THE GEOCHEMISTRY AND MOBILITY OF ZINC IN THE REGOLITH

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INTRODUCTION

The mobility of zinc in the regolith is important for several reasons, including the weathering of zinc deposits, formation of non-sulphide zinc deposits and contamination of soils and waters from human impact. The mobility of zinc is also important more generally to geologists and geochemists, both exploration and otherwise, because of the need to understand the formation of zinc ore deposits, such as Mississippi Valley Type (MVT), volcanic-hosted massive sulphide (VHMS), zinc oxide and others in which zinc occurs. This means that exploration geochemists, economic geologists and environmental scientists need to understand how zinc exists in the regolith, different lithologies and water, how it is mobilized or trapped, how far it can be transported and whether it is bioavailable and acts as either a micronutrient or a toxin to plant and animal life. In economic geology, there is presently an increasing interest in the formation of zinc oxide, or non-sulphide zinc deposits, and this is reflected in a recent special issue in the journal Economic Geology (Sangster 2003).

Although the mobility of zinc in the regolith depends on the transporting process (e.g., groundwater advection or convection, sediment or airborne physical transport, biotic), it depends substantially on the geochemistry of zinc, i.e., how does zinc exist in groundwater and the regolith materials and what are the important geochemical reactions between water and solid. It is clear that we need to know the aqueous speciation of zinc, the solubilities of zinc-bearing minerals and sorption of zinc to mineral surfaces, in order to be able to understand and predict how zinc behaves during weathering and other processes in the Earth's crust. In this paper we review the low-temperature aqueous geochemistry of zinc and the solubilities of important zinc minerals, present preliminary results of solubility experiments for an important zinc silicate mineral, hemimorphite, discuss the environmental conditions that are most likely to mobilize and/or trap zinc and outline some of our ongoing and future studies.

GEOCHEMISTRY OF ZINC

There are many geochemical variables that can affect the concentration of zinc in waters, brines, because of how they affect the solubilities of zinc minerals and the sorption of zinc onto mineral and/or organic material surfaces. The geochemical variables that have direct affects on solubility and sorption are temperature, pressure, pH, redox (e.g., Eh, log f $_{O2\,(g,\,aq)}$), concentrations of elements, ions or compounds that complex with zinc (e.g., Cl^-, 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, there are elements and compounds that indirectly affect dissolved zinc concentrations and mineral solubility, e.g., increasing carbonate concentrations and partial pressures of $CO_2(g)$ tend to stabilise smithsonite and other carbonate-bearing zinc minerals and increasing sulphide and sulphate concentrations stabilise sphalerite, other sulphide minerals and zinc sulphate minerals. Adsorption, ion exchange or precipitation of zinc on mineral surfaces may be important in controlling the transport and mobility of zinc, e.g., (García-Sánchez & Álvarez-Ayuso 2002). At low temperature, e.g., < 200°C, kinetics of reactions can also be important, although there is a growing number of examples where mineral solubility and equilibrium models agree with measured concentrations of elements in waters at room temperature, especially in acid drainage environments (e.g., Parsons *et al.* 2001).

Zinc minerals

There are many low-temperature zinc minerals, including sulphides, silicates, oxides, carbonates, phosphates and arsenates. For example, the supergene minerals identified at the Skorpion deposit in Namibia are sauconite (zinc smectite; dominant mineral), hemimorphite ($Zn_4Si_2O_7(OH)_2 \bullet H_2O$), smithsonite ($ZnCO_3$), hydrozincite ($Zn(CO_3)_2(OH)_2$), tarbuttite ($Zn_2(PO_4)(OH)$), scholzite ($CaZn_2(PO_4)_2 \bullet 2H_2O$) and other secondary minerals that contain zinc (Borg *et al.* 2003). Other zinc minerals that may be relevant more generally are hydrated zinc carbonate ($ZnCO_3.H_2O$), zinc sulphates (anhydrous and several hydrated varieties), zinc hydroxide polymorphs, other zinc oxides (franklinite, ferrite-Zn, zinc titanite, zinc chromate), zinc arsenate and zinc phosphate, as well as the common sulphide sphalerite. There are other zinc silicate clay minerals that may be important, such as zincsilite ($Zn_3Si_4O_{10}(OH)_2 \cdot 4H_2O$; uncertain composition; smectite group), fraipontite ($(Zn,Al)_3(Al,Si)_2O_5(OH)_4$; kaolinite-serpentine group), zinalsite

($Zn_2AlSi_2O_5(OH)_4 \cdot 2H_2O$; uncertain composition; halloysite-like?) and baileychlore ("$Zn_5Al_2Si_3\,O_{10}(OH)_8$"; idealised composition; chlorite group). There are other zinc minerals that may be important in some, probably very unusual geological, environments, i.e., zinc chlorides and hydrated zinc chlorate, zinc fluoride, zinc bromides, zinc iodide and iodate, zinc borate and mixed zinc chloride ammines. Interestingly, atacamite ($Cu_2Cl(OH)_3$) has been reported as an alteration mineral in the Skorpion zinc deposit (Kärner & Borg 2001), suggesting oxidising, acidic, chloride-rich (e.g., greater than seawater) altering fluids (see Brugger *et al.* 2001).

Zinc aqueous species

There are many zinc aqueous species, and only a brief description is given here of the ones likely to be most relevant for zinc transport in the regolith. The aqueous species of zinc, in addition to the zinc and zincian minerals, affect how much zinc can be solubilized and transported. In general, zinc can be easily solubilized and transported under acidic conditions, and with increasing concentrations of zinc with increasing acidity. This is because the zinc ion, Zn^{2+}, is the predominant aqueous species of zinc. Under very alkaline conditions, i.e., pH > 10, zinc can also be transported because of the predominance of the zinc hydroxide complexes $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$. Zinc chloride, bromide and iodide complexes can predominate in hypersaline (> seawater) brines and can enhance the transport of zinc. Zinc sulphide complexes are unlikely to be important in transporting much zinc because the solubility of sphalerite is very low and will precipitate in the presence of reduced sulphur. Zinc may transport as a sulphate complex in sulphate-rich brines and zinc carbonate/bicarbonate complexes may be important in carbonate-rich waters. Zinc ammine complexes are strong and may be important in transporting zinc in waters with reduced nitrogen (ammonia/ammonium), at least in cases where dissolved sulphide concentrations are low. Zinc may be transported in organic-rich waters and brines as acetate complexes or many other organic complexes.

PREDICTION OF ZINC SPECIATION AND SOLUBILITY

Predicting the aqueous speciation of zinc and the solubilities of zinc minerals indicates how much zinc can be transported in groundwater as well as showing the geochemical conditions (*e.g.,* pH, redox, chloride, sulphur and carbonate concentrations and partial pressures) that are important in affecting zinc leaching, transport and precipitation. Thermodynamic properties are available for many of the low-temperature zinc minerals (*e.g.,* sphalerite – Helgeson *et al.* 1978, willemite – Robie *et al.* 1979, wurtzite – Cox *et al.* 1989, hydrozincite - Mercy *et al.* 1998, zincite - Wesolowski *et al.* 1998, zincite - Bénézeth *et al.* 1999, smithsonite - Preis *et al.* 2000, hydrozincite - Preis & Gamsjäger 2001a, Preis & Gamsjäger 2001b). However, no properties are available for two important minerals in non-sulphide zinc deposits, sauconite and hemimorphite. There are also no properties for other potentially important minerals such as other silicate clay minerals and franklinite. Thermodynamic properties for aqueous species are available from many studies (*e.g.,* zinc bisulphide – Bourcier & Barnes 1987, zinc chloride – Ruaya & Seward 1986, zinc carbonate – Bourcier & Barnes 1987, Zachara *et al.* 1987, zinc hydroxide – Shock *et al.* 1997, zinc sulphate – Brugger *et al.* 2003, other zinc species – Wagman *et al.* 1982, Shock & Koretsky 1995, Sverjensky *et al.* 1997). There has been little critical assessment of the reliability of the published properties; however, Brugger *et al.* (2003) compared predicted and measured zinc mineral solubilities where possible and found that in many cases predicted solubilities were within one log unit of measured values.

Example speciation and solubility diagrams are shown here to depict the effects of chloride, pressure of $CO_2(g)$ and degree of quartz saturation. All figures were calculated using Geochemist's Workbench (Bethke, 1998) using thermodynamic properties distributed with the program (thermo.com.v8.r6+.dat compiled at Lawrence Livermore National Laboratory). Figure 1 shows the effect of chloride on the solubility of zincite. The solubility of zincite increases with increasing chloride concentration, especially at concentrations greater than seawater (log a $_{Cl^-} \sim$ -0.2), as a result of zinc chloride complexes predominating at higher chloride concentrations. This effect will be the same for any zinc mineral. Two other important factors that affect zinc mobility, pressure of $CO_2(g)$ and the absence or presence of silica, are shown in Figure 2. With increasing pressure of $CO_2(g)$ carbonate-bearing zinc minerals are stabilised and hence can limit zinc mobility. The presence or absence of silica limits the stability of the carbonates, where in the presence of quartz, willemite is predicted to be the stable zinc mineral. Unfortunately we do not have properties for hemimorphite, limiting our understanding of zinc mobility in the regolith.
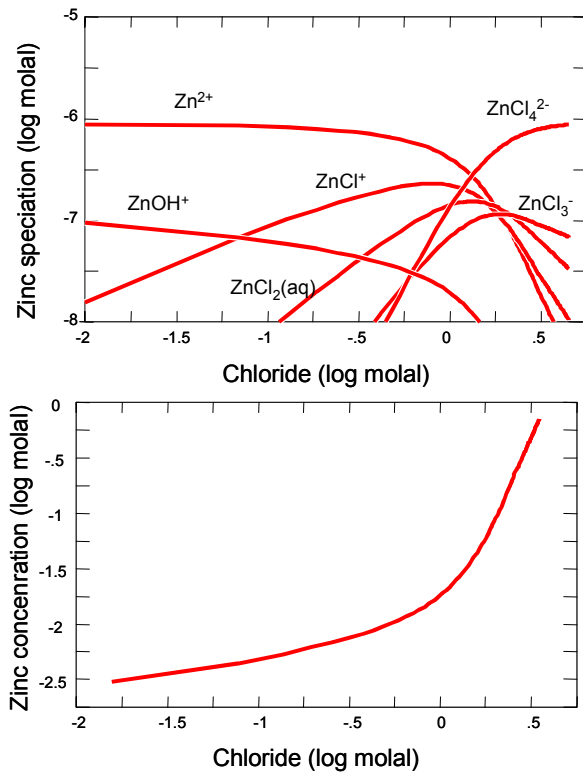
Figure 1: Speciation and zincite solubility in NaCl solutions. Top – speciation of zinc chloride complexes. Bottom – solubility of zincite. Diagram calculated for pH = 8. Note: chloride concentration of seawater is approximately log m = –0.2.
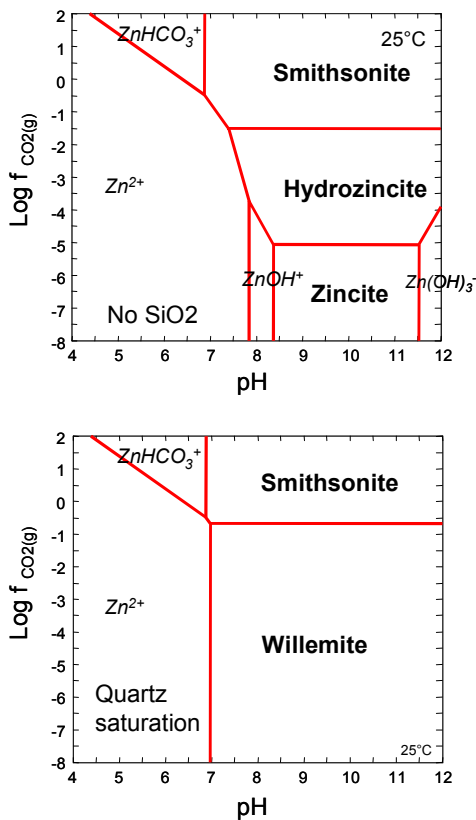

Figure 2: Zinc mineral stabilities in the chemical system Zn – O – H – C. a "Zn species" = 10^{-5}. Atmospheric $CO_2(g)$ is log f $_{CO2(g)}$ = -3.5. Top diagram is drawn assuming no silica and bottom diagram is drawn assuming waters are saturated with quartz.

SOLUBILITY OF HEMIMORPHITE

The solubility of hemimorphite has been measured in order to derive its thermodynamic properties and understand how it affects zinc mobility. Figure 3 shows the preliminary measurements of hemimorphite + quartz solubility at 50°C (chosen to speed reaction times) in pH-buffered solutions. Hemimorphite samples

were obtained from the South Australian Museum and are from Mapima, Mexico. They were crushed, hand-picked and cleaned using sodium dithionite and sodium citrate. Trace amounts of calcite and smithsonite remained; however, measured calcium concentrations in solubility experiments were less than several 10s of ppm, well below the measured zinc concentrations, and are unlikely to alter hemimorphite solubility. The calculated solubility of willemite is shown for reference, but it was calculated assuming Zn^{2+} as the only dissolved zinc species and unit activity coefficients. At lower pH, e.g., < 5.5, hemimorphite solubility is less than the calculated willemite solubility, indicating that hemimorphite would precipitate instead of willemite at these condition. At higher pH, the experimental data clearly indicate the presence of zinc hydroxide complexes in the experiments, and more complete calculations and interpretation are necessary.
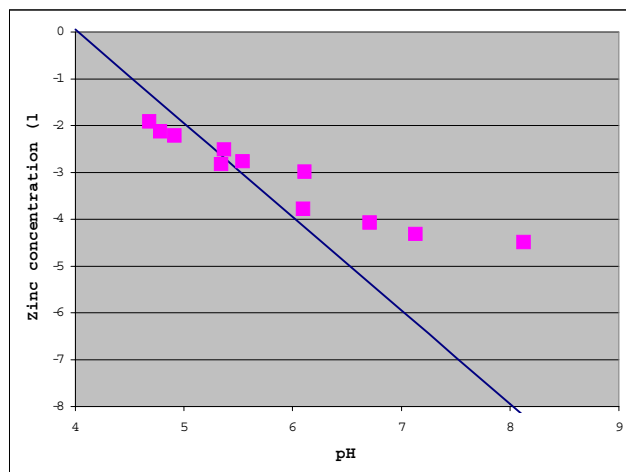
Figure 3: Solubility of hemimorphite + quartz as a function of pH at 50°C. pH was buffered using either acetate + sodium acetate (4.5<pH<6.1) or tris(hydroxymethyl)-aminomethane + HNO_3 (6.0<pH<8.2). Symbols are experimental data and line represents calculated solubility of willemite at 50°C, assuming unit activity coefficients.

ONGOING STUDIES

We are continuing studies of zinc geochemistry and mobility, in addition to our experimental solubility and geochemical modeling studies. Zinc dispersion in the regolith is being studied at the Reliance non-sulphide deposit discovery in South Australia, in collaboration with the Perilya mining company. The regolith has been sampled along a transect that crosses from areas with no surface geochemical expression to the highest concentrations over the mineralisation, as well as a depth profile from diamond core that intersected the ore zone. Zinc concentrations range up to 100s of ppm and we will use a combination of selective extraction, probe and laser ablation, and microscopy techniques to identify which minerals the zinc is associated with in the regolith sasmples. In another part of our research, we are studying samples from the Billy Spring Mine in the northern Flinders Ranges of South Australia. There are reported occurrences of hemimorphite and other low-temperature zinc and related minerals from the mine, and samples are currently being characterised to identify the minerals and their textures. We will use the information to interpret the geochemical conditions of formation for low-temperature zinc mineral formation at that site. The sorption of zinc onto mineral surfaces, especially goethite, is likely to be important in affecting zinc mobility. Although we are not studying this at present, a related study on Cu(II) sorption onto goethite is presently underway (Gunton, 2003; this volume) and preliminary results show clearly that metal mobility is limited by sorption at higher pH (*e.g.,* >5), something that is already known, but also that increasing salinity can also increase sorption and potentially limit metal mobility. Cu(II) and Zn(II) are likely to behave similarly as their chemistry in chloride solutions is similar.

SUMMARY AND CONCLUSIONS

The geochemistry of zinc, both mineral and aqueous, affects the solubility of zinc minerals and ultimately the mobility of zinc. We are using a combination of experimental, numerical modeling and field studies to study the geochemistry and mobility of zinc. Results of our studies in addition to previous ones show that zinc mobility is enhanced by low pH, oxidized conditions (sulphide-poor) and high salinity (depending on the importance of sorption). High $CO_2(g)$ partial pressures and low silica concentrations result in zinc carbonate and hydroxycarbonate minerals being stable and potentially limit zinc mobility. In environments where silica concentrations approach quartz saturation, zinc silicate minerals are likely to limit zinc mobility. Hemimorphite solubility experiments will allow us to derive reliable thermodynamic properties for that

mineral and help us to understand its importance in affecting the mobility of zinc over a wide range of conditions. Ultimately the development of numerical models of zinc leaching, transport and deposition will lead to improved understanding of zinc mobility and successful exploration strategies for zinc ore bodies.

REFERENCES

BÉNÉZETH P., PALMER D.A. & WESOLOWSKI D.J. 1999. The solubility of zinc oxide in 0.03 m NaTr as a function of temperature, with in situ pH measurement. *Geochimica et Cosmochimica Acta* **63(10)**, 1571-1586.

BETHKE C.M. 1996. *Geochemical Reaction Modeling: Concepts and Applications*. Oxford University Press, New York.

BETHKE C.M. 1998. *The Geochemist's Workbench Release 3.0: A User's Guide to Rxn, Act2, Tact, React and Gtplot*. Hydrogeology Program, University of Illinois.

BORG G, KÄMER K., BUXTON M., ARMSTRONG,R. & VAN DER VERWE S.W. 2003. G*eology of the Skorpion superene zinc deposit, Southern Namibia. Economic Geology* **98**, 749-771.

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. *Geochimica et Cosmochimica Acta* **65(16)**, 2691-2708.

COX J.D., WAGMAN D.D. & MEDVEDEV V.A. 1989. *Codata key values for thermodynamics*. Hemisphere Publications, New York, 271 p.

GARCÍA-SÁNCHEZ A. & ÁKVAREZ0ATYSI E. 2002. Sorption of Zn, Cd, and Cr on calcite. Applications to purification of industrial wastewaters. *Minerals Engineering*.

GUNTON C. 2003. The role of salinity on the formation of geochemical anomalies in the regolith. *In:* ROACH I.C. ed. *Advances in Regolith*, pp. 154-158. CRC LEME.

HELGESON H.C., DELANY J.M., NESBITT H.W. & BIRD D.K. 1978. Summary and critique of the thermodynamic properties of rock-forming minerals. *American Journal of Science* **278a**, 229 p.

KÄMER K. & BORG G. 2001. Relationship between non-sulphides and sulphides at the Skorpion zinc deposit, Namibia. *GSA Annual Meeting, Boston*, Geological Society of America.

MERCY M.A., ROCK P.A. et al. 1998. Gibbs energies of formation for hydrocerrusite [Pb(OH)2.(PbCO3)2(s)] and hydrozincite {[Zn(OH)2]3.(ZnCO3)2(s)]} at 298 K and 1 bar from electrochemical cell measurements. *American Mineralogist* **83(7-8)**, 739-745.

PARSONS M.B., BIRD D.K. 2001. Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California. *Applied Geochemistry* **16**, 1567-1593.

PREIS W. & H. GAMSJÄGER H. 2001a. (Solid + solute) phase equilibria in aqueous solution. XIII. Thermodynamic properties of hydrozincite and predominance diagrams for (Zn2+ + H2O + CO2). *Journal of Chemical Thermodynamics* **33**, 803-819.

PREIS W. & GAMSJÄGER H. 2001b. Thermodynamic investigation of phase equilibria in metal carbonate-water-carbon dioxide systems. *Monatshefte für Chemie* **132**, 1327-1346.

PREIS W., KONIGSBERGER E. & GAMSJÄGER H. 2000. Solid-solute phase equilibria in aqueous solution. XII. Solubility and thermal decomposition of smithsonite. *Journal of Solution Chemistry* **29(7)**, 605-618.

ROBIE R.A., HEMINGWAY B.S. & FISHER J.R. 1979. Thermodynamic properties of minerals and related substances at 298.15 K and 1 Bar (105 Pascals) pressure and at higher temperatures. *U.S. Geological Survey Bulletin* **1452**, 456 p.

SANGSTER D.F. 2003. A special issue devoted ot nonsulphide zinc deposits: A new look. *Economic Geology* **98**, 683-684.

SHOCK E.L. & KORETSKY C.M. 1995. Metal-organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. *Geochimica et Cosmochimica Acta* **59**, 1497-1532.

SVERJENSKY D.A., SHOCK E.L. & HELGESON H.C. 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000 C and 5 Kb. *Geochimica et Cosmochimica Acta* **61**, 1359-1412.

WAGMAN D.D., EVANS W.H., PARKER V.B., SCHUMM R.H., HALOW I., BAILEY S.M., CHURNEY, K.L. & NUTTALL R.L. 1982. The NBS tables of chemical thermodynamic properties, selected values for inorganic and c1 and c2 organic substances in SI units. *Journal of Physical Chemistry* **Reference Data 11, supp. 2**, 392p.

WESOLOWSKI D. J., BÉNÉZETH P. & PALMER D.A. 1998. ZnO solubility and Zn2+ complexation by chloride and sulfate in acidic solutions to 290°C with in-situ pH measurement. *Geochimica et Cosmochimica Acta* **62(6)**, 971-984.