ON THE MOBILITY OF GOLD IN THE REGOLITH: RESULTS AND IMPLICATIONS FROM EXPERIMENTAL STUDIES

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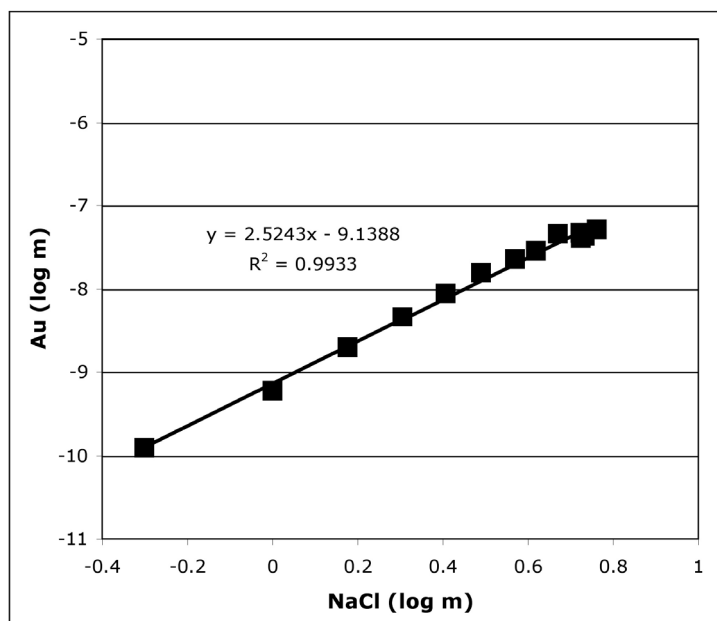[3]CSIRO Exploration and Mining, Adelaide

INTRODUCTION

At the present price of approximately US\$600/troy oz, gold is clearly a valuable commodity. In order to develop improved geochemical methods to explore successfully for new gold deposits, especially in areas covered by transported regolith, we need to understand the processes by which gold is dispersed and/or concentrated in the regolith. This understanding is also important in developing improved methods for processing gold ore. Recent experimental studies, highlighted below, show the concentrations of gold that may be expected in pore and ground waters, the speciation of dissolved gold and the effect of microbiota on the solubilisation and/or sequestration of gold.

SOLUBILITY OF NATIVE GOLD

We need to know the solubility of native gold in pore, ground and surface waters, as part of understanding how much gold can be dissolved, precipitated and transported. Gold solubility has been measured in many studies, but mainly under hydrothermal conditions (150-600°C and 500-1800 bar, *e.g.* Benning & Seward 1996; Stefansson & Seward 2003a,b; Tagirov *et al.* 2005). Low-temperature studies of gold solubility are difficult because of slow reaction kinetics and the very low and difficult to measure concentrations of dissolved gold; however, there have been a few experimental studies of gold solubility at low temperature, but only in sulfide solutions (25°C, *e.g.* Renders & Seward 1989; Tagirov *et al.* 2006). We need solubility data for native gold under the oxidising, sulfide-absent and chloride-rich conditions that are commonly found in brines in near-surface environments in Australia and other parts of the world. In this study, we have measured the solubility of native gold at 50°C, pH = 4 (acetate buffer), 1 ppm $O_2(g)$ and 0-5.8 m NaCl, in 365-day experiments. All samples were filtered using 0.45 μm filters. Equilibrium concentrations appear to have been reached after approximately 120 days. We measured the low concentrations of dissolved gold using a newly refined technique consisting of activated carbon sachets and subsequent neutron activation analysis. The detection limit of this method is approximately 4 ppt (log m_{Au} = -10.7)

Figure 1 shows the measured solubility varies from approximately log m_{Au} = -10 (~10 ppt) at low NaCl (0.5 m NaCl) to approximately log m_{Au} = -7.3 (~10,000 ppt) at high NaCl (5.8 m). The increase in log m_{Au} versus log m_{NaCl} is nearly linear with a slope of approximately 2.5. The slope greater than 2 indicates that the dissolved gold was present as a mixture of $Au^{I}Cl_2^-$ and $Au^{III}Cl_4^-$ species, the latter of which is expected given the acidic and oxidised conditions of the experiments.

These results indicate that dissolved gold concentrations in ground and pore water could reach ppb levels in brines at low temperature, even in the absence of other ligands such as thiosulfate, cyanide, sulfide and S- and N-bearing organic molecules, and/or microbiota. Note that gold concentrations in brines around gold deposits have been measured in the field to be the range of 10s of ppt, *e.g.,* around a playa lake in the St. Ives

Figure inset text:
y = 2.5243x - 9.1388
R^2 = 0.9933

Axis labels: Au (log m); NaCl (log m)

Figure 1: Native gold solubilty at 50°C, pH = 4, $P_{O2(g)}$ = 10^{-6} bar. Uncertainties within symbol size.

goldfield of Western Australia (Carey *et al.* 2003). These concentrations are up to 3 log units lower than observed in our experiments. There is a difference in temperature (experiments at 50°C, *cf.* groundwater at approximately 20-25°C) but the solubility of gold is unlikely to change by 3 orders of magnitude over this small temperature range. The difference in gold concentrations could indicate that native gold is not available to the groundwater, or other processes are operating, *i.e.,* adsorption on mineral surfaces and/or organic matter and/or kinetics. At pH less than approximately 8.5, micromolar concentrations (~200 ppb) of oxidised gold (Au^{III}) have been shown to adsorb onto goethite, smectite and kaolinite (Cohen & Waite 2004); however, the adsorption behaviour of reduced gold (Au^{I}) – likely to be the valence state of dissolved gold in most groundwater environments – is unknown, and could be very different from its oxidised counterpart. Kinetics could limit the dissolution of gold, but equilibrium was reached in the experiments after approximately 120 days and slow rates of groundwater movement (*e.g.* centimetres/yr) might allow enough contact time.

SOLUBILISATION OF GOLD BY BACTERIA

Recent studies have shown that bacteria have the capacity to solubilise and/or precipitate gold from soils (Reith & McPhail, 2006; Reith *et al.,* 2006). In biologically active and parallel sterilised microcosm experiments the solutions were sampled periodically over 70 days, filtered through No. 4 Whatman paper and analysed for gold. The solutions contained little or no chloride. The maximum gold concentrations in the biologically active experiments were reached between 20 and 40 days (maximum values shown on Figure 2). In all cases, the gold concentrations dropped to below detection (approximately 3 ppb (log m_{Au} = -7.8) by the ICP-MS method used in Reith *et al.* (2006)) by the end of the experiments. Many of the sterilised experiments had gold concentrations below detection, but some had up to approximately 50 ppb (log m_{Au} = -6.6), nearer to the values in the gold solubility experiments. The maximum gold concentrations in the biologically active experiments are up to 4 log units higher than measured in the low chloride gold solubility experiments shown above. There are three possible reasons: i) the gold in the solutions of the microcosm experiments was colloidal (because microcosm samples were not filtered through 0.45 µm filters); ii) microbiota solubilized gold while active and then the microbial community changed; or iii) there were ligands, *e.g.,* amino acids (analysed and detected in one microcosm experiment; Reith & McPhail 2006) or other organic complexing agents in the microcosms. Although microbiota were clearly shown to solubilise gold in the experiments of Reith & McPhail (2006), subsequent culturing experiments using *Ralstonia metallidurans* showed that gold can be sequestered by this bacteria (observed on gold grains from field sites; Reith *et al.* 2006). Thus, it is unclear if the gold will stay in solution and be available for transport in regolith environments.
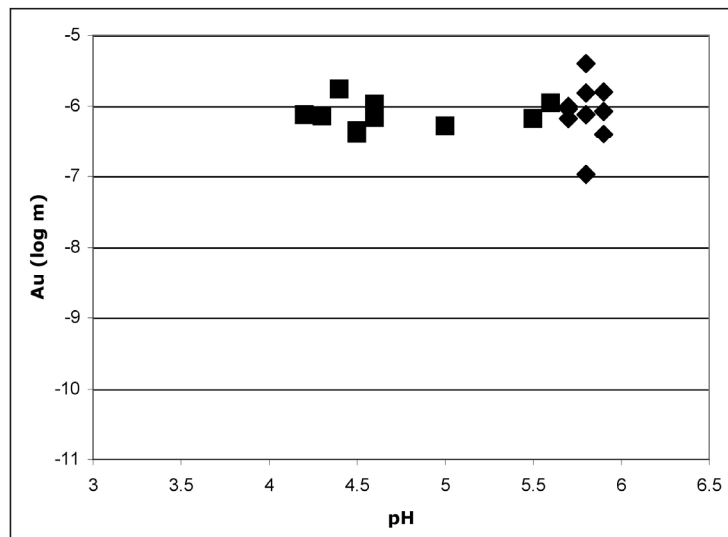

Figure 2: Gold in solutions of microcosm experiments with A-horizon (diamonds) and B-horizon (squares) soils from the Tomakin Park Gold Mine, NSW.

MOBILITY OF GOLD IN PORE AND GROUND WATER

The results of both types of experiments suggest that groundwater, especially brines, can contain much higher concentrations of gold than has been observed so far in groundwater. This may indicate that gold concentrations higher than a few 10s of ppt could be present on a local scale, such as in pore water or groundwater in contact with native gold, but it is not transported far under present environmental conditions. It might indicate that there have been periods where gold has been transported more effectively than indicated by observed gold concentrations in groundwater under present-day conditions, perhaps during episodic deep weathering periods in Australia, as suggested by paleomagnetic dating (*e.g.* Pillans & Craig 2005). It is likely that other processes, particularly adsorption of gold on mineral surfaces and/or organic material, could limit the mobility of gold; however, determining this will be extremely difficult given the low concentrations of aqueous and colloidal gold found in natural environments, and even at the higher concentrations observed in experiments using dissolved Au^{I} species and/or colloidal gold.

CONCLUSIONS

The concentrations of gold, either dissolved or colloidal, are much higher in gold solubility experiments and biologically active microcosm experiments than found so far in present-day natural pore and ground waters. We conclude that there is a much higher capacity to transport gold in pore and ground water than is currently indicated, raising the possibility that there have been periods in the geological past when gold transport may have been higher. Alternatively, processes such as adsorption limit gold mobility and/or pore and groundwater do not react with enough gold to reach high concentrations.

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