SHORT COMMUNICATIONS

Deposition of Gold on Kaolinite Surfaces from $AuCl_4^-$ Solution[1]

Hong Hanlie[a] and Tie Liyun[b]

[a] *Faculty of Earth Sciences, China University of Geosciences, Wuhan, Hubei, 430074, P. R. China*
[b] *The Center for Material Research and Testing, Wuhan University of Technology, Wuhan, Hubei, 430070, P. R. China*
e-mail: honghl 8311@yahoo.com.cn

The precipitation of gold in response to changes in various intensive and extensive parameters of a hydrothermal system may be an effective means of gold ore deposition but sorption processes may also provide an exceedingly efficient mechanism for accumulating gold from solution. It is generally accepted that gold can be complexed by a comprehensive range of ligands and is relatively soluble in the supergene environment, depending on the activity of the ligand, the Eh, and the pH of the solutions. In acidic solutions, chloride is the ligand most capable of complexing Au, mainly as $AuCl_4^-$ anion, which is extremely stable in hydrothermal fluids over a wide range of pH and temperatures and is believed to be one of the principal ions responsible for leaching and transport of gold [2–6].

Adsorption of gold on mineral surfaces is an important mechanism for the formation of gold ore deposits [7–11]. Gold-bearing complexes can be adsorbed onto the surface of sulfides and can be reduced by the sulfur atoms at the mineral surface; i.e., metal cations are leached and sulfur is oxidized on forms polysulfides [12]. However, since the 1970s, "invisible gold" deposits, as well as rare-sulfide gold deposits and supergene invisible gold deposits, were found and the intimate association of gold with clay minerals was noticed. It is generally assumed that clay minerals, such as kaolinite and hydromica, have the capacity of adsorbing gold-bearing complexes from solutions and, thus, result in the accumulation of gold [8, 13]. However, none of these studies have provided evidence for the reduction of gold on such nonmetallic minerals. We undertook the experiments on the adsorption and reduction of gold from $AuCl_4^-$ - solution by kaolinite, and the results indicate that kaolinite are also the potential reducing agents in that type of gold deposit.

MATERIALS AND METHODS
Preparation of Kaolinite

The kaolinite used in this study was collected from the Yangshan, Jiangsu Province, eastern China. X-ray powder diffraction and SEM evidence confirmed the kaolinite sample was of high purity. The sample was cleaned prior to undertaking the adsorption and reduction experiments to remove contaminant materials adsorbed on their surfaces. The method of Sutheimer et al. was used, whereby [14] the sample was washed repeatedly in 1 M NaCl adjusted to pH 3 with HCl, followed by water washings to increase the pH to greater than 5.5 and to decrease conductivity to below 700 µS/cm.

Reduction of Gold by Kaolinite

The $AuCl_4^-$ solution was prepared from $AuCl_3 \cdot HCl \cdot 4H_2O$ using deionized water giving a gold concentration of 1.2 mol/L; a pH of 4.5. 1 g of the cleaned kaolinite was added to 100 ml of $AuCl_4$ solution and subsequently stirred with a glass bar; then, the reaction vessel was sealed from the atmosphere. Hyland and Bancroft [12] and Mycroft et al. [15] showed that the deposition of Au(III) on pyrite was unaffected by normal room lights. The experiment was undertaken at an ambient temperature of 25°C (±6°C), and the reacted kaolinite sample was removed from the solution after a reaction time of one week, which was sufficient for the reduction and deposition of gold from $AuCl_4^-$ solutions by the mineral surfaces. The kaolinite was collected by filtration through 0.22-µm polycarbonate filters.

Microscopic Observations of Gold on the Mineral Surfaces

For TEM investigations, the reacted kaolinite was immersed in methanol and dispersed with the ultrasonic equipment for 10 min, then was collected with a copper net, and dried under an infrared light. The samples were studied using a PHILIPS-CM12 transmission electron microscopy equipped with an EDAX-PV9100 energy-dispersive spectrometer (EDS) system. The TEM was operated at 120 kV and the camera constant was 25.48 µA for electron diffraction.

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[1] The text was submitted by the authors in English.

RESULTS AND DISCUSSION

The analytical TEM analyses show that, occasionally, the image of a particle displays an obvious darker background than the surrounding minerals (Fig. 1). EDS analysis of the particles shows evidence for no elements other than Au (Fig. 2). But elements with an atomic number of less than 11 are not detected by this EDS analytical system. However, electron diffraction of the particles shows that they are native gold (Fig. 3). As shown in Fig. 3a, the electron diffraction pattern of a selected thin spot at the margin of gold-coated kaolinite shows that gold occurs as a single crystal; in Fig. 3b, the electron diffraction pattern shows that gold occurs as an aggregate of small crystals. However, most of the gold occurs as relatively large single crystals. The metallic gold is deposited on the crystal surfaces of kaolinite. As shown in Fig. 1, kaolinite usually occurs as a hexagonal flake, and the gold coated on the substrate, and, therefore, displays the plate nature. In addition, it was occasionally found that gold is deposited on the edge surface of kaolinite (Fig. 1).

Kaolinite is one of the most abundant aluminosilicate minerals at the Earth's surface. Natural kaolinite exhibits a range of characteristics, such as degree of crystallinity and concentrations of impurities. Crystallinity of kaolinite has been mainly attributed to the combination of various defects, such as stacking faults related to layer rotation ($\pm 120°$) or layer translation ($\pm b/3$ shift), occurrence of enantiomorphic layers, or vacancy displacement [16–17]. Impurities of kaolinite are predominantly the isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedral sites [18–19]. Defects and isomorphous substitution in the crystal would contain additional electrons and, hence, facilitate the reduction of Au^{3+} on the surface. Electron transfer from kaolinite has been proposed by Haderlein and Schwarzenbach [20]. They pointed out that adsorption of nitrobenzenes and nitrophenols onto kaolinite may result in the formation of an electron donor–acceptor complex between electron donor functioning at the siloxane surface and the aromatic ring system of nitrobenzenes and nitrophenols; the siloxane surface acts as an electron donor and the aromatic compounds as an electron acceptor in the complex [20]. Gold-bearing complex ion, $AuCl_4^-$, tends to be adsorbed predominantly onto the edge surface of kaolinite. Quantum chemistry calculations using the SCF-DV method demonstrated that $AuCl_4^-$ could be readily adsorbed on the edge surfaces, especially at Al sites of kaolinite, and simultaneously electron transfer from the kaolinite surface to Au has already taken place [21]. At first, fourfold-coordinated $AuCl_4^-$ - complexes will be chemisorbed onto the kaolinite surface by releasing one of the Cl atoms and, hence, form a kaolinite-$AuCl_3$ surface complex, followed by a reduction of Au(III) to Au(I), and then Au(0), which is stabilized by the formation of gold dimers and islands due to the formation of gold–gold metal bonds [22].
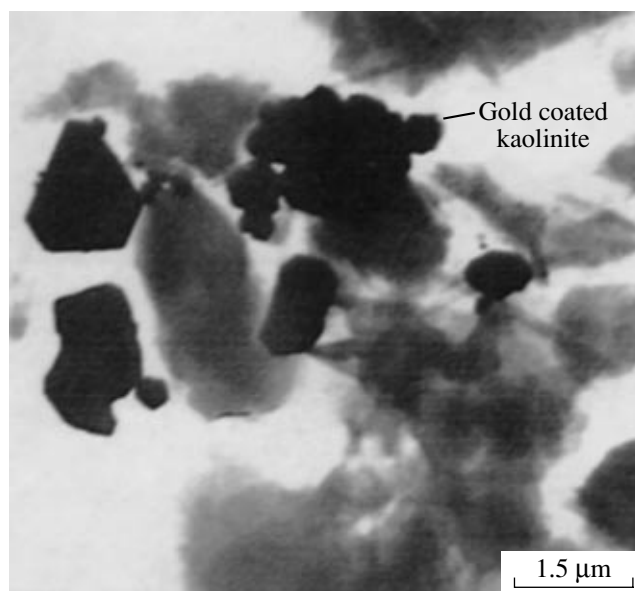

Fig. 1. TEM image shows that gold has coated kaolinite surfaces and is occasionally deposited on the edge of kaolinite.

Gold is the most electronegative transition element known, in part due to the strong relativistic effect [23]; thus, as Au^{3+} is a strong oxidizer, it can be reduced almost by all metals and their ions [8]. This may explain the electron transfer from kaolinite to gold species.

On the edge surfaces of kaolinite where there is enhanced chemisorption of the charged species, the disruption of bonding on the surfaces due to defects would also lead to enhanced chemical bonding of the ionic species, thus facilitating the precipitation of gold onto
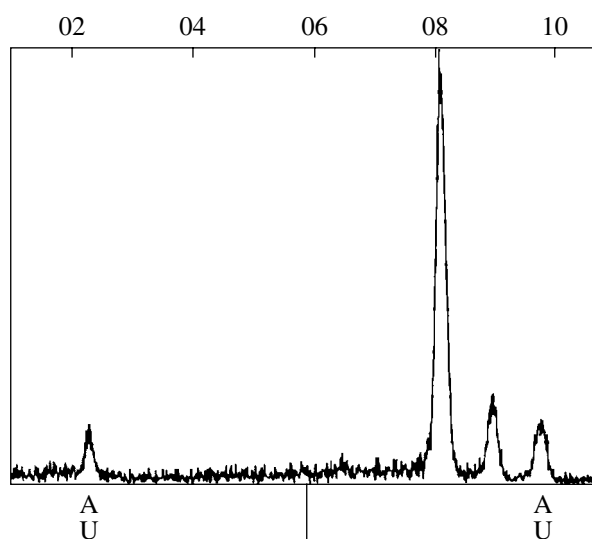

Fig. 2. EDS pattern of the coated kaolinite shows that there are no elements other than gold.
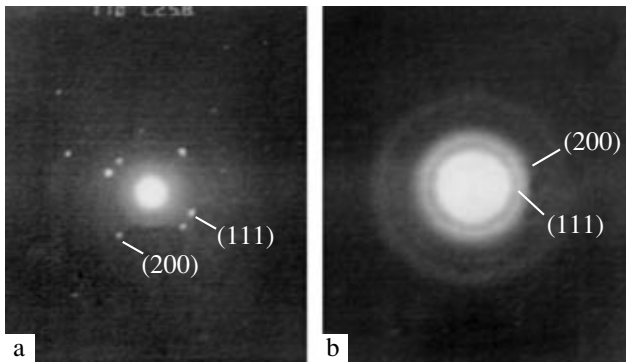
Fig. 3. Electron diffraction patterns of the gold. (a) the spots with diffraction indexes (111) and (200) of gold show that the deposited gold occurs as a single crystal; (b) diffraction rings with d-spacings consistent with (111) and (200) of gold show that gold also occurs as an aggregate of crystals.

the edge surfaces. Defects or isomorphous substitutions only collect finite additional electrons, however, the continued precipitation of the gold must eventually have been due to the presence of structurally favorable epitaxial sites in the new gold substrate. The high electrical conductivity of the gold would ensure transmission of the electronic characteristics of the nucleation site to the neighboring surface of kaolinite, thus facilitating the widespread gold plating of the kaolinite analogous to that generated by the low-temperature experimentation of Hyland and Bancroft [12]. As shown in Fig. 3a, the electron diffraction pattern of Au(111) and (200) shows that the gold coated on the kaolinite surface mainly occurs as single crystals, and, especially in Fig. 3b, the electron diffraction corona of Au-aggregate is unaffected by kaolinite, indicating that gold film extends beyond the kaolinite flake, which obviously demonstrates that the growth of gold on the kaolinite surface underwent the significantly widespread process, and gold merely coats the surface of kaolinite due predominantly to the low gold content of the solution [12].

CONCLUSIONS

The reduction of gold from gold-bearing solutions onto kaolinite surfaces demonstrates that nonmetallic minerals can play an important role in the reduction and deposition of gold. The gold mainly occurs as single crystals and merely coats the surface of the minerals, which suggests that the deposition of gold underwent the widespread process in the low gold content solution. Reduction and deposition of gold on kaolinite surfaces may be defect-induced.

Pre-existing kaolinite in contact with gold-bearing solutions can adsorb and reduce gold from the solution, resulting in gold adsorption and gold deposition on the surfaces of kaolinite. This is frequently encountered and, therefore, facilitates a better understanding of the processes by which gold is concentrated in sulfide-free gold deposits and supergene invisible gold deposits.

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