EXPERIMENTAL METHODS IN GEOCHEMISTRY AND MOBILITY OF METALS IN THE REGOLITH

D. C. "Bear" McPhail

CRC LEME, Australian National University
bear@ems.anu.edu.au

INTRODUCTION

The dispersion of metals in the regolith around ore deposits, and hence the formation of geochemical anomalies, is controlled by metal mobility. Understanding mobility requires knowledge of the geochemistry of metals in regolith, water and biota (i.e., what mineral and aqueous species of metals are important, not just their concentrations), and the leaching, transport and trapping processes. We need a much deeper understanding of the mineralogy and speciation of metals and related elements as well as the processes, in order to develop successful exploration methods that allow us to decipher observed geochemical patterns, and to distinguish between anomalies indicating ore bodies and those that do not. In Australia, this is especially important because of the need to explore in areas covered by transported regolith. Metal mobility is important more generally to geologists and geochemists because it is a critical link in the formation of lateritic and hydrothermal ore deposits. In addition, understanding the mobilisation and trapping of metals is important to mineral processing, *e.g.,* hydrometallurgy, and environmental science, *e.g.,* potential contamination of regolith and waterways and impacts on ecology. This means that exploration geochemists, economic geologists and environmental scientists need to understand how metals exist in the regolith, different lithologies, water and vapour, how they are mobilized or trapped, how far they can be transported and whether they are bioavailable and can be transported by biota and/or act as micronutrients or toxins to plant and animal life.

Although the mobility of metals in the regolith depends on the transporting process(es), *e.g.,* groundwater advection or convection, diffusion, gaseous, sediment or airborne physical transport, micro- and/or macro-biotic, it depends substantially on the geochemistry of the individual and collective metals, *i.e.,* how they exist in groundwater and regolith materials and what are the controlling geochemical reactions between water and minerals, organic matter and biota. It is clear that we need to know the aqueous speciation of metals, the solubilities of metal-bearing minerals and sorption of metals to mineral surfaces, in order to understand and predict how metals behave during weathering and diagenetic processes in the Earth's crust.

How do we gain the necessary knowledge and understanding of metal geochemistry and mobility? Detailed field studies have been done and are currently underway, especially in LEME, to research how metals exist in regolith material, groundwater and plants – largely made possible by advances in microanalytical technology, *e.g.,* Laser Ablation Inductively Coupled Plasma Mass spectrometry (LA-ICP-MS). This is important in understanding which minerals host which metals and what the best sampling media are for geochemical exploration. Although critical in developing our understanding, field studies and sophisticated analytical techniques are insufficient to understand how metals have dispersed and concentrated in the regolith, and in turn how geochemical anomalies have formed. Experimental studies provide another approach that leads to understanding the geochemistry of elements are transported. In this presentation, I highlight several examples of current experimental studies in LEME that are focused on understanding the geochemistry of metals in waters and the reactions between dissolved metals and regolith materials.

GEOCHEMISTRY AND MOBILITY OF GOLD

Gold geochemistry, i.e., the speciation of gold in solid and aqueous forms, is complicated because it is affected by pH, redox, salinity and organics, as well as temperature. Gold has three valence states in natural systems, *e.g.,* Au(0) in native gold, electrum and colloids, Au(I) in waters under reduced conditions and Au(III) in waters under very oxidized (atmospheric), acidic conditions.

Dissolved gold can exist as ions (Au^+, Au^{3+}) or as many possible complexes with, for example, chloride, iodide, sulphide, thiosulphate, cyanide, ammine and other organic ligands and chelates. The nature and properties of colloids, other particles and the dissolved gold complexes affect how much gold can be leached, transported and precipitated. These depend directly or indirectly on several geochemical variables, *i.e.,* temperature, pressure, pH, redox (*e.g.,* Eh, log f $_{O2 (g, aq)}$), concentrations of elements, ions or compounds that complex with gold (*e.g.,* Cl^-, I^-, HS^-, SO_4^{2+}, and more), and partial pressures of gases (*e.g.,* O_2, CO_2, H_2S, S_2, NH_3). In addition to the physical and chemical variables, biota can affect gold geochemistry and mobility. At the ANU, there are several current experimental and field projects focused on some of the important aspects.

EFFECT OF BACTERIA ON GOLD MOBILITY
Ph.D. student, Frank Reith, is studying how microbiota (bacteria and fungi) affect gold mobility in the regolith. He has two main field sites in areas of gold mineralisation, one at Tomakin, NSW and the other at Palmer River, Qld, chosen to compare areas with different climates. His results show a strong correlation between gold concentrations and populations of *Bacillus cereus* in both areas. Individual microcosm experiments with natural samples have either no added material, added gold (dissolved or solid) and/or added organics (energy source for bacteria). The results show that gold is mobilised into solution after several to tens of days, in contrast to sterilised samples that showed no gold mobilisation (Figure 1). In more recent experiments, Frank has monitored not only gold mobilisation, but also changes in microbial ecology, probably the first ever experiments of this kind. Preliminary interpretation of the results suggests the microbial ecology does change during the course of the experiments; however, more interpretation is necessary to confirm the nature of the changes. His current, equally exciting research is focussed on molecular microbiology studies to identify particular DNA/RNA sequences of the microorganisms from field and experimental samples. He has found that there are different microbial populations associated with gold grains from the different field areas, and he has evidence of microorganisms that have not been identified anywhere else. Frank Reith's research has already enhanced our understanding of how microbiota affect gold mobility in the regolith and there is potential to develop exploration methods using bioindicators.

GEOCHEMISTRY OF GOLD IN SALINE TO HYPERSALINE BRINES
The geochemistry of dissolved gold is being studied by several experimental methods, mainly by Ph.D. student Alistair Usher. UltraViolet-Visible (UV-Vis) spectrophotometry is being used to identify oxidised Au(III) chloride and iodide complexes in chloride and iodide solutions. Iodide forms strong complexes with Au, and could be important in transporting gold in saline brines. Oxidised Au(III) complexes may be important in transporting gold in acidic, very oxidised (atmospheric conditions), but the results will also provide a window into the more complicated Au(I) complexes, more likely to be the transporting gold complexes in many groundwater environments. Other experimental methods are currently being developed, *i.e.,* mineral solubility (native gold) under well controlled atmosphere (redox) and pH conditions with variable chloride, thiosulphate and iodide salts used to understand the importance of all three types of complexes. Another part of Alistair's Ph.D. research is focussed on improved methods of measuring low levels of dissolved gold in water, something that will benefit mineral exploration using hydrogeochemistry.

SORPTION AND MOBILITY OF BASE METALS ONTO IRON OXYHYDROXIDES
The concentrations of metals in surface and groundwater can be controlled by sorption onto mineral and/or organic matter surfaces, and therefore could be the controlling process in metal dispersion in the regolith around ore bodies. We are using experiments to study the effect of pH and salinity on the sorption of Cu and Zn on goethite, and have found some surprising results.

Ph.D. student Chris Gunton has completed a study of how NaCl affects the sorption of oxidised copper (CuII) on goethite. The experimental conditions cover a range of pH (~2-7) and NaCl concentration (~0 to 5 m, or 0 to >30 wt%). The results show that adsorbed copper increases with increasing pH, where the sorption edge is approximately pH = 4.5. This is well known behaviour,

but we have found that copper sorption increases up to 20-fold with increasing NaCl concentration (Figure 2), a result of Cu chloride complexes on the goethite surface. The increased sorption with NaCl has important ramifications for metal transport in the regolith, particularly in prospective saline and arid Australian environments. For instance, it suggests that copper haloes are likely to be intense and small during weathering of sulphide ore bodies in saline to hypersaline environments where goethite and likely other iron oxyhydroxide minerals are present.

We have extended these experiments to study zinc sorption on goethite under similar ranges of conditions. The results show that zinc is adsorbed to goethite at higher pH (i.e., pH approximately 7 for the sorption edge) than copper (Figure 3), and that the effect of NaCl is smaller. This means that zinc will likely disperse farther than copper during the weathering of an ore body and that zinc will be less affected by salinity. We have also completed preliminary experiments to study the effect of sulphate on the sorption of zinc, which suggest that sulphate has little or no effect. These results suggest that metal ratios in goethite could be a useful indicator in exploring for new ore deposits, but further research is needed to understand how different metals react with goethite.

New experimental techniques are now being established to study how metals can move through the regolith. Column experiments will be used to pump metal-bearing solutions through regolith material (e.g., goethite- and hematite-coated sand) under different pH and salinity conditions to study how the metals are trapped and/or released under dynamic flow conditions. This is a step towards taking our knowledge of sorption from batch experiments to help understand how metals move in groundwater and the regolith.

GROUNDWATER FLOW AND ELEMENT DISPERSION
The geochemistry of metals and other elements is critical in understanding the dispersion and anomaly formation in groundwater systems, but the other necessary part is knowing the groundwater flow, *i.e.,* pathways, volumes and velocities.

Although not part of LEME, recent experimental studies at Monash University by Michelle Carey (Ph.D. supervised by Dr. McPhail) demonstrate how hypersaline plumes form under playa lakes and can affect the dispersion of gold and other elements in groundwater systems. This was part of her Ph.D. research on the use of hydrogeochemistry as an exploration tool. She studied the St. Ives gold fields near Kambalda, WA, installing a well field of approximately 100 km^2, sampling and analysing the saline to hypersaline groundwater, numerically modelling the geochemistry of gold under hypersaline conditions and experimentally determining and numerically modelling the density-driven convective flow around the playa lake and the gold mineralisation. Figure 4 shows an example cross-section indicating the variation in groundwater salinity, schematic groundwater flow directions and groundwater region where elevated levels of dissolved gold were found (Condenser survey on Figure 4)

The experiments were conducted in a tank 105 cm long, 60 cm high and 5 cm thick, filled with 100 μm diameter glass beads and constant head was imposed on each end of the tank, one end to simulate regional flow of saline brine and the other end to simulate the playa lake. The experimental conditions are scaled to represent the conditions in St. Ives goldfields bordering Lake Lefroy. The results demonstrated the shape and extent of the hypersaline plume (Figure 5), as well as the timeframe of the plume development, and the process of density-driven convection. Numerical models were used to predict the density-driven convection and then the results were compared with the experimental data. The comparisons allowed us to refine and verify the numerical models, so that we could apply them to the field area with more confidence. The applications showed that the present playa lake could form in a timeframe of tens of thousands of years, a short time compared to the millions of years of relatively stable geological environment in the area. The results of experiments and field studies indicate that any gold signature in the groundwater is affected by the extent of the convection cell.

SUMMARY AND FUTURE STUDIES

A combination of experimental techniques is being used to understand the geochemistry of gold, copper, zinc and other elements, as well as their mobility and dispersion patterns in the regolith. Although there are already some direct links to field studies, *i.e.,* Frank Reith's research on microbes and gold, we need to take the results from experimental studies to help understand the dispersion patterns observed in regolith and groundwater. For gold mineralisation, the likely field areas are in the Yilgarn (*e.g.,* Lancefield, Mt. Gibson, St. Ives, Whirling Dervish), Gawler Craton (*e.g.,* Tunkillia), Lachlan Fold Belt (e.g., Cobar basin, Lake Cowal) and the Tanami, in collaboration with Drs. David Gray and Mark Pirlo of CSIRO Exploration and Mining in Perth, and Dr. Dirk Kirste (ANU) and Dr. Patrice de Caritat (Geoscience Australia). In other studies we are measuring the solubilities of low-temperature zinc minerals (*i.e.,* hemimorphite, a hydrated zinc silicate) and researching the dispersion of zinc around zinc oxide deposits in the northern Flinders Ranges, SA. We strive to choose field areas to combine forces with other LEME projects and scientists working on different aspects of regolith science, especially so we can build our understanding of geochemical and physical processes of dispersion in the context of landscape, regolith and climate evolution. In addition to studies focussed on aspects related to mineral exploration, we are also studying with experiments the impacts of biota (microbial, fungal, tree and their roots) and organic acids on weathering processes in the regolith (Drs. Sue Welch, John Field and others), mobility of salt in regolith (Drs. Andrew Fitzpatrick, Dirk Kirste and others) and the formation and degradation of acid sulphate systems in inland areas (Drs. Sue Welch, Sara Beavis, Sebastien Lamontagne, Steve Rogers, Rob Fitzpatrick, and others). What we learn from mineral exploration studies will help in environmental and salinity studies, and *vice versa*.
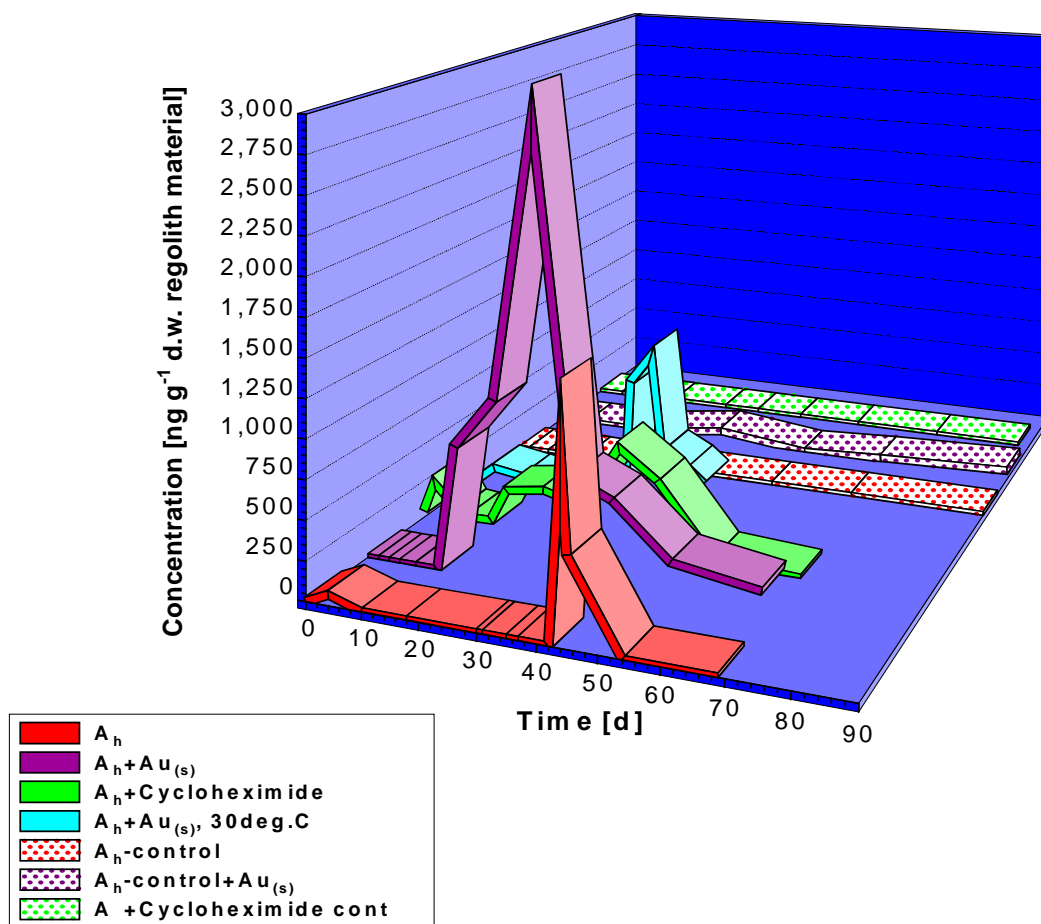
Figure 1. Results from microcosm experiments at mainly 25°C showing gold solubilisation in samples from the Mogo Gold Mine, Tomakin, NSW. A_h refers to samples from that soil horizon. Cycloheximide limits organisms other than bacteria. Samples from the 3 control experiments were sterilized before running.
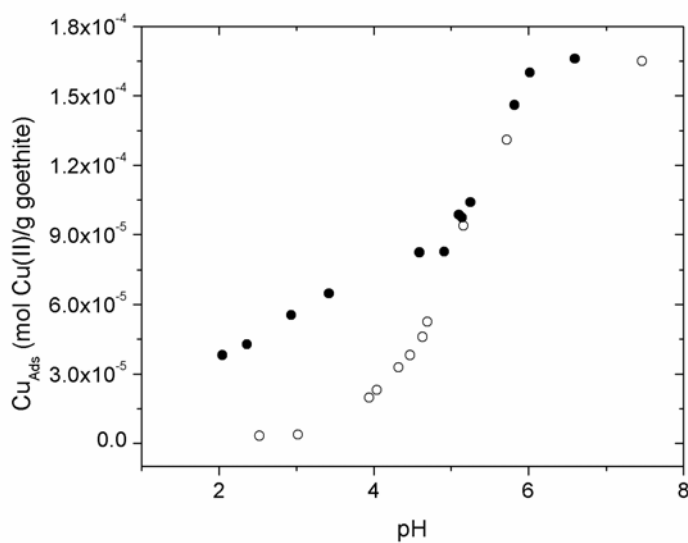

Figure 2. Effect of NaCl on the adsorption of copper onto goethite at 25°C. The open circles are for experiments with no NaCl and the filled circles are for experiments with 5 molal NaCl (seawater is 0.6 molal and halite saturation is approximately 6 molal). Note that most of the increase in adsorption occurs between 0 and 1.5 molal NaCl. Initial dissolved copper concentration in experiments was 10 ppm.
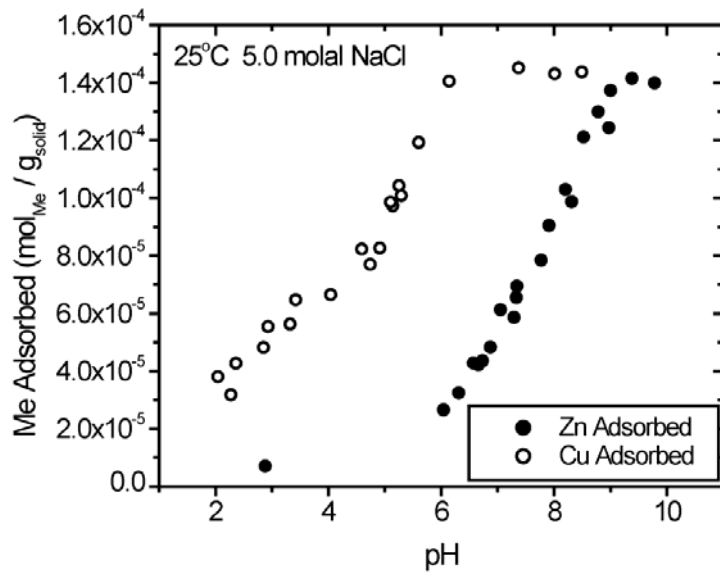
Figure 3. The effect of pH on the adsorption of copper and zinc on goethite. Initial dissolved metal concentrations in experiments was 10 ppm. Note that the effect of NaCl on copper adsorption is less than it is for zinc.
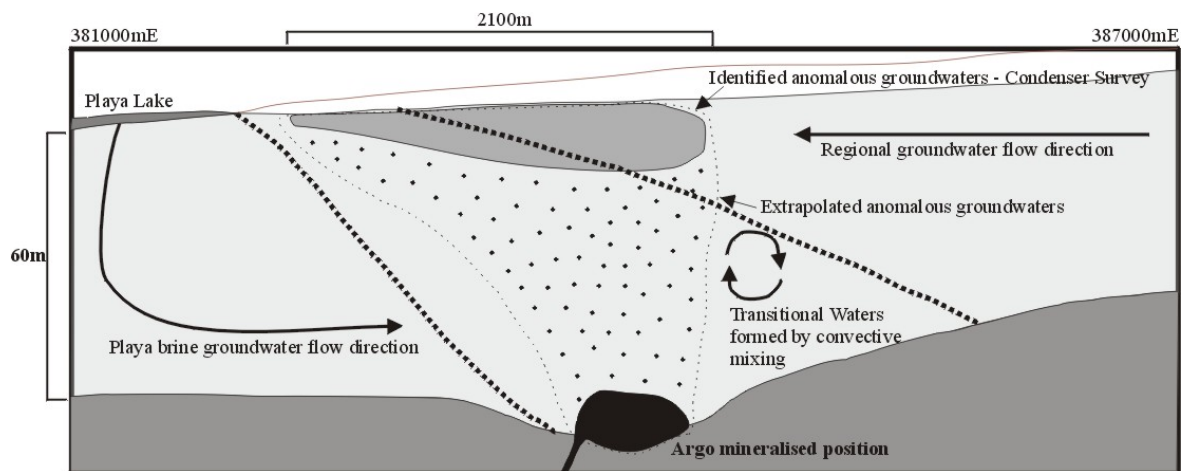

Figure 4. Schematic diagram of density-driven convection under Lake Lefroy and the St Ives area, Western Australia. (Taken from Carey et al., 2003; Geochemistry: Exploration, Environment and Analysis, 3, 57-71).
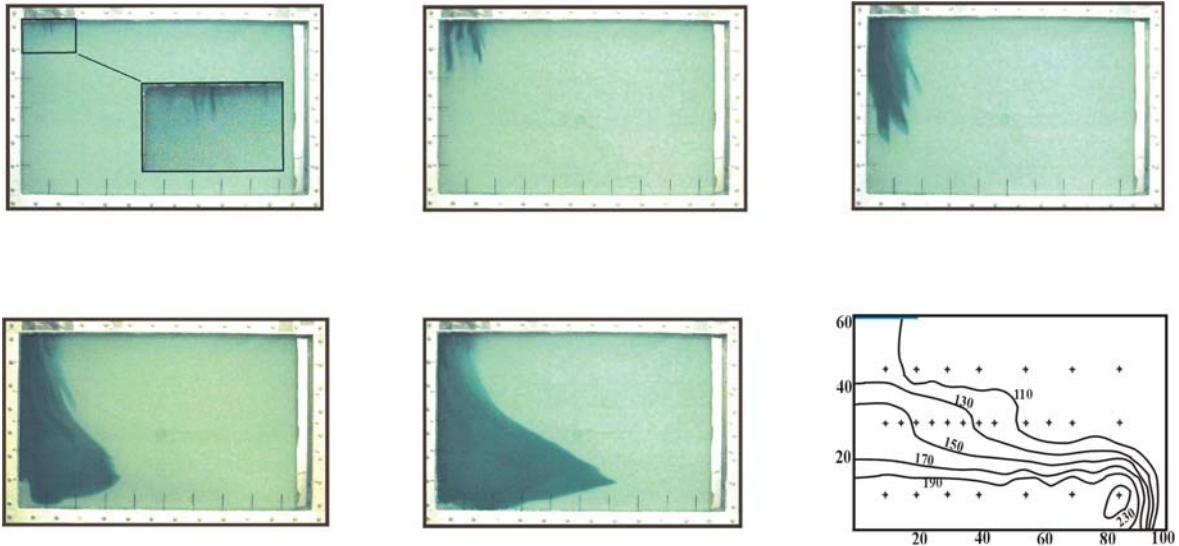
Figure 5. Snapshots of plume development in a 105 cm wide and 60 cm high tank. Total length of time for experiment was approximately 24 hours. The bottom right diagram shows contours of salinity measured at points shown in diagram at the end of the experiment.