

SPECTROPHOTOMETRY OF GOLD(III) HALIDES

Alistair J. Usher¹, D.C. “Bear” McPhail¹ & Joël Brugger^{2,3}

¹CRC LEME, Department of Earth and Marine Sciences, Australian National University, Canberra, ACT, 0200

²CRC LEME, School of Earth and Environmental Sciences, University of Adelaide, SA, 5005

³South Australian Museum, North Terrace, Adelaide, SA, 5000

INTRODUCTION

Understanding the behaviour of gold in the Earth’s crust will aid the development of informed and effective exploration strategies. Alteration of primary deposits in the weathering zone is of particular importance to the Australian gold industry, and knowledge of the geochemical behaviour of the element during weathering is essential for the discovery of new deposits and to interpret the history and genesis of known mineralisation.

A number of complex processes are involved in the formation of gold deposits. Investigation of the chemical and thermodynamic properties of the metal during the three critical processes of mobilisation, transport and deposition in the regolith will lead to an improved theoretical basis for understanding observed mineralisation and dispersion patterns. Developing this understanding is of practical utility for geochemical prospecting in the regolith, having applications to the discovery of placer deposits, supergene mineralisation and the location of primary ore deposits under cover.

Despite the perception of gold as a “noble” metal and highly resistant element, it is mobile in a range of weathering environments in a variety of forms and has been directly observed to exist in three oxidation states in the natural environment: Au(0); Au(I); and, Au(III) (Boyle 1979). All of these states are potentially mobile so knowledge of the speciation behaviour of the element in a given environment is a prerequisite for understanding its mobility.

The mobility of gold in the regolith is mediated by water as both a solvent and mass transport medium. The form and speciation of the metal is determined by the initial state of the primary deposit as well as the physical and chemical properties of the solution. Fine-grained elemental gold has been observed to be more physically mobile than coarse-grained nuggets, as would be expected for any mineral subject to physical transport. However, explaining the mobility of dissolved gold species is a far more complex problem requiring information about the solubility of each form of gold as well as the distribution of species and reaction chemistry of gold-containing complexes.

Hydrometallurgical techniques for gold extraction are becoming increasingly important in the modern gold industry as the majority of new deposits being mined are low grade ore bodies containing 1-3 g/tonne total gold (Sparrow & Woodcock 1995). Knowledge of the speciation and reaction chemistry of the element in aqueous solution is potentially of twofold economic significance, leading to advances in both finding and harnessing the resource.

In order to develop informed and effective exploration strategies and optimise hydrometallurgical extraction techniques, we must obtain an understanding of the fundamental chemical properties of gold and how these affect solubility, speciation and transport processes. There is a long history of controversy over the form, speciation and oxidation state of gold in most environments (Peck *et al.* 1991). It is generally accepted that hydrothermal fluid systems involved in the formation of gold deposits are unlikely to be oxidising enough to stabilise Au(III) species and geochemical research has increasingly focussed on Au(I) complexes (e.g., Stefansson & Seward 2003 and references therein). However, Au(III) halide species (such as the AuCl₄⁻ and AuBr₄⁻ ions) are stable in air even at high concentrations for many years at ambient temperatures and pressures and may therefore play a significant role in gold transport in near-surface, regolith environments (Mann 1984, Sharps *et al.* 1993). Further, Au(III) halides continue to be used as experimentally accessible starting materials for sorption, biological and reactive transport experiments (e.g., Berrodier *et al.* 2004 and references therein), so a deeper understanding of their physical, chemical and thermodynamic properties will allow improvements in the design and interpretation of such experiments. This study describes a detailed spectrophotometric investigation of Au(III) complex formation and Cl/Br competition in the Au-H₂O-Cl-Br system and hopes to contribute to the confusion in the literature about gold geochemistry in general.

EXPERIMENTAL DESIGN

Spectrophotometric methods are suitable for a variety of metal ions in solution, although a number of requirements exist for the collection of reliable data. Ultra-violet (UV) and visible (Vis) spectrophotometry is

ideally suited to the study of Au(III) complexation and speciation for two reasons. First, Au(III) centres absorb strongly in the UV-Vis region and display changes in spectra with variable pH and ligand activity. Second, aqueous Au(III) halides remain mononuclear so obey the Beer-Lambert Law. This provides a well characterised conditionality linking measured spectra to speciation, thus providing a mathematical framework within which to interpret data. The remaining requirement for reliable data is that interferences from other species in solution can be eliminated, background corrected or included and accounted for in the model.

In this study, ligand-to-metal and metal-to-ligand charge transfer bands overlap with ligand-to-solvent charge transfer bands and can be accounted for by two means. First, each spectrum was collected in dual beam mode with a background solution of the same composition but *without* gold present. This largely eliminates interference from ligand to solvent bands in cases where the concentration of ligand is much greater than gold and it can be assumed that free ligand concentrations are very nearly equal. Second, where background correction was ineffective due to differences in free ligand concentration between the two similar solutions, a wavelength range was chosen such that interfering bands were not included in the analysis. The effect of spectral window selection on the thermodynamic properties derived using this technique was investigated in the Au-H₂O-Cl subsystem (relatively free of charge transfer band overlap) in order to establish the validity of this method.

Changes in the shape and intensity of absorbance bands can be attributed to changes in speciation of the gold in solution and appropriate models developed to solve for equilibrium constants of absorbing species. Rigorous, quantitative methods for the deconvolution of series of systematically varying spectra have been developed by Brugger (2001) and are not covered here. Hydrolysis of metal ions may also cause significant changes in spectra, but this can be tightly controlled by solution pH or avoided altogether in highly acidic media.

SPECTROPHOTOMETRIC METHODS

All spectra were recorded on a temperature-controlled Cary 100 spectrophotometer equipped with a six cell changer run in dual beam mode to account for instrument drift and baseline corrected prior to data analysis. The concentration of gold used in the solutions in this study ranged from $3 \times 10^{-5} < [\text{Au}] < 1 \times 10^{-4} \text{ m}$ in order to produce absorbance maxima in the range of 0.2-1.2 absorbance units. No interference was observed from chloride concentrations from 0 to 6 M total Cl or bromide concentrations from 0 to 3 M total Br. All spectra presented here were recorded within these ranges. The effect of temperature on molal absorbance spectra was also investigated from 25-80 °C, although unless otherwise stated data given here relates to series collected at 25°C. Baseline corrected spectra were reproducible to 0.01 absorbance units.

CHLORIDE/BROMIDE COMPETITION STUDIES

A typical data set displaying systematic changes in the absorption spectrum of $1 \times 10^{-4} \text{ m}$ Au(III) with systematically increasing $[\text{Br}^-]/[\text{Cl}^-]$ ratio from 0 to 1 is shown in Figure 1. This is clearly a systematically varying series of spectra suitable for further analysis.

A plot of residuals versus the number of factors used in principle component analysis is shown in Figure 2, where it can be seen that five factors (absorbing species) are required to explain the data. If instrument noise is perfectly random, the system can be effectively subject to principle component analysis to find the number of absorbing species, or factors, required to explain the observed data. Each factor that is actually contributing to the spectra should result in a significant and rapid decrease in residuals.

Excess factors that may not carry any physical meaning

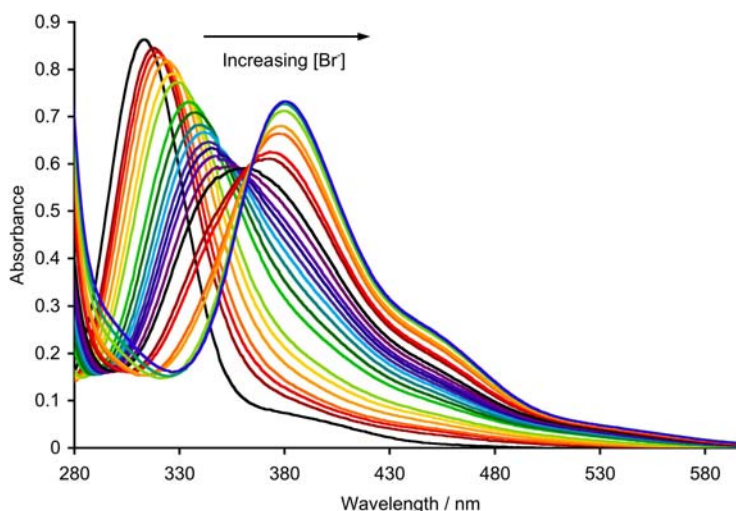


Figure 1: Effect on increasing bromide/chloride ratio (from 0 to 1) on the absorption spectrum of $1 \times 10^{-4} \text{ m}$ gold.

simply serve to account for random noise and result in a lesser, slower decrease in residuals. This is in excellent agreement with chemical reasoning, as five complexes arise from the successive replacement of Cl⁻ ligands for Br⁻ ligands from AuCl₄⁻ to AuBr₄⁻ with increasing bromide.

Quantitative analysis of the spectra requires developing a chemical speciation model (mass balance and mass action equations) and fitting an equilibrium constant to each absorbing species that contributes to the measured spectra. Five gold-containing species ([AuCl_{4-n}Br_n]⁻, where n = 0, 1, 2, 3, 4) were included in the model based on results from PCA and chemical reasoning, and the model was fitted to the data. A distribution of species plot resulting from the fitted speciation model is shown in Figure 3. It is noted that mixed Cl/Br complexes rapidly become dominant over AuCl₄⁻ with even slight increases in Br⁻ content.

Similar analysis techniques may in principle be used to examine the effect of pH in the Au-H₂O-Cl-Br system, enabling more comprehensive modelling of natural systems by allowing series of spectra to be measured over a wide range of pH. Such a series is shown in Figure 4, recorded at constant [Au] (1 × 10⁻⁴ m) and [Cl] (0.1 m) with progressively increasing pH from 0.9 to 12.

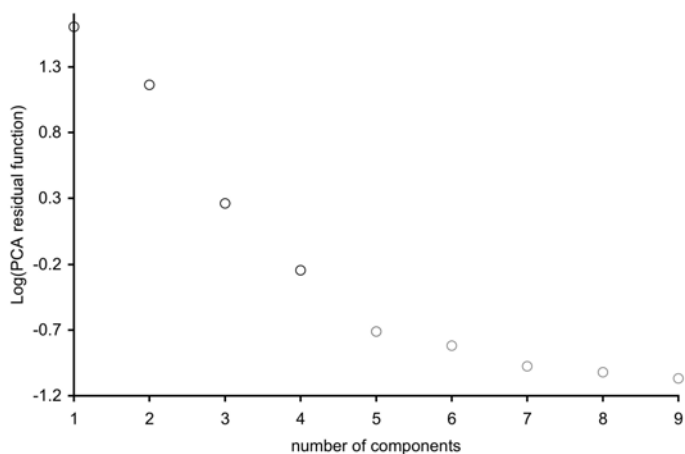


Figure 2: Plot of the PCA residual function versus number of factors used to model the data from Figure 1. Note the change of slope around 5.

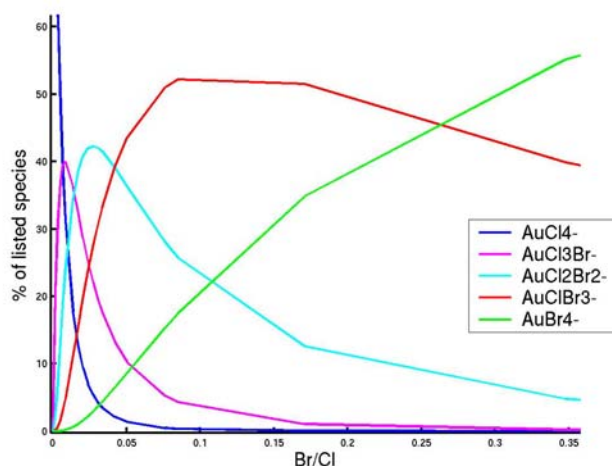


Figure 3: Preliminary distribution of species model based on quantitative interpretation of the data from Figure 1. Note the range of mixed ligand intermediates.

IMPLICATIONS OF HALIDE COMPETITION ON GOLD TRANSPORT

Gold transport in near-surface environments with low organic content and high salinity has long been assumed to be dominated by aqueous chloride complexes (Mann 1984). Based on this assumption, conventional modelling has typically included AuCl₄⁻ as the only Au(III) species considered, and the importance of intermediate mixed-ligand complexes has been overlooked.

It is immediately obvious from our results that no one species completely dominates the Au-Cl-Br-H₂O system, even in solutions with high chloride and relatively low bromide concentration. The original assumption is therefore only a half-truth (there may not be enough bromide in natural waters to allow the formation of AuBr₄⁻), but the possibility of intermediate complexes can no longer be denied.

Aqueous speciation can have a profound effect on the crucial processes involved in gold mobility in the regolith, in particular solubility, sorption and biological

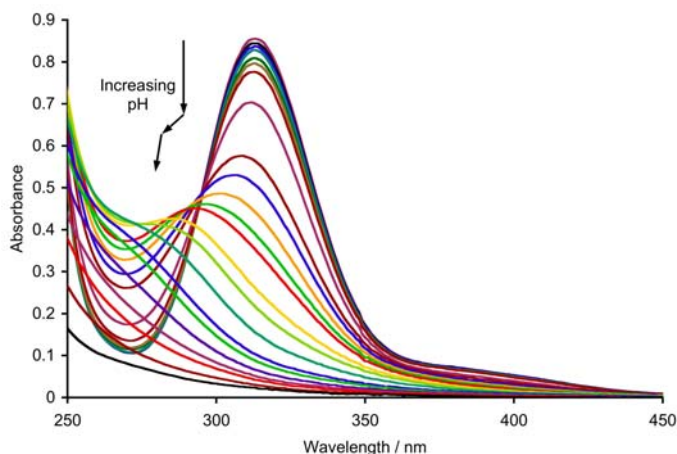


Figure 4: Effect of increasing pH on the absorption spectrum of 1 × 10⁻⁴ m gold.

interactions. Attempts to model these processes without an understanding of the nature of each complex will at best be approximate, and at worst be misleading. In order to develop a sound theoretical understanding of gold transport for exploration purposes, there is a clear need for further study in the field of aqueous speciation of gold.

REFERENCES

- BERRODIER I., FARGES F., BENEDETTI M., WINTERER M., BROWN JR G. E. & DEVEUGHÈLE M. 2004. Adsorption mechanisms of trivalent gold on iron- and aluminium-(oxy)hydroxides. Part 1: X-ray absorption and Raman scattering spectroscopic studies of Au(III) adsorbed on ferrihydrite, goethite and boehmite. *Geochim. Cosmochim. Acta* **68(14)**, 3019-3042.
- BOYLE R.W. 1979., The geochemistry of gold and its deposits. In: *Geological Survey of Canada Bulletin* **280**.
- BRUGGER J., MCPHAIL D. C., BLACK J. & SPICCIA L. 2001 Complexation of metal ions in brines: application of electronic spectroscopy in the study of the Cu(II)-LiCl-H₂O system between 25 and 90°C. *Geochim. Cosmochim. Acta* **65(16)**, 2691-2708.
- MANN A.W. 1984. Mobility of gold and silver in lateritic weathering profiles: some observations from Western Australia. *Econ. Geol.* **79**, 38-49.
- PECK J.A., TAIT C.D., SWANSON B.I. & BROWN G.E. JR 1991 Speciation of aqueous gold(III) chlorides from ultraviolet/visible absorption and Raman/resonance Raman spectroscopies. *Geochim. Cosmochim. Acta* **55**, 671-676.
- SHARPS J.A., BROWN G.E. JR & STEBBINS J.F. 1993. Kinetics and mechanism of ligand exchange of Au(III), Zn(II) and Cd(II) chlorides in aqueous solution: An NMR study from 28-98°C. *Geochim. Cosmochim. Acta* **57**, 721-731.
- SPARROW G.J. & WOODCOCK J.T. 1995. Cyanide and other lixiviant leaching systems for gold with some practical applications. *Extractive Metallurgy Review* **14**, 193-247.
- STEFANSSON A. & SEWARD T.M. 2003 Stability of chloridogold(I) complexes in aqueous solutions from 300 to 600°C and from 500 to 1800 bar. *Geochim. Cosmochim. Acta* **67(3)**, 4559-4576.