

ADSORPTION: SHOULD WE CARE?

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INTRODUCTION

When we consider the movement of metals in the regolith, it is often thought of as a three stage process. Firstly, the dissolution of metals into solution, followed by the transportation of metal away from the parent material, where the metal is finally removed from solution.

The removal of a metal from solution is commonly assumed to be due to the precipitation of a new mineral phase, and this is certainly the case with the formation of secondary carbonate and sulfate minerals such as malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), smithsonite (ZnCO_3) or anglesite (PbSO_4). However, a chemical process that is often overlooked when describing the removal of metals from solution is adsorption.

Adsorption is the removal of a metal from solution by the electrostatic forces of a mineral surface, forming a mono-molecular layer on the mineral surface. It is well known that metal solutes exhibit a charge when dissolved in a solution and like these dissolved species, mineral surfaces may also exhibit charge properties. Therefore, if a dissolved ion or complex approaches within a given distance of a mineral surface, it may be attracted to and stuck on the mineral surface (Figure 1).

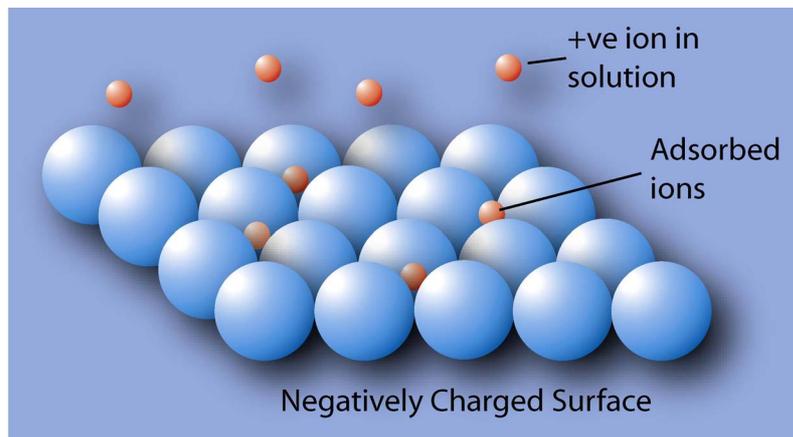


Figure 1: Illustration showing the adsorption of positively charged ions in solution to a negatively charged surface.

Our understanding of how adsorption works in nature is still limited despite the large number of applications in environmental geochemistry and mineral exploration. However, with the aid of experimental studies in a wide range of chemical systems we are beginning to understand the factors that influence the adsorption of metals onto mineral surfaces.

This presentation aims to highlight the major factors that influence metal adsorption and illustrate why this is such a crucial process when trying to understand the movement of chemical elements in natural systems.

CONTROLLING FACTORS ON ADSORPTION

There are three major components that must be considered when examining the adsorption of metals onto mineral surfaces:

- 1) The type of mineral and its surface properties;
- 2) The metal species in solution;
- 3) The chemistry of the surrounding solution.

Each of these components plays an important part in determining the adsorptive capacity of a system.

Mineral Properties

There are a number of important properties that make minerals ideal for adsorbing metals, but two of the more important factors are:

- 1) Surface area and site density – which controls the amount of metal a mineral may adsorb;
- 2) Charge properties – which determine how effectively a mineral may adsorb various elements.

While there are a number of other factors that control adsorption such as crystal morphology, chemical composition and particle size distribution, these are not described here.

The ability of a mineral to adsorb chemical elements is strongly dependent upon the surface area per unit mass of the mineral. The surface area ultimately determines the concentration of a chemical element that can be adsorbed to the mineral surface. Therefore, minerals with a high surface area are able to adsorb higher concentrations of metals. For example, goethite with a surface area of approximately 36 m²/g, can adsorb up to approximately 55 mg of copper per gram of mineral.

The charge properties of a mineral determine how effectively a mineral is able to adsorb chemical species from solution. Most mineral surfaces have one of two main surface charge types, either a permanent structural charge or a non-permanent surface charge (Davis & Kent 1990).

Minerals with a permanent structural charge normally acquire a charge due to the isomorphous substitution of elements in their structure. For example, Al³⁺ in smectite may be substituted by Si⁴⁺, creating a net positive charge due to the surplus of protons. The opposite may also occur if Al³⁺ is substituted by Mg²⁺, producing a surplus of electrons and a net negative charge. In general, minerals that have a permanent structural charge are not affected by changes in pH.

However, minerals with a non-permanent surface charge acquire their charge based on surface hydroxyl reactions and are therefore highly dependent on pH. In solutions with a low pH, H⁺ ions from solution will adsorb onto the mineral surface, thereby creating a strong positive net charge. When the pH of the solution is increased, H⁺ ions desorb from the mineral surface and the surface charge decreases (Figure 2).

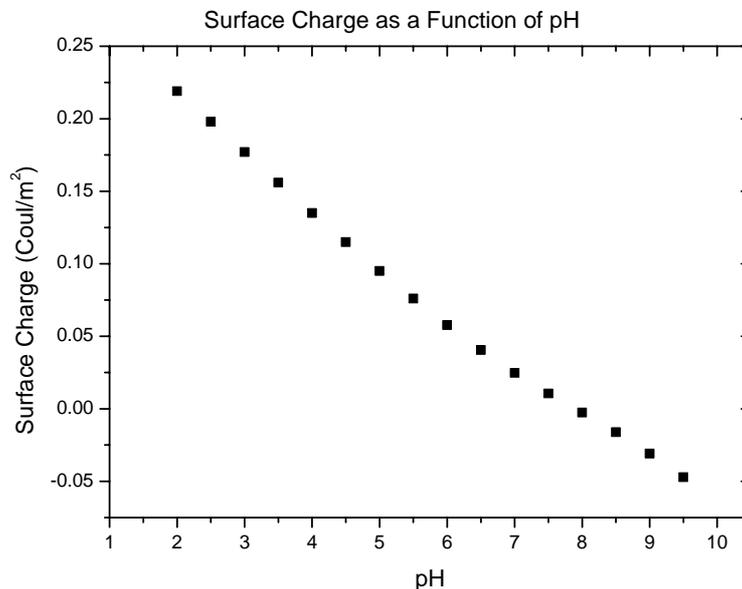


Figure 2: Schematic illustration of the change in surface charge of a mineral as a function of pH.

Examples of non-permanently charged minerals include iron oxides and oxy-hydroxides such as ferrihydrite, goethite and hematite. Manganese oxy-hydroxides are also an important non-permanently charged mineral commonly found in natural environments. Goethite is the most commonly used mineral used for adsorption studies due to its high abundance in natural systems and ideal adsorption properties. Therefore, references to adsorption studies made in this paper relate to the adsorption of elements onto goethite unless otherwise stated.

Adsorbent Characteristics

The adsorption behaviour of different metals varies based upon their dominant speciation in solution.

Single ion cations and positively charge complexes tend to adsorb in more alkaline solutions. This is due to the mineral surface having a strong positive charge in solutions of low pH with a high concentration of H^+ , which repel positively charged aqueous species away from the surface.

The type of element will also have an impact on how well it may adsorb. For example, Cu^{2+} and Zn^{2+} may adsorb as single ions to a mineral surface, however, the hydrolysis of these metals changes the pH range in which they adsorb (Figure 3).

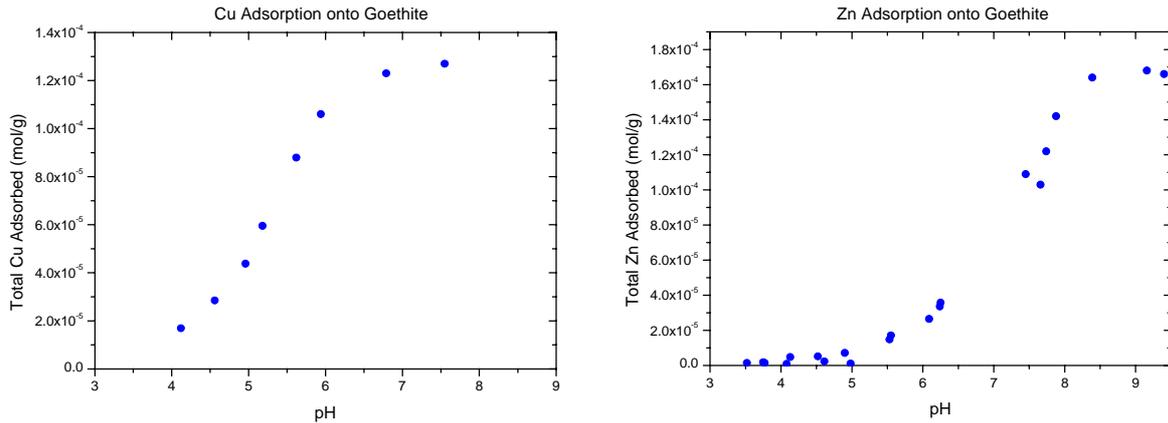


Figure 3: Adsorption of Cu^{2+} and Zn^{2+} ions onto goethite as a function of pH.

However, not all metals are stable as single ions in solution. Arsenic⁵⁺ forms AsO_4^{3-} , Mo^{5+} forms MoO_4^{3-} and Se^{4+} forms SeO_3^{2-} . The negative charge of these complexes means they are considered as anions, and exhibit the opposite adsorption behaviour as cations such that they adsorb in acidic conditions, and will desorb in more alkaline solutions (Dzombak & Morel 1990).

Solution Chemistry

The chemistry of metal-bearing solutions is known to influence the mobility of elements in natural systems. For example, the solubility of many elements is enhanced in solutions with NaCl due to the formation of stable metal-chloride complexes (Figure 4).

However the effect of solution chemistry on adsorption is poorly understood. Many experimental studies have been conducted using simple low ionic strength solutions in an attempt to isolate the adsorption behaviour of the element of interest (e.g., Balistrieri & Murray 1982, Forbes *et al.* 1982, Kovacevic *et al.* 2000, Padmanabham 1983, Peacock & Sherman 2004, Rodda *et al.* 1993, Sen *et al.* 2002). As a result, most of the adsorption data available is for systems with low concentrations of $NaNO_3$ or $NaClO_4$, as these electrolytes are considered unreactive with mineral surfaces (Balistrieri & Murray 1982). While this data is vital for understanding the basic adsorption process, such conditions are highly unlikely in nature.

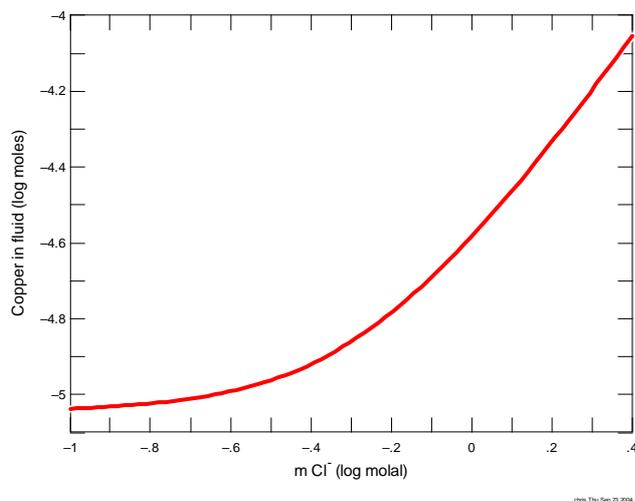


Figure 4: Cuprite solubility as a function of NaCl concentration (pH 7).

EXAMPLE: INFLUENCE OF Cl^- ON Cu^{2+} ADSORPTION ONTO GOETHITE

Experimental work presented by Gunton (2003) examined the effect of Cl^- ions on the adsorption of Cu^{2+} onto goethite. Detailed systematic mapping of Cu^{2+} adsorption onto goethite as a function of NaCl concentration and pH indicated that Cu^{2+} adsorption onto goethite was enhanced as the NaCl concentration was increased. This suggests that the speciation of metals in solution plays an important role on the formation of surface complexes.

Based on the experimental results, numerical modelling of the data has assisted in understanding the reason for the enhanced adsorption in the presence of NaCl. Figure 5 outlines the predicted surface speciation in a solution containing 0.1 mol/kg NaCl. The surface speciation is dominated by non-chlorinated Cu^{2+} species when the pH is low. However, when the pH of the system is increased, a change in the dominant surface species occurs such that SOCuCl becomes the more stable complex.

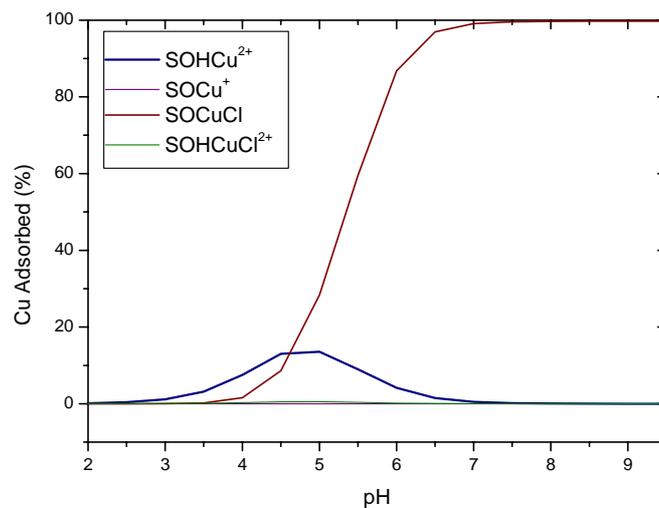


Figure 5: Surface speciation of copper on goethite in 0.1 mol/kg NaCl solution.

If the Cl^- concentration is increased to 5.0 mol/kg, the surface speciation is dominated by the SOHCuCl_2 species at low pHs, but as the pH increases, the dominant surface species changes to SOCuCl (Figure 6).

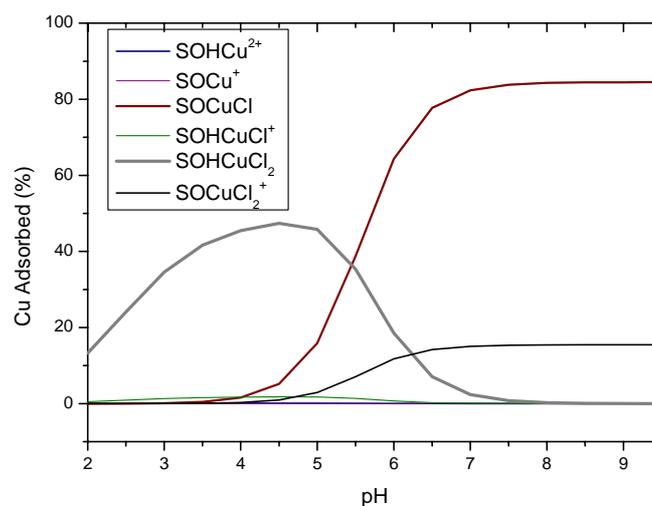


Figure 6: Surface speciation of copper on goethite in 5.0 mol/kg NaCl.

SUMMARY

The main controlling factors that control adsorption have been briefly described here, while results presented from experimental data and numerical modelling have indicated how metal speciation in solution can influence the adsorption of metals onto mineral surfaces.

The implications for the enhancement of metal adsorption in the presence of common ligands, such as Cl⁻, may change our understanding of how metals move through the regolith. As described earlier some metal-chloride complexes, such as copper-chloride and zinc-chloride, increase the solubility of these metals in solution. Therefore, we assume that these metals are capable of being transported further away from the parent source. However, the presence of chloride complexes also enhances the adsorption of these metals onto minerals such as goethite. Proving that mineralogy and fluid compositions are favourable, it is possible that the enhanced adsorption of these metals may actually decrease the relative mobility of these elements, possibly forming smaller, more concentrated geochemical anomalies.

Understanding how chemical elements interact with each other in solution and with mineral surfaces is an important part of understanding the formation of geochemical anomalies in the regolith. By understanding geochemical processes such as adsorption, it will provide mineral explorers with another known variable in the formation of geochemical anomalies in the regolith.

REFERENCES

- BALISTRERI L.S. & MURRAY J.W. 1982. The adsorption of Cu, Pb, Zn, and Cd on goethite from major ion seawater. *Geochimica Et Cosmochimica Acta* **46**, 1253-1265.
- DAVIS J.A. & KENT D.B. 1990. Surface Complexation Modeling in Aqueous Geochemistry. *Reviews in Mineralogy* **23**, 177-260.
- DZOMBAK D.A. & MOREL F. 1990. *Surface complexation modeling : hydrous ferric oxide*. Wiley.
- GUNTON C.G. 2003. The Role of Salinity in the Formation of Geochemical Anomalies in the Regolith. In: ROACH I.C. ed. *Advances in Regolith*. CRC LEME, pp. 154-158.
- KOVACEVIC D., POHLMEIER A., OZBAS G., NARRES H.D. & KALLAY M.J.N. 2000. The adsorption of lead species on goethite. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **166(1-3)**, 225-233.
- PADMANABHAM M. 1983. Adsorption-Desorption Behavior of Copper(Ii) at the Goethite-Solution Interface. *Australian Journal of Soil Research* **21(3)**, 309-320.
- PEACOCK C.L. & SHERMAN D.M. 2004. Copper(II) sorption onto goethite, hematite and lepidocrocite: A surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy. *Geochimica Et Cosmochimica Acta* **68(12)**, 2623-2637.
- RODDA D.P., WELLS J.D. & JOHNSON B.B. 1996. Anomalous adsorption of copper(II) on goethite. *Journal of Colloid and Interface Science* **184(2)**, 564-569.
- SEN T.K., MAHAJAN S.P. & KHILAR K.C. 2002. Adsorption of Cu²⁺ and Ni²⁺ on iron oxide and kaolin and its importance on Ni²⁺ transport in porous media. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **211(1)**, 91-102.