

EXPRESS LETTER

Migration mechanisms of gold nanoparticles explored in geogas of the Hetai ore district, southern China

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Several studies have shown that gas flows (namely “geogas”) ascending from the Earth’s interior can, while passing through concealed orebodies, assimilate ore nanoparticles and carry them to the surface. The orebodies might be detected by measuring nanoparticle contents in soil gas or in the atmosphere. However, the mechanism by which geogas carries gold nanoparticles from orebodies to the surface is not well understood. To investigate these migration mechanisms, suspended particles from deep gas in the Hetai gold ore district in southern China were collected, gold nanoparticles artificially added, and the distribution of the gold nanoparticles studied using a transmission electron microscope. This study showed that gold nanoparticles migrate by 1) adsorption onto other particles suspended in the geogas, including needle, spherical and flower-like shaped iron-bearing particles, spherical aluminous particles, and calcite; and 2) in aggregated form.

Keywords: geogas, gold, concealed ores, gas migration, nanoparticles

INTRODUCTION

Because of the worldwide shortage of mineral resources, development of new exploration methodologies is needed, in order to meet the requirements of economic development. With the current decrease in the number of surface deposits being found, and of operating surface mines, concealed orebodies are becoming increasingly important, and there is a need to develop effective methods to explore them. Geogas prospecting is a relatively new technique in exploration for concealed mineral deposits (down to 1 km depth) developed by Kristiansson and Malmqvist (1980, 1982, 1987), Kristiansson *et al.* (1990) and Malmqvist and Kristiansson (1984). Geogas is a flow of gas containing N₂, O₂, CO₂, CH₄, and inert gases (Tong and Li, 1999). It has been widely reported from many ore deposits worldwide (Xie *et al.*, 1999). The so-called “geogas theory” includes the following features: (1) Geogas may originate from degassing of the upper mantle and lithosphere (Gold and Soter, 1980; Morner and Etiope, 2002; Annunziatellis *et al.*, 2003). (2) Significant Earth outgassing processes are accomplished by the ascent of enhanced microflow of endogenous gases through faults and fractures in the crust not only in active

areas but also within sedimentary basins, shields, and forelands (Malmqvist and Kristiansson, 1984; Etiope and Lombardi, 1996). (3) The principle of geogas prospecting rests on the premise that geogas derived from the Earth’s interior carries nanoparticles from orebodies to the Earth’s surface and into the atmosphere. However, the mechanism by which geogas carries nanoparticles is still poorly understood.

The behavior of gold during transport by geological processes has been a controversial subject for decades. It is generally accepted that transport is predominantly in the form of gold complexes associated with HS⁻, H₂S, and Cl⁻ in natural hydrothermal solutions (e.g., Hayashi and Ohmoto, 1991; Loucks and Mavrogenes, 1999; Stefansson and Seward, 2004). Reduced sulfur complexes may play an important role in the transport of gold in the vapor phase of hydrothermal systems (Pokrovski *et al.*, 2006; Zevin *et al.*, 2007). However, these studies have focused mainly on the mechanisms of transport and deposition of gold by hydrothermal fluids at high temperatures and pressures in the Earth’s crust. There has been little research on the transport and deposition of gold in fluids at low temperatures, close to the surface. Diffusion and groundwater (advective) transport have long been considered the main mechanisms for element migration from deep orebodies to the surface (Zhou *et al.*, 2003).

To study the transport mechanism of gold by geogas, suspended particles were collected from deep gas in the

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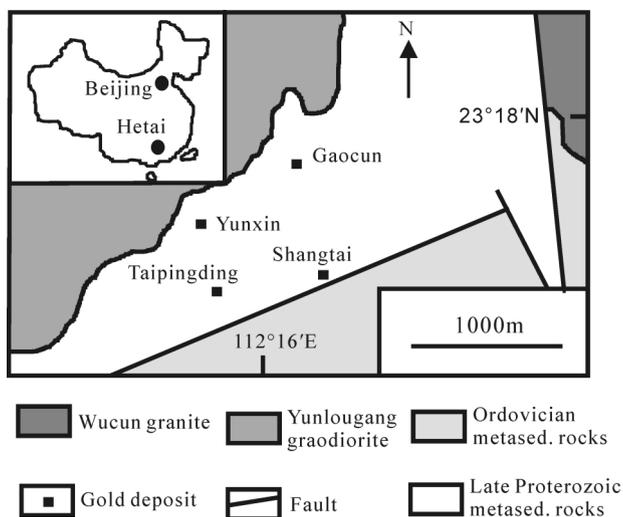


Fig. 1. Geological map of the Hetai gold deposit area, Guangdong province, China (modified from Yang *et al.*, 2003).

Hetai gold ore district, to which gold nanoparticles were added, and the distribution of the added gold nanoparticles on the original particles observed using a transmission electron microscope (TEM). The results of this research contribute to geochemical transference theory and to understanding of the genesis of metallic ore deposits.

GEOLOGICAL SETTING

The Hetai gold ore district is located in the Guangdong Province, southern China. The ore district lies within the Yunkai uplift area northwest of the intersection of the Sihui–Wuchuan and the Guangning–Luoding fracture zone. Orebodies are typical ductile shear-zone-hosted gold deposits. Outcrops consist mainly of metamorphic rocks of the Late Proterozoic Yunkai Group, which includes mica schist, quartz-micaschist and biotite granulite. Ordovician flysch consisting of interbedded slates, metaclastics and quartzite outcrops in the south of the district (Yang *et al.*, 2003). There are two major intrusive bodies in the Hetai district: the Yunlougang granodiorite in the northwest, and the Wucun at the east of the district (Yang *et al.*, 2003). Main deposits of the Hetai gold ore district are at Gaocun, Yunxi, Shangtai, and Taipingding (Fig. 1). The focus of this study is the Yunxi deposit, which is located in the northwest of the district where the orebodies are associated with mylonites. The major ore zones of the Yunxi deposit occur as veins in the middle and lower parts of the mylonite zone. They are silicified, sericitized, pyritized, chalcopyritized and sideritized mylonites or ultramylonites. Yunxi gold deposits are auriferous chalcopyrite-pyrite mylonites and auriferous veins. Gangue minerals of mylonite-related deposits are

mainly quartz and feldspar. Gangue minerals of auriferous veins are quartz and calcite, with minor amounts of feldspar and sericite. Gold occurs mainly in the form of native gold. Sulfides are predominantly pyrite, with minor amounts of chalcopyrite and pyrrhotite. Iron-bearing minerals associated with the Yunxi gold deposit are goethite, hematite, magnetite, and siderite.

SAMPLING AND ANALYTICAL METHODS

Particles were collected from gas vents in a mine within the Yunxi gold deposit using a total suspended particle sampler (TH-150C Series Intelligent Medium Air Flow, China) with sampling film for particle collection. Three sampling sites were selected, two close to the ore body (sample Nos. HT01 and HT02) and one above the ore body (sample No. HT03). Because that upward migration of geogas is controlled by faults and fractures (Morner and Etiope, 2002; Annunziatellis *et al.*, 2003), all sampling sites were selected in fault zones. To ensure that samples included only natural particles, the sampling sites were chosen in areas that had not been mined for a long time. The three sampling sites were at depths of 300, 250, and 50 m and the temperatures at these depths were 37.0, 35.1, and 29.3°C, respectively.

Particles from each sample were placed in a 150-ml beaker and 50 ml of high-purity water was added. After soaking for 24 h, samples were treated ultrasonically for 30 min and then 10 ml of medium were aspirated from each beaker and divided into two portions. One portion was retained for use as a blank sample, and 1 ml of a solution containing gold nanoparticles (preparation described below) was added to the other. The pH of the mixed solution was 5.4. This solution was stirred for 10 min at room temperature and then treated ultrasonically for a further 10 min. Samples for TEM analysis were prepared by dip-coating carbon-film Cu grids in the solution. TEM analyses were carried out at the Sun Yat-sen University using a JEM-2010HR instrument (JEOL LTD, Japan) connected to an energy dispersive spectroscope (Energy TEM 200, OXFORD-INCA). This TEM has a lattice image resolution of 0.14 nm and a point image resolution of 0.28 nm and can be operated at a magnification of 2000–1500000×.

The solution containing gold nanoparticles was prepared using a chemical reducing method (Song *et al.*, 2002): 2.5 ml of 1% aqueous HAuCl_4 solution was placed in a 250 ml volumetric flask, diluted with high-purity water to volume, and mixed well. After boiling for 10 min, 6.65 ml of freshly prepared trisodium citric acid was quickly stirred into the HAuCl_4 solution. Average grain size of the gold nanoparticles was determined to be of 20 nm by a UV-visible spectrophotometer (Shimadzu UV 2501PC).

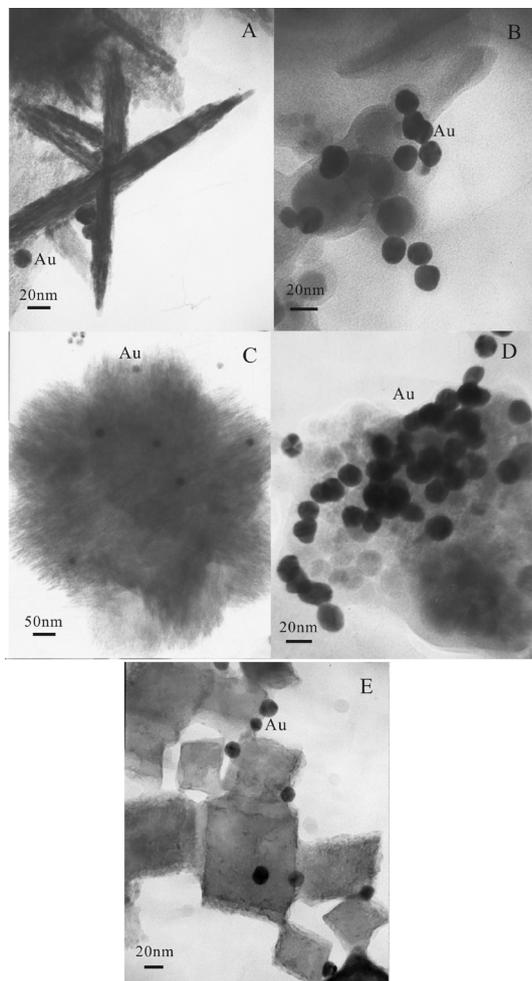


Fig. 2. TEM photographs of gold nanoparticles adsorbed on (a) needle-shaped iron-bearing particles; (b) on spherical iron-bearing particles; (c) on flower-like iron-bearing particles; (d) on spherical aluminum-bearing particles; (e) on calcite particles.

RESULTS

TEM observations (Fig. 2) showed spherical gold nanoparticles with diameter ranging from 18 to 20 nm. The gold nanoparticles were adsorbed onto iron-bearing particles having three characteristic shapes: needle, spherical, and flower-like. The needle particles (Fig. 2a) were 100 to 300 nm in length and their maximum width was 35 nm. Energy dispersive spectroscope analysis (EDS) revealed that their main components are Fe (54.30%) and O (31.56%), with minor amounts of Tb (4.57%), Ca (2.66%), Al (3.78%), P (1.26%), Si (0.94%) and As (0.93%). This suggests that the iron particles are goethite. Gold particles were observed at the intersection of needle crystals, or on the needle crystal surfaces. The diameters of the spherical iron-bearing particles range

from 15 to 50 nm (Fig. 2b). EDS analysis revealed that the composition of the spherical iron-bearing particles is Fe (67.55%) and O (30.85%), with minor amounts of Si (1.60%), implying that the particles are hematite (Fe_2O_3). Gold nanoparticles look adsorbed onto the surface of the spherical iron-bearing particles. Spherical iron-bearing particles adsorbed the largest number of gold nanoparticles. The flower-like iron-bearing particles (Fig. 2c) were observed to be 500 to 800 nm in diameter, and most were larger than the spherical and needle-shaped particles. The flower-like particles are aggregates of very fine elongate particles. EDS analysis revealed that they are essentially composed of Fe (63.49%) and O (31.40%), with minor amounts of Al (2.80%), Ca (0.39%), Si (1.05%), and As (0.87%). Gold nanoparticles are embedded below the surface of the flower-like clusters (Fig. 2c). TEM showed that the diameter of the spherical particles ranges from 15 to 20 nm (Fig. 2d). EDS analysis revealed that their major components are Al (50.42%) and O (47.26%), with minor amounts of Fe (0.33%) and Si (1.99%). These aluminous particles adsorbed abundant gold nanoparticles (a rough calculation showed that 1 gold nanoparticle is adsorbed per the surface area of 710 nm^2), indicating their stronger adsorptive capability. Other particles onto which gold nanoparticles were adsorbed are rhombohedral in shape with sizes ranging from $50 \times 60 \text{ nm}^2$ to $100 \times 130 \text{ nm}^2$ (Fig. 2e). EDS analysis revealed that their main elements are Ca (56.58%), O (42.32%) and probably C (it was difficult to distinguish C content of the sample from C originating from the carbon-film Cu grid), with minor amounts of Si (1.10%). Consequently, these rhombohedral particles appear to be calcite crystals. Most of the gold nanoparticles were adsorbed along the contacts between calcite particles. TEM observations suggest that in some instances gold nanoparticles aggregated without being adsorbed directly onto other particles.

DISCUSSION AND CONCLUSIONS

Kristiansson and Malmqvist (1980) postulated that ascending geogas (or gas microbubbles) passing through deep orebodies could assimilate and carry matter from orebodies to the surface. Malmqvist and Kristiansson (1984) observed ascending gas in 26 out of 30 tested boreholes at three different sites and found that flow rates varied between 0.006 to $4 \text{ cm}^3/\text{min}/\text{m}^2$ of borehole cross-section.

The matter transported by geogas can be in the form of individual nanoscale particles with sizes ranging from several nanometers to hundreds of nanometers, or aggregations of these particles (Tong *et al.*, 1998). Mineralization processes can form large quantities of nanoparticles of metallogenic and associated elements

(Tong and Li, 1999). As the nanoparticles from concealed ore deposits and surrounding rocks interact with ascending geogas flows they are transported, and can form geogas anomalies on the surface of the ores (Xie *et al.*, 1999; Tong and Li, 1999). Kristiansson and Malmqvist (1982) and Kristiansson *et al.* (1990) demonstrated that geogas bubbles collect and transport trace elements (as solid particles) for long distances. They found evidence of natural transport of Au, Cu, Zn, As and Pb by upward geogas via faults above buried ore deposits. A laboratory experiment by Etiope and Lombardi (1996) showed that air, bubbled through a 2 m natural sand column, can transport solid ultra-small metallic and radioactive particles. However, the mechanism for migration of gold nanoparticles in ascending geogas is still an open question. Nanoparticles differ from bulk matter in their surface's structure. The ratio of surface atoms to interior atoms in nanoparticles is higher and their surfaces are charged (Guo *et al.*, 2001; Barnesa *et al.*, 2002; Jiang *et al.*, 2003). Nanoparticles also exhibit high absorption capacity (Ding, 1998). These properties imply that the migration mechanism of gold nanoparticles in geogas flows should be different to those of hydrothermal ore-forming fluids. The experimental results reported here indicate that gold nanoparticles migrate in geogas by adsorption onto iron-bearing particles (needle-shaped, spherical, and flower-like), onto spherical aluminum-bearing particles, and onto calcite crystals. The results also show that gold nanoparticles can form aggregates, without being directly adsorbed onto other particles, and may also migrate in geogas in this form. Brownian motion of the gold nanoparticles may overcome the force of gravity so that the nanoparticles can ascend with the geogas flow above the groundwater table, along dried fault and fracture in rocks (Cao *et al.*, 2010). Adsorbed or aggregated gold nanoparticles ascended with the geogas were partially adsorbed by the Quaternary sediments. The ratio between adsorbed versus flowed nanoparticles depends from the mineral compositions and the pH conditions of the Quaternary sediments.

The migration mechanism of gold nanoparticles in geogas has an important influence on their behavior in terms of both precipitation and mobility. The mechanism of precipitation of gold nanoparticles within geogas flows is different from that in ore-forming fluids, where the precipitation of gold is related to the variation of conditions including temperature, pressure, pH, and Eh.

Au anomalies have been detected in surface geogas associated with concealed deposits of gold, copper, and silver, with oil and gas accumulations, and with concealed faults (Tong *et al.*, 1998; Wang *et al.*, 1999; Yang *et al.*, 2000, Ge *et al.*, 2000), the results of this study are important to exploration for concealed deposits and studies of concealed faults. Moreover, toxic materials from deep

sources may be transported to the earth's surface by geogas (Etiope, 1998; Etiope and Lombardi, 1996; Etiope and Martinelli, 2002); therefore, this research has implications for studies on the toxic materials in geogas.

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