIRONG & HU RUIZHONG (1999): Occurrence and distribution of invisible gold in the Shewushan supergene gold deposit, southeastern Hubei, China. *Can. Mineral.* **37**, 1525-1531.

________ & YE XIANXIAN (1998): Study on characteristics of the gold in the lateritic gold mine. *J. Chin. Electron Microsc. Soc.* **17**, 267-271 (in Chinese).

HYDE, S.T. (1993): Hyperbolic and elliptic layer warping in some sheet alumino-silicates. *Phys. Chem. Minerals* **20**, 190-220.

JEAN, G.E. & BANCROFT, G.M. (1985): An XPS and SEM study of gold deposition at low temperatures on sulfide mineral surfaces: concentration of gold by adsorption/reduction. *Geochim. Cosmochim. Acta* **49**, 979-987.

NECHAYEV, Y.A. & NIKOLENKO, N.V. (1986): Effects of surface charge on the adsorption of gold (III) chloride complexes on oxides. *Geochem. Int.* **23**(9), 142-146.

PENNELL, K.D., RHUE, R.D. & HARRIS, W.G. (1991): The effect of heat treatments on the total charge and exchangeable cations of Ca-, Na-, and Li-saturated kaolinite. *Clays Clay Minerals* **39**, 306-315.

QIAN DINGFU & DIAO SHUQIN (1986): Mode of occurrence of gold in a certain gold deposit, China. *Geochimica* **1**, 58-65 (in Chinese).

RENDERS, P.J. & SEWARD, T.M. (1989): The stability of hydrosulfido- and sulfido complexes of Au (I) and Ag (I) at 25°C. *Geochim. Cosmochim. Acta* **53**, 245-253.

ROSLIYAKOV, H.A. (1990): Occurrence of Au in soil and its indicative significance. *Tech. Sci. Gold Geol.* **23**, 32-37 (translated in Chinese).

SHENBERGER, D.M. & BARNES, H.L. (1989): Solubility of gold in aqueous sulfide solutions from 150 to 350°C. *Geochim. Cosmochim. Acta* **53**, 269-278.

WARD, D.B. & BRADY, P.V. (1998): Effect of Al and organic acids on the surface chemistry of kaolinite. *Clays Clay Minerals* **46**, 453-465.

WILLIAMS, D.J.A. & WILLIAMS, K.P. (1978): Electrophoresis and zeta potential of kaolinite. *J. Colloid Interface Sci.* **65**, 79-87.

YE XIANXIAN, WANG GUANGQUAN, SUN ZHENYA, LIU YONGKAN, ZHOU LINDI, LIU SHIRONG, XUE DEJUN, RIVERS, L. & JONES K.W. (1994): Microscopy study on submicrometer gold in a Carlin-type gold deposit, southwestern Guizhou, China. *Sci. Chin.* **B 24**, 883-889 (in Chinese).

ZHANG ZHENRU, YANG SIXUE & YI WEN (1987): Studies of submicro-gold and lattice-gold in some minerals. *J. Cent. South Inst. Mining Metall.* **18**, 355-361.

ZHOU, ZHIHONG & GUNTER, W.D. (1992): The nature of the surface charge of kaolinite. *Clays Clay Minerals* **40**, 365-368.

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