ADSORPTION BEHAVIOR OF GOLD(I)-THIOSULFATE COMPLEX ANIONS ON THE SURFACE OF ALUMINA AND SILICA GELS: APPROACH TO THE FORMATION MECHANISM OF LOW-SULFIDATION EPITHERMAL GOLD DEPOSITS

K. YONEZU[1], T. YOKOYAMA[2] Y. OKAUE[2], A. IMAI[1] & K. WATANABE[1]

[1]Department of Earth Resources Engineering, Kyushu University, Fukuoka, Japan
[2] Department of Chemistry, Kyushu University, Fukuoka, Japan

SUMMARY – In order to elucidate the chemical relationship between gold and aluminum in quartz veins of low-sulfidation epithermal gold deposits, it is important to investigate the role of aluminum for the enrichment of Au(I) ions. Adsorption behavior of $[Au(S_2O_3)_2]^{3-}$ complex anions (Au(I)-S) on the surface alumina and silica gels was examined in this study. In the pH range of 4 to 9, the amount of Au(I)-S adsorbed on alumina gel decreased with increasing pH and the amount abruptly decreased between 6 and 7. The amount became almost zero at pH 8 and 9 under 30 °C. Based on the zeta potential of the alumina gel, its isoelectric point was around pH 7, indicating that its surface charge was positive below pH 7. The results suggest that the adsorption of Au(I)-S on the alumina gel was mainly controlled by electrostatic interaction. While, Au(I)-S were significantly adsorbed under 60 °C even at pH 8 and 9. This fact suggests that they were adsorbed due to formation of Al-O-Au bonds (chemical adsorption) at 60 °C. On the other hand, only a little adsorption of Au(I)-S occurred on the surface of silica gel at 30 °C and 60 °C. We deduce us that aluminum may play a more important role for enrichment of gold than silica (quartz) during the formation of low-sulfidation epithermal gold deposits.

1. INTRODUCTION

In low-sulfidation epithermal gold deposits, gold is macroscopically observed in quartz veins. Therefore, it has been believed for along time that silica minerals interact with Au complex anions contained in hydrothermal ore-forming fluid. However, no specific reaction between Au complex anions and silica minerals has been known yet. Recently, our research group found high concentration parts of gold nearby aluminum minerals such as adularia or smectite in ore deposits (Honda, 2003). They also found that there is a good correlation between contents of Al and Au in siliceous deposits formed from geothermal waters (Hayashi 1996).

From experimental results of gold solubility, it is considered that gold is transported as Au(I) complex anions such as $[Au(HS)_2]^-$ complex anion in hydrothermal forming liquid and geothermal water (Renders and Seward 1989; Seward 1991). Accordingly, it is essential to investigate the reaction between Au(I) complex anions, and silica or aluminum minerals to elucidate the enrichment mechanism of gold during the formation of low-sulfidation epithermal gold deposits. In this study, we selected $[Au(S_2O_3)_2]^{3-}$ complex anions as the Au(I) complex anions for convenience and examined the adsorption behavior of $[Au(S_2O_3)_2]^{3-}$ on the surface of alumina and silica gels at 30 °C and 60 °C.

2. EXPERIMENTAL

2.1 Reagents

Alumina gel powder (200 m^2/g, ICN Alumina N-Super I) and silica gel powder (450 m^2/g, Wako gel C-200) were used as adsorbents and were commercially obtained from ICN Biomedicals and Wako. Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) was also obtained from Wako. As a gold(III) stock solution, the gold standard solution (1000 mg dm^{-3} as Au) for atomic absorption spectrophotometry (AAS) was used ($HAuCl_4$ in 1 mol dm^{-3} HCl, Wako).

2.2 Preparation of sample solutions

The stock solution of sodium thiosulfate was prepared by dissolving sodium thiosulfate in deionized-distilled water to have a concentration of 4×10^{-2} mol dm^{-3}. Au(I)-thiosulfate solution was prepared from a mixture of both gold(III) and thiosulfate stock solutions in a volume ratio of 9:1 with the concentration 1×10^{-3} mol $dm^{-3}$and 4×10^{-2} mol dm^{-3}, respectively. To complete the formation of $[Au(S_2O_3)_2]^{3-}$ complex, this solution was kept at pH range of 7 - 8 for at least 24 hours with stirring prior to adsorption experiments. The $[Au(S_2O_3)_2]^{3-}$ complex is stable in solution in the pH range of 2 to 12. Sample solutions (500 ml) containing 25 to 250×10^{-6} mol dm^{-3} of gold with 0.12 to 1.2 mol dm^{-3} NaCl were prepared by diluting the standard solution with deionized-distilled water immediately before each adsorption experiment.

2.3 Adsorption experiments

Adsorption experiments were conducted at 30 and 60 °C as follows. The pH of sample solutions ($[Au(S_2O_3)_2]^{3-}$ complex solution) was adjusted between 4 and 9 and subsequently 1-10 g of alumina gel or silica gel was added to the solution. The pH was continuously monitored and maintained within ±0.1 pH with NaOH solution or HNO_3. Suspensions were magnetically stirred. After a predetermined time, an aliquot of the suspension was collected and filtered with a 0.45 µm membrane filter. The gold concentration in the filtrate was determined by flame AAS and the amount of gold adsorbed on the gels was estimated from the difference in gold concentration before and after adsorption.

3. RESULTS & DISCUSSION

3.1 pH effect

Figure 1 shows the effect of pH in 0.12 mol dm^{-3} NaCl solutions at 30 and 60 °C. The vertical axis indicates % of Au adsorbed on alumina and silica gels. In alumina gel, high adsorption range is from 4 to 6, with the maximum adsorption at pH 4. Above pH 6, the amount of adsorbed gold rapidly decreased with increasing the pH. Fedoseyeva and Strel'tsova(1987) also conducted the adsorption experiments of Au(I)-S on Al_2O_3 and reported a similar result as the Figure 1. In comparison, only a little adsorption of Au(I)-S took place on silica gel.

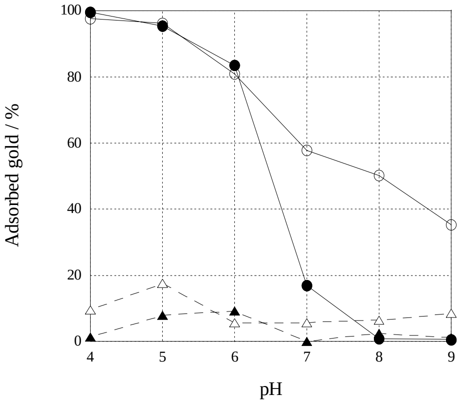

Figure 1. Variation of % of gold adsorbed on alumina and silica gels with pH after 24 hours at 30 and 60 °C.

● : Alumina gel at 30 °C. ○ : Alumina gel at 60 °C.▲ : Silica gel at 30 °C. △ : Silica gel at 60 °C. Initial gold concentration: 2.5 ×10^{-5} mol dm^{-3}. NaCl concentration: 0.12 mol dm^{-3} NaCl.

3.2 Zeta potential of adsorbents

The zeta potential corresponding to the surface charge for alumina and silica gels in aqueous solution is shown in Figure 2. For alumina gel, the zeta potential was positive in the pH range 2 to 6.4. In contrast, the zeta potential of silica gel was almost zero or negative in the pH range 2 to 6.4. From the fact that negatively-charged Au species could be adsorbed on alumina gel but not on silica gel (see Figure 1.), it appears that electrostatic force has an influence on adsorption. Au(I)-S were not adsorbed on silica gel in the pH range 4 to 9 due to electrostatic repulsion between negatively-charged Au complex ions and the negative surface charge on silica gel, while the complex was attached electrostatically to the positively-charged surface of alumina gel. These results indicate that alumina plays a more important role for enrichment of gold than silica.

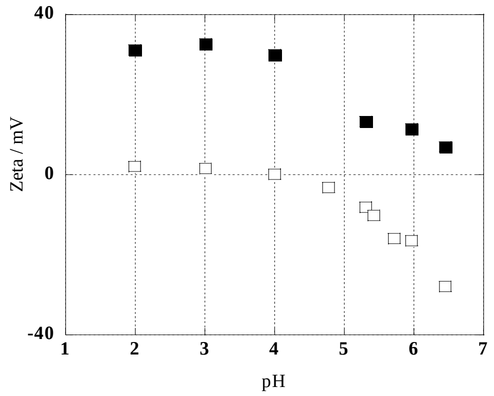

Figure 2. Zeta potential as a function of pH for alumina (■) and silica (□) gels in NaCl solutions. NaCl concentration: 0.12 mol dm^{-3}.

3.3 Adsorption rate

Figure 3 shows variation of % of adsorbed gold on alumina gel with reaction time. The adsorption occurred very rapidly (in half hour) and reached at maximum adsorption. Once the adsorption attained the maximum, it was kept a constant value even after 120 hours.

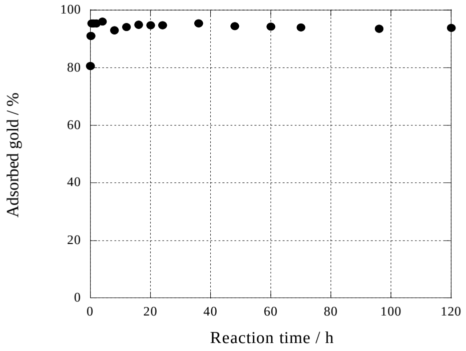

Figure 3. Variation of % of the amount of gold adsorbed on alumina gel with reaction time in 0.12 mol dm^{-3} NaCl solution at pH 4. Initial gold concentration: 2.5×10^{-5} mol dm^{-3}. The amount of adsorbent: 10 g.

3.4 Adsorption isotherm

Figure 4 shows an adsorption isotherm at 30 °C for alumina gel. It seems that the isotherm is matches a Freundlich-type.

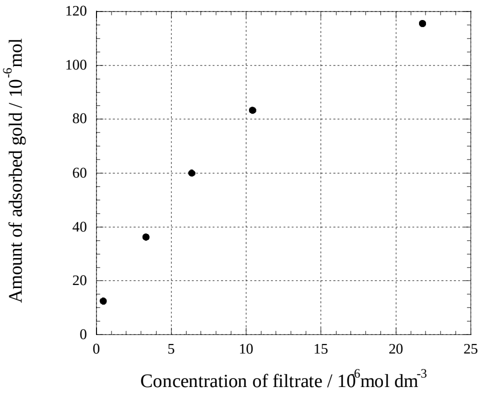

Figure 4. Adsorption isotherm for alumina gel at 30 °C in 0.12 mol dm^{-3} NaCl solution at pH 4. Reaction time 24 hours.

3.5 Effect of NaCl concentration

Figure 5 shows the effect of ionic strength on adsorption of Au(I)-S. The amount of gold adsorbed decreased abruptly with increasing concentration of NaCl. This fact indicates that chloride ions prevent adsorption of Au(I)-S on alumina gel.

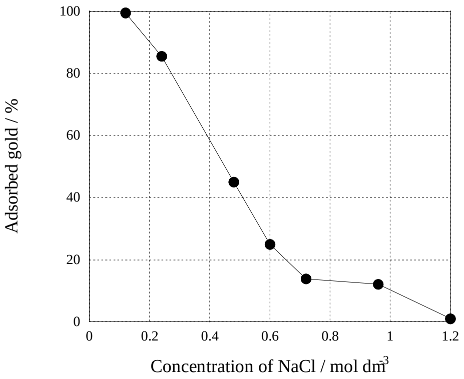

Figure 5. Variation of the amount of gold adsorbed on alumina gel as a function of concentration of NaCl reacted for 24 hours at pH 4. Initial gold concentration: 2.5×10^{-5} mol dm^{-3}. The amount of adsorbent: 10 g.

3.6 XANES spectra for Au

Solid samples (alumina gel after reactions) on the filter were air-dried in a dark room at room temperature. To identify the chemical state of gold adsorbed on alumina gel, some of the solid samples were examined by X-ray absorption spectroscopy (XANES spectra). In Figure 6, XANES spectra for three standard materials are shown [(b): metal gold as Au(0), (c): $KAu(CN)_2$ as Au(I), (d): $KAuCl_4$ as Au(III)]. The XANES spectrum ‘a’ corresponds to the spectrum for gold adsorbed on alumina gel. From comparison of spectral pattern between the standards and the sample, it is reasonably concluded that the adsorbed gold exists as elemental gold, suggesting that Au(I)-S was spontaneously reduced to Au(0) (atomic Au) by disproportionation (Gammons, et al. 1997) because the resulting Au(III) complex ions are easily reduced to atomic gold after adsorption on the surface of alumina (Uchida 2001).

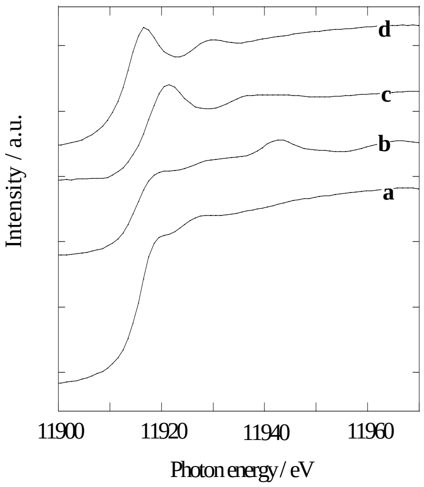

Figure 6. XANES spectra for standard materials and the solid sample.
(a): Solid sample reacted for 24hours shown in Figure 4 at pH4. (b): Au(0) standard, metal gold. (c): Au(I) standard, $KAu(CN)_2$ crystal (d): Au(III) standard, $KAuCl_4$ crystal.

4. GEOLOGICAL IMPLICATION

This study showed that the adsorption capacity of alumina gel for Au(I) complex is better than that of silica gel. In addition, gold ions were reduced to elemental gold on the surface of alumina. These facts explain why high-grade gold occurs intimately with minerals containing aluminum. It is widely accepted that $[Au(HS)_2]^-$ is the dominant species of Au in hydrothermal water (Renders and Seward 1989). Gammons et al. (1997) reported that Au(I) ions disproportionate to Au(0) and Au(III) ions by cooling. Based on the above description, the concentration and reduction of gold in quartz containing adularia and clay minerals, and the formation of low-sulfidation of gold deposits, can be explained by the following. Gold exists as a form of Au(I) complex in hydrothermal water. Upon its mobilization through cracks and fissures of crust, hydrothermal water containing gold is boiled and degassed. Consequently, increased pH and cooling cause large amounts of quartz to precipitate with aluminum hydrous oxides. At the same time, Au(I) complex becomes unstable and disproportionates to Au(0) and Au(III) species on the surface of aluminum hydrous oxide, as suggested in this study. These gold species with negative charge are concentrated on the surface of aluminum minerals providing positive sites. Lastly, Au(III) ions are also reduced to Au(0) spontaneously. In this way, aluminum plays an important role for the enrichment and reduction of gold during the formation of low-sulfidation epithermal gold deposits.

5. REFERENCES

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