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OCCURRENCE AND DISTRIBUTION OF INVISIBLE GOLD IN THE SHEWUSHAN SUPERGENE GOLD DEPOSIT, SOUTHEASTERN HUBEI, CHINA

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Abstract

The Shewushan gold deposit, eastern Hubei, China, hosted in weathered mantle above the Shewushan thrust zone, is probably an example of a type of deposit where all the ore-grade gold is related to surficial weathering processes of a previously uneconomic gold deposit. Electron-probe micro-analysis (EPMA) and analytical electron microscopy (AEM), optical microscopy, and chemical dissolution were done to determine the occurrence and distribution of gold in the ore. The optical microscopy study demonstrates that gold is invisible in ordinary light. Fire assay yielded 4.34 g/t Au for clay-mineral separates. The AEM analyses show that gold associated with clay minerals occurs as submicrometric particles at the rim of clay-mineral grains. EPMA data show that gold in goethite occurs as micrometric granules of native gold or as an adsorbed phase (or both). The gold content of other minerals, such as quartz, "chalcedony" and barite, is generally below the detection limit of EPMA (0.05%). The characterization of invisible Au in this supergene gold deposit is beneficial to the design of a metallurgical process for Au recovery and to our understanding of the transport and accumulation of Au during the process of weathering under supergene conditions.

Keywords: occurrence, distribution, gold, invisible gold, clay minerals, goethite, electron-probe micro-analysis, analytical electron microscopy, Shewushan deposit, Hubei, China.

Sommaire

Le gisement d'or de Shewushan, dans la partie orientale de Hubei, en Chine, est situé dans une zone météorisée supérieure à la zone de cisaillement de Shewushan; il serait un exemple d'un type de gisement dans lequel l'enrichissement du minerai en or est entièrement dû au lessivage de surface d'un gisement non économique au départ. Des analyses à la microsonde électronique (AMSE) et par microscopie électronique analytique (MEA), microscopie optique et les expériences de dissolution chimique ont été faites pour déterminer le mode de formation et la distribution de l'or dans le minerai. La microscopie optique montre que l'or est invisible en lumière ordinaire. Les analyses au feu des concentrés d'argiles ont donné 4.34 g/t d'or. Les analyses MEA montrent que l'or associé aux argiles se présente en particules submicrométriques en bordure des grains. Les données AMSE montrent que l'or dans la goethite se présente sous forme de granules micrométriques d'or natif ou de phase adsorbée (ou les deux). La teneur en or des autres minéraux, par exemple quartz, "chalcédoine" et barite, est en général au dessous du seuil de détection de la méthode AMSE (0.05%). La caractérisation de l'or invisible dans ce gisement supergène est bénéfique à la fois pour la planification du processus métallurgique d'extraction de l'or et pour une meilleure compréhension du transfert et de l'accumulation de l'or au cours du lessivage dans un milieu supergène.

(Traduit par la Rédaction)

Mots-clés: caractérisation, distribution, or, or invisible, argiles, goethite, données de microsonde électronique, microscopie électronique analytique, gisement de Shewushan, Hubei, Chine.

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Introduction

The Shewushan area, located in south Hubei, central China (Fig.1), is of particular geological significance because it is a new type of economically viable gold deposit presently being worked in China. A tectonic mélange hosts a low-grade deposit containing mostly invisible gold. Ore of economic grade is confined largely to the lower portion of the 30-m-thick weathering profile rather than to the fresh, unweathered parts of the deposit. The gold in the ore is not visible by reflected- and transmitted-light microscopy at high magnification. It is, therefore, extremely difficult to study the occurrence of gold and its distribution by conventional means.

It is possible to assay hand-picked mineral separates to obtain the average content of Au in each mineral. However, such analyses of mineral separates convey no information as to whether the Au is homogeneously distributed within and among the mineral crystals, is in solid solution, or is present as submicroscopic inclusions, *i.e.*, the studies provide no direct and convincing evidence about its occurrence and distribution. Using an electron-probe micro-analyzer (EPMA) and analytical electron microscopy (AEM) with an energy-dispersion X-ray technique, we investigated the occurrence and distribution characteristics of invisible Au in Au-bearing minerals.

Sample Preparation

The deposit occurs in the Shewushan Thrust Zone, which was a conduit for epithermal mineralization as well as the present site of formation of the weathered mantle formed at the expense of the mineralized tectonic mélange (Fig. 1) (Ding 1992). The orebodies are located mainly in the lower portion of the weathered mantle, which comprises brown to red-brown clay and gravelly clay, and consists of an assemblage of illite, kaolinite, goethite, quartz, and oxides of Fe and Mn (Hong 1995).

The ore samples were collected from pits in many parts of the deposit. The total weight of the ore samples was 297.35 kg. This material was dried in the sun, and blocks of sample were selected for the preparation of the polished sections and thin sections, which were used for mineralogical studies by reflected- and transmitted-light microscopy and EPMA investigations. The rest of the sample was crushed and ground to ≤200 mesh; a portion of the sample was used to prepare a goethite concentrate by panning, then selected grains of goethite from the concentrate were studied under a microscope. This yielded a goethite separate for Au assay and EPMA studies.

A clay-mineral separate with a grain size of <5 μm and a total mass of 400 g was prepared using the pulverized ore sample and a method of precipitation.

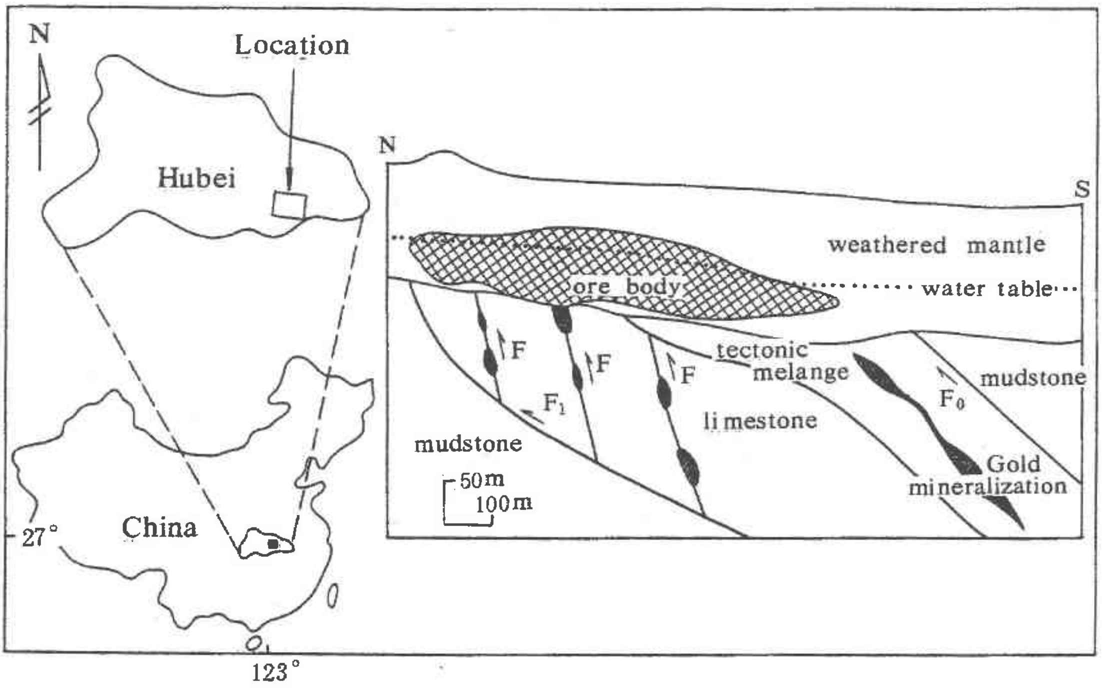

FIG. 1. A generalized map showing the location of the Shewushan gold deposit and the distribution of gold.

The grain size was estimated from the speed of precipitation and not measured accurately. This separate was used for Au assay and AEM observation.

EXPERIMENTAL METHODS

Optical microscopy

The mineralogical composition of the ore was determined by examining a large number of polished sections and thin sections in reflected and transmitted light; it was also confirmed by observing all the fractions of panning and calculating the mineral components from bulk-chemical analyses.

EPMA and AEM analyses

The analyses of goethite and other minerals were performed on a JEOL JCXA–733 electron microprobe coupled with a TN5500 energy-dispersion spectrometer (EDS) system and TN5600 automation system. The analyses were performed at 25 kV (accelerating voltage) with a beam current (cup reading) of 20 nA and a beam diameter about 1 μm using the following X-ray lines and standards: Au$L\alpha$ (metal) and Fe$K\alpha$. Trace quantities of Au could be measured by wavelength-dispersion spectrometer (WDS). In our work, a crystal of pure goethite free of Au was employed as a standard for the measurement of background, and the background count-rate was measured at the Au$L\alpha$ peak position on this blank goethite standard. One wavelength-dispersion spectrometer with a LiF crystal was dedicated to the determination of Au concentration, so that during the entire procedure, the spectrometer was not moved from the Au$L\alpha$ position. To reduce the detection limit and the error due to counting statistics, the counting time for detection of trace Au was set at 100 s. The TASK program provided by Tracor Northern is capable of doing EDS and WDS measurements simultaneously and then performing the quantitative corrections for atomic number, absorption, and fluorescence effects with the ZAF program included in TASK. Because there is some overlap between Au$M\alpha$ and the third-order Fe$K\alpha$, Au$L\alpha$ was chosen as the analyzed line in our study. In routine work, the following expression is used to calculate the detection limit (C_{DL}) for a given element (Toya & Kato 1983): $C_{DL} = 3\sqrt{I_B} / [(I_P - I_B)\sqrt{t}]$, where I_P is the peak count-rate, I_B is the background count-rate, both in counts per second (cps), and t is the counting time in seconds. Under the operating conditions mentioned above, I_P for Au is approximately 8950 cps, I_B is approximately 80 cps, t is 100 s, and the calculated value of C_{DL} in this expression is 0.03%. Taking into account uncertainties such as instrumental instability or imperfections in sample polishing, a practical C_{DL} value for trace Au in goethite is estimated to be 0.05%. Therefore, a gold concentration less than 0.05% measured in any analyzed spot is considered to be zero.

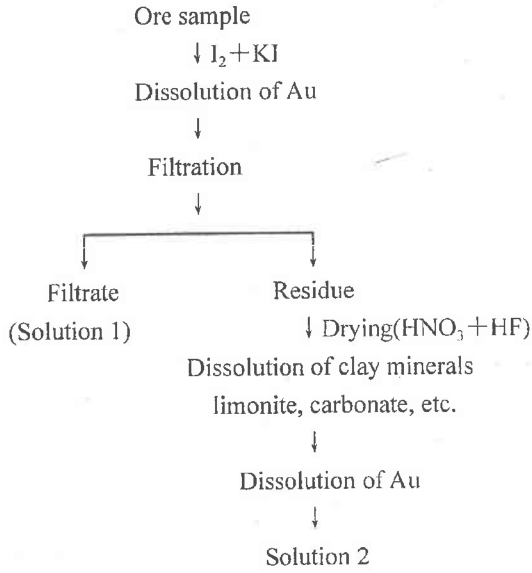

FIG. 2. Flow chart of dissolution experiment on ore sample.

The analyses of clay minerals were performed on a Hitachi 800 analytical electron microscope equipped with a TN5500 energy-dispersion spectrometer system. The instrument was operated at 120 kV. In our work, the Au$L\alpha$ line was used to qualitatively identify the gold particles less than 1 μm in diameter.

Chemical dissolution

Chemical dissolution experiments on ore were carried out as shown in the flow chart (Fig. 2) using an ore sample with a grain size <0.074 mm and a total mass of 4 g. The Au in solution was concentrated by fire assay, and the bead was analyzed by atomic absorption spectrometry (AAS). The Au in solution 1 is representative of gold as invisible particles between mineral grains, and the Au in solution 2 is indicative of gold as submicroscopic inclusions within minerals.

RESULTS

Mineralogical and chemical composition of the ore

The mineralogical study by optical microscopy showed that the common minerals present in the ore sample are quartz, kaolinite, halloysite, illite, "chalcedony", goethite and barite; the accessory minerals are rutile, muscovite, dolomite, anatase, pyrite and apatite. Modal analysis, point-counting statistics and calculation

TABLE 1. BULK CHEMICAL COMPOSITION OF THE WEATHERED MANTLE, SHEWUSHAN SUPERGENE GOLD DEPOSIT

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	FeO	MnO	MgO
71.06	14.16	5.35	0.30	0.00	0.00	0.15
CaO	K_2O	Na_2O	P_2O_5	CO_2	SO_3	H_2O^+
0.04	0.90	0.06	0.15	0.07	0.42	5.41
Ba	Au*	Ag*	Hg*	Sb*	As*	Sr*
0.43	2.26	0.89	34	100	400	577

The results are quoted in wt.% and in ppm (*).

of standard minerals gave 40 wt.% quartz, 39% clay minerals, 15% "chalcedony", 5% goethite, and 0.5% barite.

The quartz occurs as euhedral crystals and anhedral granules, with a grain size varying from 0.03 to 0.10 mm. Chalcedony is present as fan-shaped aggregates. The clay minerals kaolinite, halloysite, and illite are mixed together, with a single-crystal size less than 2 μm. The Fe oxides occur mostly as amorphous grains pervasively distributed in the ore; only a minor amount occurs as irregular granules or as a pseudomorph after pyrite; the barite is present as platy aggregates.

Wet-chemical analyses indicate that the ore is dominantly composed of SiO_2, Al_2O_3 and Fe_2O_3, which is characteristic of a weathered residue (Table 1). Fire-assay analyses yielded 4.34 g/t Au in clay minerals, 0.04 g/t Au in "chalcedony", 0.11 g/t Au in barite, and <0.01 g/t Au in quartz.

Au concentration in the minerals determined by EPMA

Concentrations of gold have been determined in tens of quartz grains of different sizes and shapes. Thirty-four spots were selected in different areas for the analyses. The Au concentrations at all of the 34 spots are below the limit of detection. In addition, chemical assay showed that the average Au concentration in quartz is <0.01 g/t. Of 28 analyzed spots in "chalcedony", only one had a concentration of Au (0.06%) just above the detection limit. Chemical assay indicated that the Au concentration in "chalcedony" averages 0.04 g/t.

Twenty spots were chosen for analyses in barite grains; two of the spots had Au contents just above the detection limit. Fire-assay data indicated 0.11 g/t Au in barite, which occurs very sparsely in the ore.

On the basis of the above results, the conclusion can be drawn that the amount of Au held in quartz, "chalcedony", and barite is not significant.

Most of the goethite occurs as very fine particles pervasively distributed among the other minerals in the ore, with some occurring as irregular or cubic pseudomorphs of pyrite that can be separated from the ore. Both irregular and pseudomorphic granules of goethite were chosen from the panning products by optical microscopy, and were then glued to a base and polished into sections. Grains of both types were chosen at random. Spots were randomly selected in each grain, 46 spots in irregular grains and 40 in cubic (pseudomorphic) grains, making a total of 86 spots. Among the 46 spots, 14 spots had Au concentrations higher than the detection limit, ranging from 0.05 to 0.12% (average 0.09%); among the 40 spots, only five spots had Au concentrations higher than the detection limit, with the values ranging from 0.05 to 0.08% (average 0.06%).

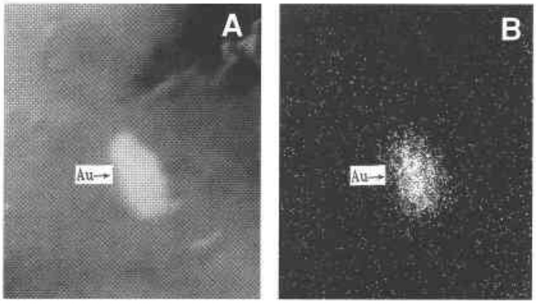

FIG. 3. a. Gold particle within goethite aggregate. b. Distribution pattern of Au*L*a X-ray scanning (EPMA). Width of the field of view: 5 mm.

To determine the mode of occurrence of trace Au in goethite, we took X-ray images of Au in grains of different shapes. Among 24 images produced, only one shows that Au is enriched in an aggregate of goethite grains (Figs. 3a, b). The X-ray image (Fig. 3a) and secondary electron image (Fig. 3b) show that there is a granule of gold about 0.6 μm in size in a particle of goethite. EPMA analysis gaves the following chemical composition (excluding Fe and summing to 100 wt.%): 99.71% Au, 0.18% Ag, 0.11% base metals, and Cu below its detection limit.

The results illustrate that some of the Au in goethite occurs as micrometric grains of native gold; most of the particles are so fine that it is not possible to characterize them by EPMA.

Au in clay minerals determined by AEM

The clay minerals are kaolinite, halloysite, and illite. For this kind of sample, the background of the image is dominantly dependent on the mass and thickness of the minerals. Usually, the image of a particle of gold displays a darker background than the surrounding silicate minerals owing to its greater mass, and it is easily identified under AEM. Particles can be located by first using the brightness contrast at lower magnification, then making determinations by EDS at higher magnification.

After identifing a number of possible particles of Au, eight very small Au-bearing particles were found at the rim of kaolinite and illite grains, with the particle size ranging from 15 to 30 nm (resolution 5 nm). The EDS

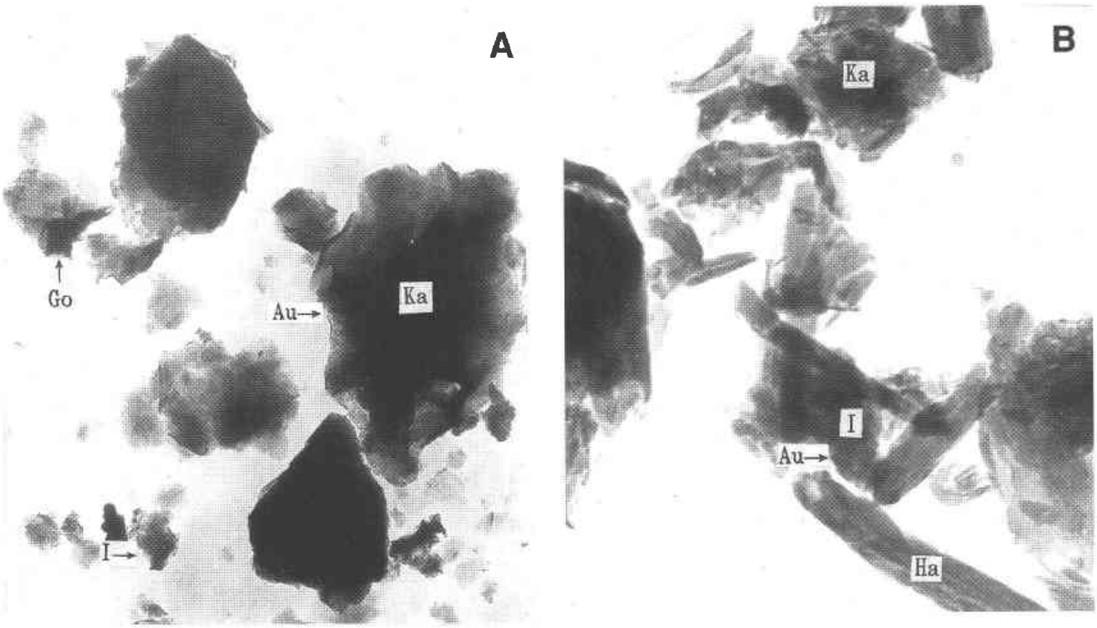

FIG. 4. a. Gold particle at the rim of kaolinite crystals (with AEM, ×50000). b. Gold particle at the rim of illite crystals (with AEM, ×30000). Symbols: Au: gold particle, Ka: kaolinite, I: illite, Go: goethite, Ha: halloysite.

spectra of the corresponding spots show that there are small peaks of Au, indicating that there are very fine Au-bearing grains present (Figs. 4a, b). Moreover, the strong peaks of common elements Si, Al, Fe, Ca, K and Ti pertain to the accompanying minerals kaolinite, illite, goethite and rutile. We believe that the Au-bearing particles among clay minerals are actually submicrometric granules of native gold.

Result of Au leaching test

To confirm the inference made from the EPMA and AEM results, that Au occurs as submicrometric particles among clay minerals and goethite in the ore, Au leaching experiments were carried out on ore, and the following results were obtained. There is 2.01 g/t Au in the I_2 + KI leaching solution and only 0.17 g/t Au in the residue after 5 hours of dissolution of an ore sample with 2.26 g/t Au, a recovery ratio as high as 92.2%. This result was confirmed in the subsequent metallurgical experiment (Wang 1993), which was undertaken by a direct cyanidation method, and led to an extraction ratio of 94.6%. The study demonstrated that the gold occurs as free granules of native metal among clay minerals and goethite.

DISCUSSION

As clay minerals constitutes 39% by weight of the ore with an Au content of 4.34 g/t, it can be inferred that there is 74.9% Au in the clay minerals, and approximately 24.8% in goethite, and that the Au content of other minerals, such as quartz, "chalcedony" and barite, are nearly all below the detection limit of EPMA. The results of chemical assays of mineral separates confirmed that there is little or no Au in those minerals.

Gold is remarkably enriched in the clay minerals; AEM observations reveal submicrometric particles at rims of grains. The leaching experiments indicate that most of the Au can be directly dissolved by leaching, which suggests that the submicrometric particles of Au may be there because of physical adsorption on clay minerals or as a mechanical mixture with them (or by both mechanisms). Clay minerals have the capability of adsorbing very fine particles because of their large specific surface-area. On the other hand, their crystal sizes are far larger than the submicrometric granules of Au. Also, clay minerals under supergene conditions usually develop as imperfect crystals. In this case, the fragmented margins and the concave surface of the clay flakes could provide suitable sites for retention of the very fine Au particles.

Experiments on submicrometric particles of gold have been performed by Japanese scientists using transmission electron microscopy (TEM). Their results have shown that artificially disseminated submicrometric particles (about 2 nm in size) subsequently transformed into single crystals, twins, and multiple twins with time. Furthermore, the smaller particles have also been proved to occur as single crystals (Dong 1988). The size range of the gold particles at Shewushan are not only remarkably larger than those created artificially, but they have also undergone a long process of weathering. We believe that the submicrometric particles at Shewushan probably occur as single-crystal particles of native gold.

EPMA analyses indicate that there are small granules of native gold in goethite; furthermore, some of the goethite grains are auriferous, but no gold particles were found within the grains. The Au in the goethite thus probably occurs as an adsorbed phase, taking into account the adsorbent nature of Fe oxyhydroxide and the geochemical characteristics of Au during weathering (Boyle 1979). Gold in goethite occurs as micrometric particles or as an adsorbed phase (or both).

Usually, secondary grains of gold present in the weathering profile exhibit a unique morphology and texture. Small crystals, flake gold and dendritic and wire growths appear to be the most common secondary occurrences in laterite and mottled clay zones of deposits (Wilson 1983, Lawrance 1988). In Western Australia, all the secondary gold in the saprolite zone of supergene gold deposits shows a total absence of impurities of other elements (<0.01 wt.%: Mann 1984, Lawrance 1988). This pure gold is generally concentrated in subhorizontal zones of accumulation of iron oxide associated with the "paleo" and present water-table.

The characteristics of supergene gold at Shewushan are similar to those of the Boddington gold deposit in Western Australia (Gao *et al.* 1995), the only difference being the degree of development of weathering. At Boddington, extensive tropical weathering has produced a well-developed complete lateritic profile, whereas at Shewushan, the weathering zone is only a subsaprolite, which is a horizon developed early in the weathering process.

In the weathering profiles overlying gold deposits, the mobility of gold has been inferred from the occurrence of surface-dispersion patterns (Lecomte 1988, Colin *et al.* 1989, Colin & Veillard 1991) or by the presence of high-purity supergene gold, either free (Wilson 1983, Lawrance 1988) or associated with Fe oxyhydroxides (Mann 1984, Vasconselos & Kyle 1989). Petrological observations and thermodynamic calculations have shown convincingly that gold can be transported and redeposited in surface waters. The transport of gold from hypogene to supergene areas may be affected by chloride in acid environments, and thiosulfate in neutral or alkaline conditions (Webster & Mann 1984, Webster 1986). Acidic chloride solutions are produced in laterites, in part by ferrolysis (oxidation and hydrolysis of iron), whereas thiosulfate solutions are produced by oxidation of pyrite in near-neutral and alkaline fluids that may be generated during the leaching of carbonate-rich ore. At Shewushan, where the weathering profile is derived from a mineralized tectonic *mélange* mainly composed of argillaceous limestone, gold – arsenic – sulfur and gold – antimony – sulfur thiosulfate complexes such as $[Au(AsS_3)]^{2-}$ and $[Au(Sb_2S_4]^{-}$ are suggested as the most likely ionic complexes that transported and redeposited gold during the weathering process, leading to the Au, As, and Sb dispersion haloes and geochemical anomalies around Shewushan (Hong 1995).

The accumulation of gold may be dominantly due to adsorption. Fan & Li (1991) performed a model experiment on gold transport in surficial conditions. They claimed that clay minerals and Fe and Mn oxyhydroxides have the capability of adsorbing colloidal gold in a pH range of 5 to 8. At those pH conditions and in the presence of clay minerals and Fe and Mn oxyhydroxides, representative of surficial conditions at Shewushan, the Au complexes may well have accumulated as they percolated downward. A negatively charged Au complex may be adsorbed irreversibly onto the positively charged edge of a clay platelet, and the decomposition of Au complexes may take place with the passage of time. As a result, the Au particles are very small in size and closely associated with clay minerals. In addition, in a pH range from 5 to 8, Fe and Mn oxyhydroxides show a strong tendency to adsorb Au (Roslyakov 1976). Fe and Mn oxyhydroxides may be associated with the adsorption of Au complexes precipitated in the lower portion of a weathering profile by the change of chemical conditions. With time, some of the gold could be expected to desorb from Fe and Mn oxyhydroxides as they were aging, forming the small particles of native gold, most of which would be retained in the oxides as adsorbed phases or small grains mixed with the oxides (Boyle 1979). The intimate association of gold and goethite clearly indicates supergene transport and accumulation.

Acknowledgements

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References

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

Colin, F., Minko, E. & Nahon, D. (1989): L'or particulaire résiduel dans les profils latéritiques: altération géochimique et dispersion superficielle en conditions équatoriales. *C.R. Acad. Sci. Paris* **309**, *Sér.* **II**, 553-560.

________ & Veillard, P. (1991): Behavior of gold in the lateritic equatorial environment: weathering and surface dispersion of residual gold particles at Dondo Mobi, Gabon. *Appl. Geochem.* **6**, 279-290.

DING QIXIU (1992): Some new ideas on the stratigraphy of the Shewushan area. *Hubei Geol.* **8**, 4-6 (in Chinese).

DONG DEJI (1988): Value and control on observation of submicrometer particle and microstructure by transmission electron microscopy (TEM). *Japanese Science and Technology* **1**, 31-36 (in Chinese).

FAN HONGRUI & LI ZHAOLIN (1991): A model experiment on gold under supergene conditions. *Gold J.* **12**, 12-16 (in Chinese).

GAO, Z.L., KWAK, T.A.P., CHANGKAKOTI, B.H. & GRAY, J. (1987): Supergene ore and hypogene nonore mineralization of the Nagambie sediment-hosted gold deposit, Victoria, Australia. *Econ. Geol.* **90**, 1747-1763.

HONG HANLIE (1995): Study on the geological characteristics of the oxidized zone at Shewushan. *Gold J.* **16**, 1-7 (in Chinese).

LAWRANCE, L.M. (1988): Behavior of gold within the weathering profile in the Yilgarn Block, Western Australia. *In* Advances in Understanding Precambrian Gold Deposits **II** (S.E. Ho & D.I. Groves, eds.). *Publ. Geology Department and Extension Service, Univ. Western Australia* **12**, 335- 351.

LECOMTE, P. (1988): Stone line profiles: importance in geochemical exploration. *J. Geochem. Explor.* **30**, 35-61.

MANN, A.W. (1984): Mobility of gold and silver in lateritic weathering profiles: some observations from Western Australia. *Econ. Geol.* **79**, 38-49.

ROSLYAKOV, N.A. (1976): Gold in the zone of hypergenesis of gold ore deposits of East Trans-Baikal, and gold behavior in the hypergene processes of an oxidizing series. *In* Gold and Rare Elements in Geochemical Processes (Yu.G. Scherbakov, ed.). Nauka Publ. House, Siberian Branch, Novosibirsk, Russia (113-140; in Russ.).

TOYA, T. & KATO, A. (1983): Practical techniques for microprobe analysis. JEOL Training Center, Tokyo, Japan.

VASCONSELOS, P. & KYLE, J.R. (1989): Supergene geochemistry and crystal morphology of gold in a semiarid weathering environment: application to gold exploration. *In* Int. Geochem. Explor. Symp., Rio '89, 22 (abstr.).

WANG YUZHONG (1993): Metallurgical test on Shewushan auriferous ore. Unpubl. Rep.

WEBSTER, J.G. (1986): The solubility of gold and silver in the system Au–Ag–S–O_2–H_2O at 25° and 1 atm. *Geochem. Cosmochim. Acta* **50**, 1837-1845.

________ & MANN, A.W. (1984): The influence of climate, geomorphology and primary geology on the supergene migration of gold and silver. *J. Geochem. Explor.* **22**, 21-42.

WILSON, A.F. (1983): The economic significance of non hydrothermal transport of gold, and the accretion of large gold nuggets in laterite and other weathering profiles in Australia. *Geol. Soc. S. Afr., Spec. Publ.* **7**, 229-234.

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