THE ROLE OF SALINITY ON THE FORMATION OF GEOCHEMICAL ANOMALIES IN THE REGOLITH

Chris Gunton

CRC LEME, Department of Geology, Australian National University, Canberra, ACT, 0200

INTRODUCTION

In the current economic climate with weak base metal process and moderate gold prices, mining companies are relying on the discovery of large 'World Class' ore deposits. The search for these deposits is becoming increasingly difficult due to the fact that most of these large deposits that are close to or exposed at the surface have been discovered. Therefore companies are being forced to explore in regions where there is a thick transported sediment cover.

Geochemical sampling programs developed in the past were based on the theory that exposed mineral deposits undergo weathering, thereby shedding material from the mineralised zone and depositing it down hill from its origin (Figure 1). Often these geochemical anomalies may be detected in stream environments, flood planes or alluvial fan deposits and traced back to their original source.

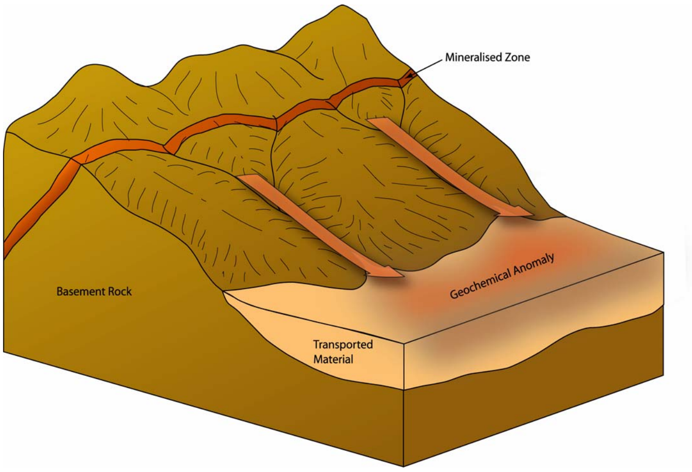

Figure 1: Illustration showing the formation of a geochemical anomaly in sediments associated with the weathering of material above. Gravity is the main driving force behind the migration of the anomaly.

This type of sampling model is still valid in some regions of the world that are relatively unexplored such as some South American countries. However, in Australia, much of the remaining prospective Proterozoic basement rock is covered by younger sediments of various thicknesses deposited in shallow marine environments. Unfortunately, many sampling practices have not been altered to reflect the changing geological environment.

Research into alternative methods of geochemical anomaly formation has been undertaken in recent times. One possibility is the formation of geochemical anomalies in young transported regolith profiles from underlying rocks (Radford & Burton 1999). Formation by this method would require the transportation of metals in an upwards direction, where the metal can then be deposited in the overlying material. For a geochemical anomaly of this nature to form, several key components are required:

1. *Metal Source*: An underlying source of metal with economic value (such as Cu, Zn, Au) is the most important component when forming a geochemical anomaly.
2. *Transporting Media*: Assuming that there is an underlying mineral deposit, a means of dissolving and transporting metal ions is required. One of the most common mediums for element transportation in the regolith is groundwater, however other fluids such as hydrothermal fluids may also be likely transporting mediums.
3. *Transportation Paths*: Assuming that a fluid is capable of dissolving metal ions, the flow path of the fluid needs to be able to concentrate these ions in an area whereby a detectable anomaly can form which is ideally close to the surface.
4. *Metal Traps*: The final process in forming an anomaly is the removal of the metal from the solution. This may happen if the solution conditions change, possibly precipitating the metal as a new mineral in the regolith, or the regolith material may change such that the metals adsorb to minerals or organic matter.

The emphasis of research in this project has been to better understand the trapping of metals in the regolith, highlighting the role of adsorption in the retention of metals onto mineral phases. The adsorption of copper (II) onto goethite in highly saline conditions has been studied in detail during this study. The properties of

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copper are well known, as the formation of copper chloride complexes has been studied in detail quite recently, while the surface characteristics of goethite have been well documented. The interactions between copper and goethite have been studied in the past making the development of an experimental methodology easier and allowing a baseline comparison for highly saline conditions.

While it is recognised that organic matter is as equally important when examining adsorption, detailed studies of the interaction between metals and organic materials is beyond the scope of this study. However, it is believed that the mineralogical phases in the regolith have a critical role to play when it comes to preventing the transportation of metals through the regolith. Understanding the adsorption of metal-mineral associations in the regolith may aid in the development of more effective sampling practices.

PREVIOUS ADSORPTION STUDIES

Experimental studies to data have focussed on the adsorption of copper (II) onto synthetic goethite. A large information base regarding this system is known with studies conducted in the past by Barrow *et al.* (1982), Balistrieri & Murray (1982), Swallow *et al.* (1980), Rodda *et al.* (1996), Dzombak & Morel (1990), Padmanabham (1983a) and Padmanabham (1983b). These studies focussed primarily on the interactions between copper (II) ions and the goethite surface as a function of pH. Therefore the conditions of these experiments were set to minimise the influence of the surrounding solution with the reactions occurring at the solid solution interface and low concentrations of an inert background electrolyte such as $NaNO_3$ or $NaClO_4$ were used (Table 1).

Table 1: Summary of Experimental Conditions for studies examining the adsorption of Cu (II) onto goethite.

Author	Goethite conc. (g/kg)	Cu^{2+} conc. (mg/kg)	Background electrolyte
Balistrieri & Murray (1982)	0.56	$3.1x10^{-5}$ $3.2x10^{-7}$	$NaNO_3$ Seawater
Barrow *et al.* (1982)	2.00	?	NaCl KNO_3
Padmanabham (1983)	?	?	NaCl $NaNO_3$
Swallow *et al.* (1980)	0.0089	$1.0x10^{-5}$	$NaClO_4$ NaCl

Balistrieri & Murray (1982) and Swallow *et al.* (1980) studied the effect of NaCl as a background electrolyte, concluding that the presence of Cl^- does not influence the adsorption of Cu (II) onto goethite. This is contradictory to the results of Padmanabham (1983a) and Barrow *et al.* (1982) who concluded that the presence of Cl^- enhances adsorption. In an extensive review of empirical data, Criscenti & Sverjensky (1999), concluded that the presence of Cl^- decreases the adsorption of Cu(II).

GOETHITE SYNTHESIS

The synthesis of goethite was according to the method outlined by Schwertmann & Cornell (1991) by aging amorphous ferrihydrite. The ferrihydrite was prepared by adding 180mL of 5M KOH to 100 mL of 1M $Fe(NO_3)_3.9H_2O$ solution in a 2 litre polyethylene flask while mixing. The solution was then diluted with 1.72 litres of Milli-Q grade water, sealed and aged for 60 hours at 70°C. After cooling to room temperature the solid material was washed at least three times in deionised water and the solid was filtered using a vacuum filter with Whatman Standard Grade 4 filter papers with pore spaces of 20-25 μm before being dried and stored in a polypropylene container at room temperature. The resultant goethite consisted of fine grained euhedral asicular crystals (Figure 2) which varied from 200-300 nm in width, and 1-3 μm in length.

ADSORPTION EXPERIMENTS

0.735 g of goethite was added to 75g of 0.1-3mol/kg $NaNO_3$ or 1-3 mol/kg NaCl solution in a 125 mL glass reaction vessel. The pH of each sample was adjusted to the using 0.1M HNO_3. This ensured that any dissolution of the goethite surface occurred before the addition Cu^{2+}. A dreschler head was attached to each reaction vessel, and N_2 gas was bubbled through the solution to create a nitrogen atmosphere while simultaneously acting as an agitator to keep the goethite suspended in the solution. Each reaction vessel was submerged in a water bath set at a constant temperature of 25°C and equilibrated for 5 hours.

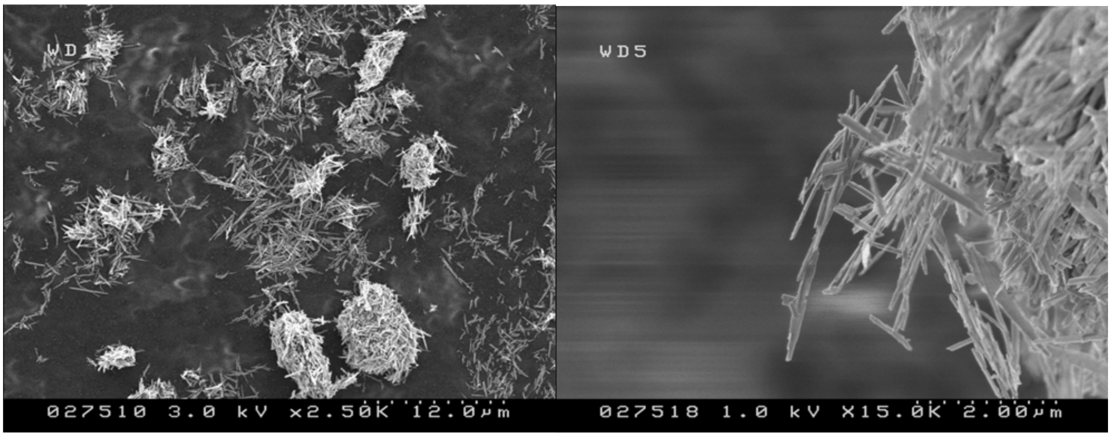

Figure 2: SEM images of synthetic goethite illustrating the fine grain size and asicular habit of crystals. The fine grained nature of the crystals increases the surface area of the mineral, promoting adsorption.

After the equilibration period, 5 g of 160 mg/kg $Cu(NO_3)_2$ solution with the same background electrolyte concentration as the sample was added to the reaction vessel. The pH was adjusted using 0.1M HNO_3 and 0.1M NaOH accordingly. The samples where then reacted for 2 hours at 25°C in the nitrogen atmosphere. At the completion of the experiment, the samples were filtered using a 0.22 µm Millipore nitrocelluose filter and analysed using ICP-AES.

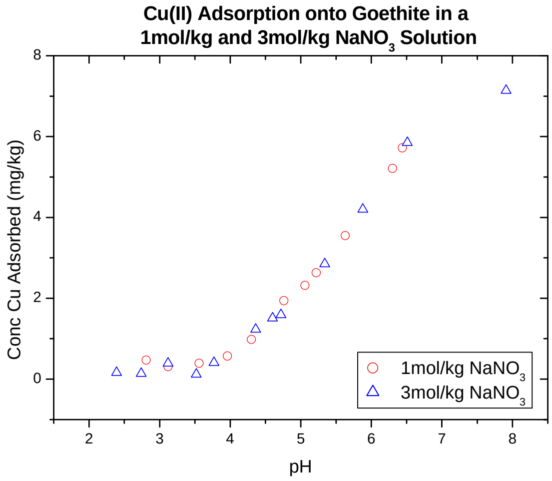

Figure 3: Adsorption of Cu(II) ions onto goethite in a 1mol/kg $NaNO_3$ and 3mol/kg $NaNO_3$ back ground electrolyte as a function of pH.

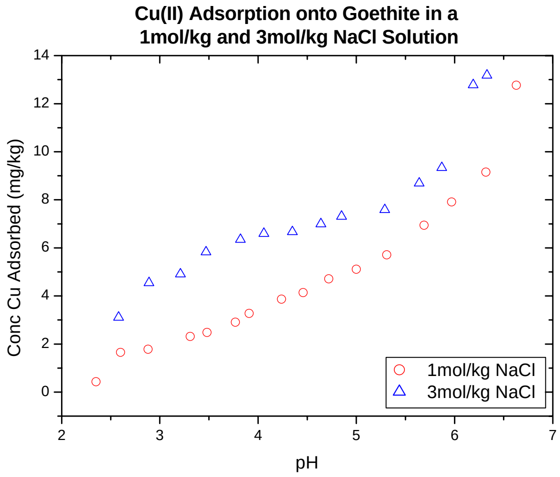

Figure 4: Adsorption of Cu(II) onto goethite in a 1mol/kg NaCl and 3mol/kg NaCl background electrolyte as a function of pH.

ADSORPTION OF Cu(II) IN $NaNO_3$

Adsorption is primarily controlled by the pH of the bulk solution. At a low pH, the activity of H^+ ions is higher, and the adsorption of Cu(II) is inhibited due to the flooding of the goethite surface by H^+, which occupy's most of the available adsorption sites. This is represented by the reaction:

$$SOH + H^+ \rightleftharpoons SOH_2^+ \qquad (1)$$

(where SOH represents the presence of a hydroxyl on the goethite surface). The formation of SOH^{2+} surface complexes results in a strong positive net charge on the surface, which repels nearby Cu^{2+} ions away from the goethite surface. As the pH of the solution increases, H^+ ions desorb from the goethite surface according to the reactions:

$$SOH_2^+ \rightleftharpoons SOH + H^+ \qquad (2)$$

$$SOH \rightleftharpoons SO^- + H^+ \qquad (3)$$

Therefore the higher the pH of the solution, the more abundant the SO^- species become, which generates a net negative charge allowing the adsorption of Cu^{2+}. The rapid increase in adsorption between pH's 4 and 7 signify the rapid formation of SO^- surface species, which facilitates the adsorption of Cu^{2+}. The adsorption of Cu(II) onto the surface of goethite can be represented by the reaction:

$$SO^- + Cu^{2+} \rightleftharpoons SOCu^+ \qquad (4)$$

Experimental results show that changes in the concentration of $NaNO_3$ in the bulk solution does not influence the adsorption of Cu(II) onto goethite (Figure 3). Therefore, increases in the ionic strength of a solution that is greater than 1M does not change the adsorption behaviour of Cu(II) on goethite, which is consistent with the findings of Criscenti and Sverjensky (1999).

ADSORPTION OF Cu(II) IN NaCl

The presence of NaCl in the bulk solution significantly alters the adsorption of Cu(II) onto goethite (Figure 4). The typical sigmoidal adsorption edge curve in the $NaNO_3$ electrolyte does not result in a NaCl solution. In a 1 mol/kg NaCl solution, adsorption of Cu(II) is suppressed. Although there is an initial rapid uptake of Cu(II) on goethite below a pH of 2.5, the adsorption of Cu(II) is slowed until the solution pH reaches 5.4, where it increases rapidly until all of the Cu(II) is adsorbed. This contradicts the conclusions of Swallow *et al.* (1980) and Balistrieri and Murray (1982) who concluded that Cl^- ions do not influence Cu(II) adsorption. These results are consistent with the conclusions of Criscenti and Sverjensky (1999), who described a decrease in adsorption as NaCl concentrations increase.

In the 3 mol/kg NaCl solution, the adsorption characteristics of Cu(II) changed significantly. A rapid uptake of Cu(II) occurs between pH's 2 to 3.8, before it is suppressed between pH's of 3.8 and 5.4, followed a rapid increase again until all of the Cu(II) is removed from solution. The increase in NaCl concentration has increased the adsorption of Cu(II) to goethite, contradicting the original idea that increasing NaCl concentration would further suppress adsorption.

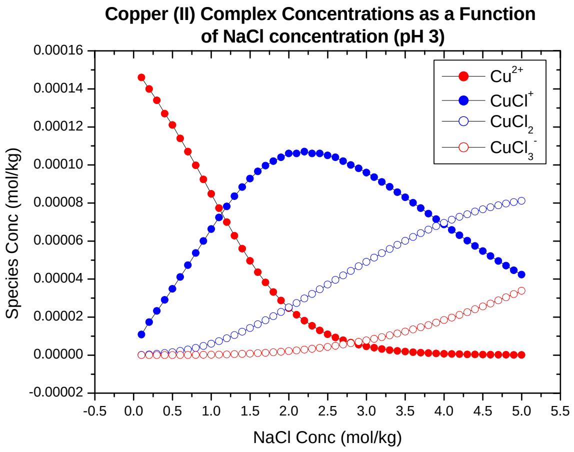

Figure 5: Concentration of copper (II) chloride species at pH 3 as a function of NaCl concentrations.

The changes in the adsorption of Cu(II) onto goethite as a function of NaCl concentrations can be described by the aqueous species of copper present in the bulk solution. Geochemical modelling of the copper chloride complexes at a pH of 3 has been conducted using PHREEQC (Figure 5). At 1 mol/kg NaCl, the dominant copper species include Cu^{2+} and $CuCl^+$, with minor $CuCl_2$. At 3 mol/kg, the copper chloride species change, with $CuCl^+$ becoming the dominant complex followed by $CuCl_2$ and $CuCl_3^-$. As the concentrations of $CuCl_2$ and $CuCl_3^-$ complexes increases, an increase in the adsorption of Cu(II) is also observed. Therefore the change in adsorption behaviour at low pH's can be explained by the preferential adsorption of copper chloride complexes.

The suppression of Cu(II) adsorption which occurs between pH 3.8 and 3.4 can be explained by the complete adsorption of $CuCl_2$ and $CuCl_3^-$ complexes from the solution. When the pH reaches 5.4, sufficient H^+ has desorbed from the goethite surface to allow the adsorption of Cu^{2+} and $CuCl^+$ to occur.

CONCLUSION

The presence of NaCl in solution alters the adsorption behaviour of Cu(II) onto goethite. At a NaCl concentration of 3 mol/kg, adsorption is promoted due to the preferential adsorption of copper chloride complexes. At 1 mol/kg, adsorption is suppressed with the uptake of Cu(II) slowing significantly until a pH of 5.4, where the remaining Cu in solution is rapidly adsorbed.

The change in adsorption of Cu(II) in NaCl is attributed to the preferential adsorption of copper chloride complexes onto goethite where:

- $CuCl_2$ and $CuCl_3^-$ are strongly adsorbed onto goethite at low pH's.
- Low concentrations of $CuCl^+$ are adsorbed onto goethite at low pH's
- Cu^{2+} adsorption does not occur until the pH reaches 3.8.

The results of this study conclusively show that goethite is an effective metal trap in the regolith which is capable of concentrating the metal on the mineral surface under highly saline conditions. This makes goethite an ideal sampling media in areas where highly saline groundwaters are present.

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