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GEOCHEMISTRY

Interaction of Elemental Gold Surface with Fluids: A Key to Understanding Mechanisms of Recondensation and Mobilization of Gold under Endogenic and Exogenic Conditions

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The inoxidizability of pure metallic gold and its stability under the influence of strong dry oxidants like oxygen, chlorine, and sulfur are universally recognized [1]. The resistance to corrosion is a characteristic feature of noble metals (NM), particularly platinum and gold. Therefore, these metals are used as jewellery materials, elements of electronic chips, and inoxidizable mats for growing crystals and films (e.g., in production of crystalline silicon in platinum crucibles). However, all these properties are related to massive NM. The situation changes drastically in the case of nano-scale particles and surface layers. Experiments with impulse radiolysis showed that the redox potential of gold atoms in water is close to –1.5 V. Therefore, gold is a strong reductant; i.e., isolated "gold atoms would be instantly oxidized in the air!" [2]. In other words, if we could isolate a monolayer of gold atoms, it would be oxidized in the air. At the surface, atoms only partially belong to the solid body. Therefore, oxidation starting with the adsorption of an oxidant should always be present to a certain extent. Indeed, under the influence of a beam of oxygen atoms on the platinum surface (111) in an ultrahigh vacuum at 250–450 K, increase in the degree of surface coating with oxygen atoms enhances both adsorption and development of surface oxygen-containing phases. When the coating reaches >0.75 of a monolayer, platinum oxide particles start to grow and the surface becomes disordered [3].

As was mentioned above, the chemical inactivity of gold is well known. Studies on catalysis also indicate that gold is among the least active metals as concerns chemical sorption of gas molecules, including oxygen. Therefore, mobilization and transfer of gold is not commonly attributed to "weak" ligands and aqua-complexes. Instead, it is suggested that the Au-transporting fluids should contain ligands like Cl^-, HS^-, and CN^-, which can react with gold and make up complex compounds. As concerns the finds of oxyhydrates and similar gold compounds under natural conditions [4], they are largely related to the supergene zone. This fact only confirms the instability of gold oxides and hydroxides at high temperatures (approximately 100–140°C). However, based on Auger electron spectroscopy and low-energy electron diffraction, Chesters and Somorjai [5] corroborated the formation of an oxide layer on the surface of metallic gold at much higher temperatures (>500°C or more) and oxygen pressure of 10^{-6}–10^{-7} Torr. This oxide was interpreted as "Au_2O_3" with an intermediate state of Au valence and a "square" surface structure of AuO_4. At the indicated oxygen pressure, such a layer can be obtained using water vapor. Oxygen chemically sorbed on gold reveals stability in the high temperature region. This was explained by the "unusual chemistry of the surface, in particular, readily changeable valence of surface atoms" [5]. Subsequently, a similar surface film with allegedly discontinuous structure [6] was revealed on native gold from placers. The occurrence of an oxygen-containing layer was deduced from the fine structure of the Au peak at an energy of 69 eV that corresponds to the Auger transition with participation of the valent 5*d*-electrons of Au $N_{6.7}O_{4.5}O_{4.5}$ metal. This fine structure is expressed in the appearance

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of a “shoulder” located in the differential Auger spectrum between two energetic minimums of the NOO-doublet. Evidence for oxidation of Au nanoparticles has also been obtained from study of their precipitation on arsenopyrite surface with scanning tunneling microscopy and spectroscopy [7]. It has been shown that the resistance to the tunnel current and the probability of the so-called Coulomb blockade related to the existence of a dielectric film on gold particles increase with decreasing size of gold particles.

The surface oxidation of NMs may affect their mobilization in rocks, transportation with fluid phases, and redistribution in the oxidation zone of ore deposits. However, this phenomenon has not been studied experimentally. The present paper is an attempt to fill this gap.

Experiments were carried out at 500°C and 1 kbar in both reducing ($H_2O + NH_3 + H_2$) and oxidizing ($H_2O + O_2$) fluids. The fluid composition was set by introduction of the necessary amount of metallic Al into the aqueous ammonia solution or by a certain concentration of hydrogen peroxide in water. Plates of the initial gold were placed in the lower portion of the autoclave. Runs lasted from 48 to 336 h. After the runs, the plates were examined with X-ray photoelectron spectroscopy (XRP) and Auger electron spectroscopy (AES). With the help of AES, we determined the oxygen content at the surface and revealed that the Au NOO Auger spectrum includes a “shoulder” indicating the presence of the Au–O bond. The surface was examined with a LAS-3000 device (Riber Company) equipped with a hemispheric analyzer of electrons with a retarding potential and the cylindrical mirror-type Auger electron spectrometer. The oxygen content profiles were obtained from the Auger spectra during ion milling of samples at a rate of ~0.06 nm/s. The etching was carried out with an argon ion beam (energy 2keV, emission current 20 mA). The vacuum in the analytical chamber was $5 \cdot 10^{-10}$ Torr. Atomic concentrations were calculated from intensities of Auger peaks by means of coefficients of elemental sensibility with an accuracy of ±10%. In addition, the surfaces of gold plates were examined with a Russian CMM-2000 multimicroscope in the regime of scanning tunneling microscopy (STM).

Figure 1 presents results of the Auger spectroscopy of the gold surface after the complete etching of carbon compounds. The time intervals between etching points were 10–15 min. The complete profile in sample 1 (~300 nm) approximately fits the maximum thickness of the oxygen-containing layer at the gold surface. The thinner, or more likely, fragmentary layers are formed under reducing conditions but in the obligatory presence of NaOH (even in the absence of water, sample 4). In all cases, the Au NOO Auger spectrum shows a fine structure in the form of a “shoulder” located at a distance of XRPS 2.3 eV toward the high-energy side from the $N_7O_{4.5}O_{4.5}$ Auger peak, indicating the formation of a Au–O chemical bond in the surface gold layer. The shoulder is expressed best in sample 1. Thus, a 100*n*-nm-thick layer of oxygen-containing compounds is formed at the Au surface in the presence of hydroxyl ion, water, and high partial pressure of oxygen (starting pressure ~200 bar at 500°C, total pressure 1000 bar). Judging from oxygen concentrations, the layer composition does not fit the common (nondissociated) adsorption of oxygen against the background of the permanent decrease in its activity in the autoclave owing to the transfer of the buffering function to the metallic surface. In this case, the amount of oxygen in the outermost layer would be minimal rather than maximal.

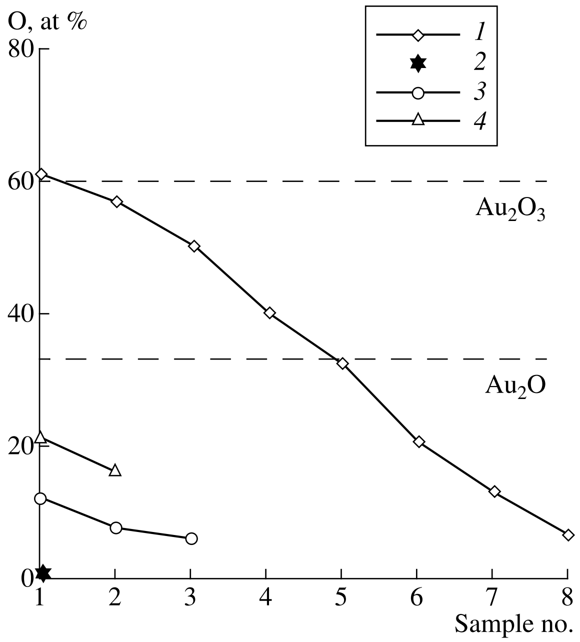

Fig. 1. Results of Auger spectroscopy of gold surface after the runs at 500°C and 1 kbar in the systems: (*1*) $80\%H_2O + 20\%O_2$ + NaOH, (*2*) $25\%H_2O + 25\%NH_3 + 50\%H_2$, (*3*) $25\%H_2O + 25\%NH_3 + 50\%H_2$ + NaOH, (*4*) $50\%NH_3 + 50\%H_2$ + NaOH. In general, the run duration for experiments 2–4 was 336 h; duration of run 1 was 72 h. Numbers plotted on the abscissa correspond to different durations of ionic etching; point 1 corresponds to the initial samples after carbon removal from their surface.

The nature of the chemical bond in the surficial gold oxides remains a matter of debate. Figure 1 shows that they are, most likely, compounds with the composition varying from Au_2O_3 to almost pure gold. The area occupied by these compounds is probably variable as well. To elucidate the character of the Au–O bond, an XPS spectrum of sample 1 (Fig. 2a) was compared with a reference spectrum (Fig. 2b). After the hydrothermal treatment of metallic gold with 80% H_2O + 20% O_2 + NaOH fluid, the chemical shift was +0.5 eV for both peaks of the $4f_{5/2–7/2}$ doublet. The shape of low-energy peak becomes more Lorentzian, and the dispersion diminishes insignificantly. The chemical shifts of simple gold compounds presented in the NIST database [8] and some other publications [9–11] allow us to con-

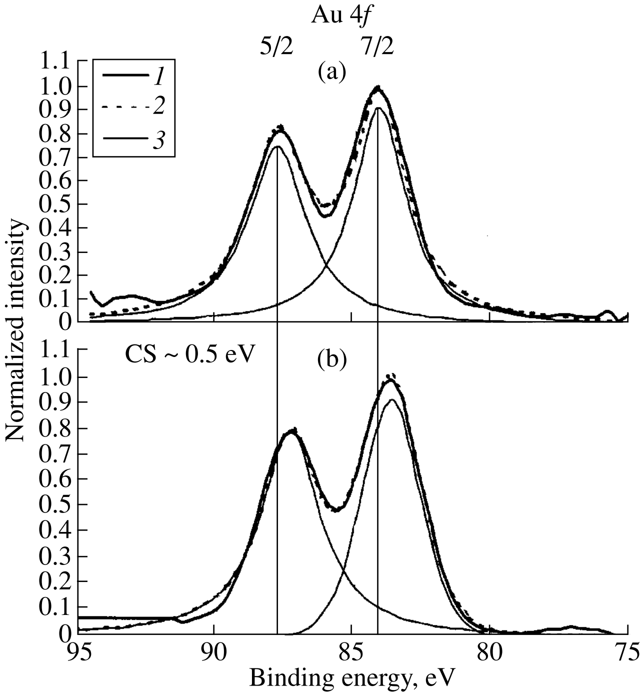

Fig. 2. Au 4*f* X-ray photoelectron spectrum. (a) Sample 1 (Fig. 1, 80% H_2O + 20% O_2 + NaOH); (b) reference sample. The chemical shift is 0.5 eV and corresponds to Au(I). (*1*) Run; (*2*) summary peaks; (*3*) particular peaks.

clude that the compounds of trivalent Au are characterized by a chemical shift of ≥3.5 eV. In the compounds with Au formally occurring in valent forms I and III (e.g., $Cs_2Au_2Cl_6$), the chemical shifts range from 0.4 to 4.0 eV. Finally, the chemical shift for Au(I) is the lowermost (0.4–0.8 eV). In our case, the chemical shift is 0.5 eV, i.e., close to Au(I).

The STM data indicate a decrease in the conductivity of the surface in the most oxidized sample 1 (probably, Coulomb blockade). Nanoscale spherules are observed on the surface of sample 4 (Fig. 3). The frequency spectrum of the height of points above the surface yields two maximums (~20 and ~25 nm). This height exceeds the minimal value of topographic surface (unfortunately, the initial roughness of the surface was not determined). Therefore, we suggest that the material is recondensed on the gold surface with the formation of Au nanoparticles under the run conditions. This mechanism is only a suggestion and cannot be considered proven. However, in light of the above reasoning, such recondensation looks quite plausible.

The oxidized state of Au at the surface may be of great importance in gold transport under high-temperature conditions and may promote mobilization of Au from rocks without obligatory participation of strong complexing ligands. Crystallites of native gold with a nonuniform nanoscale structure are detected during the formation of condensates of volcanic gases. Gold may occur as a suspension [12] with a highly developed surface of particles under conditions of nonequilibrium transport at considerable temperature and pressure gradients. In this case, the metallic and highly oxidized (at the surface) states may coexist under nonequilibrium conditions [12] giving rise to the nanoscale heterogeneity of the products and their high ability for recondensation in the supergene zone.

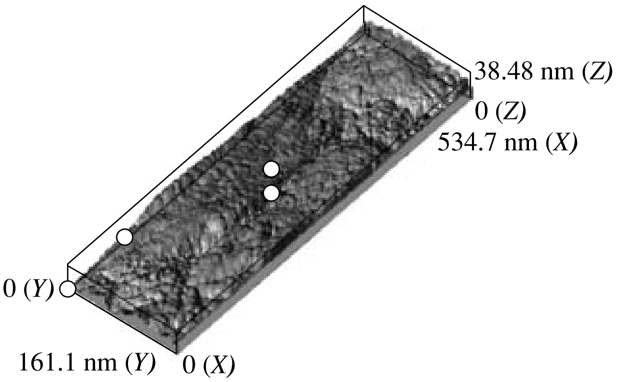

Fig. 3. 3D image of the gold plate surface in a scanning tunneling microscope. Sample 4 (Fig. 1, 50%NH_3 + 50% H_2 + NaOH). Spherical nanoparticles are seen on the right, above and below the scan.

The dissolution and recondensation of gold under supergene conditions leads to the appearance of products that are morphologically very different from the primary gold. The chemical transfer may be related to both the Au precipitation from a colloidal solution and the adsorption and surface precipitation of Au on particles of mineral substrate [13]. Anyway, supergene conditions undoubtedly promote recondensation of the primary gold and enlargement of its particles, which were often submicroscopic in the primary ore. The primary Au particles smaller than 5 μm in size are dissolved and redeposited in the process of chemical weathering [14].

In summary, we can draw the following conclusions.

(1) The hydrothermal treatment of elemental gold at 500°C and 1 kbar provides the formation of oxygen-containing surface layers under both oxidizing and reducing conditions. The layer is as thick as 300 nm in the first case and much thinner in the second case. The Au NOO Auger spectra include a "shoulder" suggesting the formation of the Au–O chemical bond in the surface layer. The oxygen content regularly diminishes inward into the layer, indicating surface Au oxidation rather than sorption of oxygen by the metallic surface. The oxidation of Au^0 requires the presence of a hydroxyl ion in the medium. The layer varies in composition probably based on a compound with a chemical bond Au(I)–O. The formal reaction of its formation may be written as $2Au^0 + \frac{1}{4}O_2 + OH^- = Au_2O + \frac{1}{2}H_2O$.

(2) The surface compound Au(I)–O retains its relative stability under oxidizing conditions. Under reduc-

ing conditions, Au(I) probably disproportionates to Au(0) and Au (III): $Au_2O + OH^- + H_2O = Au^0 + Au(OH)_3^0$. The trivalent Au passes into solution, whereas Au^0 is redeposited as nanoparticles. The oxidized film is readily removed in the acid medium created by organic and mineral acids of the supergene zone. This mechanism may function under exogenic conditions, leading to enlargement of the dispersed gold in the weathering and oxidation zones of ore deposits, on the one hand, and to the nanoscale inhomogeneity of aggregates, on the other hand. The smaller the size of particles, the greater the contribution of the surface oxide phase (hence, the intensity of recondensation). Precisely these circumstances are likely responsible for the well-known effect of gold particle enlargement in the worked-out placers and high contents of the fine-dispersed gold in the clay fraction from the weathering profile of the Novogodnee Manteau deposit (Polar Urals). Here, Au–O films (up to 0.3 μm thick) are developed on the native gold associated with the skarn–magnetite ore [15]. Under endogenic conditions, this mechanism may promote mobilization of Au from rocks without obligatory participation of strong complexing ligands.

(3) Further experimental studies are necessary to specify the temperature, as well as oxygen and alkali activities, which provides the formation of the surficial gold oxide phase.

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