EXPERIMENTAL METHODS IN GEOCHEMISTRY AND MOBILITY OF METALS IN THE REGOLITH

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INTRODUCTION

The mobility of metals in the regolith controls their dispersion, or concentration, and the formation of geochemical anomalies, especially in areas covered by transported regolith. Understanding mobility requires knowledge of the geochemistry of the metals and the leaching, transport and trapping processes. We need a much deeper understanding of all parts in order to develop successful exploration methods that allow us to decipher anomaly patterns, and to distinguish anomalies indicating ore bodies and those that do not. Metal mobility is important more generally to geologists and geochemists, both exploration and otherwise, because it is a critical link in the formation of laterite and hydrothermal ore deposits. In addition, understanding the mobilisation and trapping of metals is important to many aspects of 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 and water, how they are mobilized or trapped, how far they can be transported and whether they are bioavailable and 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 do 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 the 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 part of the puzzle, 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 how 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 is complicated because it 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 and 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 BIOTA

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 are exciting and show that gold is mobilised after several to tens of days, in contrast to samples that were sterilised and show no gold mobilisation. In his most 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 sequences of the microorganisms from field and experimental samples. 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 complexes in NaCl and LiCl solutions. These complexes may be important in transporting gold in acidic, very oxidised (atmospheric conditions), but the experiments also provide a window into the more complicated Au(I) complexes, more likely to be the transporting gold complexes under many regolith conditions. 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. Spectro-electrochemical methods are also being investigated. Another part of Alistair Usher’s Ph.D. research is focussed on alternative and improved methods of analysing low concentrations (ppt) of dissolved gold in groundwater.

GOLD MOBILITY

We are developing experimental methods to study how gold moves through regolith material. Frank Reith’s research includes column experiments under abiotic and biotic conditions, and the results already show that gold can be mobilised in the presence of microbiota. These experiments are run under similar conditions to his microcosm experiments but with solutions flowing through columns, a more dynamic system that approaches field conditions. Although in preliminary stages, we intend to use column, and perhaps tank experiments for 2-dimensional flow, to study how gold and other elements are leached, transported and trapped in synthetic and natural regolith. The results will be used to test reactive transport models, also being developed at the ANU. As we get to the stage where model and experimental results agree, the models can then be applied more confidently to predicting gold mobility and anomaly formation in the regolith.

SORPTION OF METALS ONTO IRON OXYHYDROXIDES

The concentrations of metals in solution can be controlled by sorption onto mineral and/or organic matter surfaces, but there is much more research necessary to understand the importance over the wide ranges of conditions found in the regolith. We have completed an experimental study of the impact that salinity has on the sorption of copper on goethite, with some surprising results.

Ph.D. student Chris Gunton is studying the effect of salinity on 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 the well known behaviour with pH, but the effect of increasing NaCl concentration, a controversial topic in the literature, has important ramifications for metal transport in the regolith, particularly the in prospective saline and arid Australian environments. With increasing NaCl concentration, the amount of copper sorbed onto goethite increase by a factor of two or more over the pH range typically encountered in the regolith. Preliminary quantitative interpretation of the data indicate that one or more copper chloride complexes form on the goethite surface and they are more stable than those in aqueous solutions. The increased sorption suggests that copper haloes are likely to be intense and small during weathering of sulphide ore bodies in saline to hypersaline environments.

We are extending these experiments to study zinc sorption on goethite under similar ranges of conditions, although the pH range important for the sorption of zinc is higher than for copper. We may also use different morphologies and compositions of goethite, *e.g.,* Al-bearing goethite found commonly in the regolith. Depending on time and resources, we will also extend our studies to gold; however, the concentrations of gold that can be obtained are low and may prevent us from obtaining reliable results.

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 dertermining and numerically modelling the density-driven convective flow around the playa lake and the gold mineralisation.

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 result in the hypersaline, and higher density, brine convecting. 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, as well as the timeframe of the plume development. Numerical models were used to predict the density-driven convection and then the results were compared with the experimental data. Once good agreement was obtained, the numerical models were applied to the field area. In combination with the detailed geochemistry, measured and modelled, we now understand much better the dispersion of gold in groundwater in the St. Ives area.

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 the field. For gold mineralisation, the likely field areas we will focus on are in the Yilgarn (*e.g.,* Lancefield, Mt. Gibson, St. Ives, Whirling Dervish), Gawler Craton (*e.g.,* Tunkillia), Lachlan Fold Belt and the Tanami. 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. In all cases 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 in the context of landscape and regolith 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, Steve Rogers, Rob Fitzpatrick, and others). What we learn from mineral exploration studies will help in environmental and salinity studies, and *vice versa*.