# METAL ION DISPERSION THROUGH TRANSPORTED COVER AT MOONTA, SOUTH AUSTRALIA

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## INTRODUCTION

In arid to semi-arid environments, typical of much of the prospective mineral terrains in South Australia, a thick unsaturated (vadose) zone is commonly developed above the water table (top of phreatic zone). In this situation, understanding present and past hydrologic processes particularly with respect to flow through the vadose zone is critical for modelling geochemical dispersion to surface of metal ions from a mineralised host buried beneath thin sedimentary cover. The Moonta copper mines on northern Yorke Peninsula, South Australia, are an example of anomalous Cu in transported sediment that reflect the presence of mineralisation in weathered crystalline basement buried beneath. This was recognised and successfully exploited by miners when prospecting for new lodes in the district during the late 1800s to early 1900s (Jack 1917), and later demonstrated convincingly in field studies reported by Sokoloff (1948) and Mazzucchelli *et.al.* (1980). Recent investigation of metal ion distribution in sediments sampled from sections at abandoned open pit mines at Poona and Wheal Hughes showed significant differences in Cu content in pedogenic calcrete at each mine (Hartley 2000). The results indicate that further study of the two sites might clarify the dominant mechanism of transport of metal ions through younger cover sediments in this environment. That work remains to be done and the focus of this presentation is to briefly review the historical background and key observations for each site, consider the role of capillarity and diffusion as possible dispersion mechanisms and promote discussion on what additional data need to be collected.

## BACKGROUND, GEOLOGY AND WEATHERING

The Moonta and Wallaroo districts, 120 km northwest of Adelaide, were important historic centres for copper mining and between 1860 and 1923 produced 330,000 tonnes of Cu from narrow, shear-hosted sulphide vein deposits. Recent open pit and underground mining at Poona and Wheal Hughes (1986-92) produced a further 18,000 tonnes Cu from chalcopyrite-pyrite ore grading 4.5% Cu from lodes hosted by Moonta Porphyry of Palaeoproterozoic age. The porphyry is weathered to around 15 m with a 4-6m highly weathered mottled zone of dominantly kaolin, quartz and iron oxide/oxyhydroxide megamottles over variably weathered lower saprolite and saprock. The weathered porphyry is overlain by 5-8 m of transported sediment. At Poona, these comprise 2-4 m thick terrestrial lacustrine and overbank sandy and silty, red-brown clay equated with Hindmarsh Clay of Early Pleistocene age (ca. 0.78 Ma) (Zang 2003); 1-2 m calcareous aeolian sand and silt with calcrete as nodules and platy layers; and 0.6 m calcareous clay loam topsoil. At Wheal Hughes, 1.7 km south of Poona, a 1-4 m thick Cambrian coarse-grained, arkosic sandstone (Winulta Formation) directly overlies weathered porphyry and is in turn overlain by Hindmarsh Clay, calcareous sand and topsoil, as at Poona. The post-Cambrian sediments at Wheal Hughes are only 2-4 m in thickness (Hartley 2000).

Poona and Wheal Hughes occupy an inter-drainage setting at around 40 m elevation and 4.5 km from the coast. The area is semiarid, < 400 mm annual rainfall, with flat to gently undulating topography and poorly developed surface drainage. The water table is around 20 m below ground surface and is very saline (ca. 42,000 mg/L). The water table approximates the local saprock/fresh rock boundary in the porphyry except in areas marginal to the Cu-lodes, especially the footwall, which is weathered for a further 20 m due to local highly acidic conditions from pyrite oxidation (Keeling *et al.* 2003). A zone of supergene Cu mineralisation of chalcocite and covellite to 5 m thickness also approximates the position of the present water table. Above this is a barren zone of saprock/saprolite from which copper mineralisation has been mostly leached. A broad envelope of halloysite as coating on joints and fractures was mapped around the ore zone to 80 m depth (Mauger *et al.* 1997) and is thought to have formed by precipitation from downward migrating acidic water during lowering of the water table in response to sea level fluctuations over the past 1Ma (Keeling *et.al.* 2003).

Palaeomagnetic dating of iron-rich mottles in the leached zone at Poona gave an age of crystallisation of the magnetic iron phase as 8 ± 4 Ma, Late Miocene to Early Pliocene times (Pillans *pers comm.*, 2004). The weathered profile, depleted zone and supergene Cu were, therefore, developed long before deposition of the Pleistocene clay at around 0.78 Ma. Elevated Cu concentrations were measured throughout the Hindmarsh Clay in pit sections at Poona (Figure 1). Maximum values of 300 ppm were recorded 0.3-0.5 m below the contact with aeolian carbonate and were associated with thin, 20-70 mm wide alunite seams developed in the clay. The results accord with anecdotal account of patches and nodules of radiating atacamite ($Cu_2Cl(OH)_3$) crystals encountered during overburden stripping of transported clay that overlay the back of the copper lode. This Cu-rich clay was stockpiled separately and subsequently picked over for mineral specimens by local gem and mineral clubs. Specimens lodged with the State Museum include one weighing 1.195 kg and estimated to contain over 600 gm Cu (Pring, SA Museum, *pers. comm.* 2004). By way of contrast, elevated copper values were uncommon in Hindmarsh Clay at Wheal Hughes and alunite seams were not observed in the clay (Hartley 2000). The lack of mobilisation of Cu into Pleistocene clay at Wheal Hughes is reflected in the absence of Cu above background values in near-surface calcrete (Figure 1).

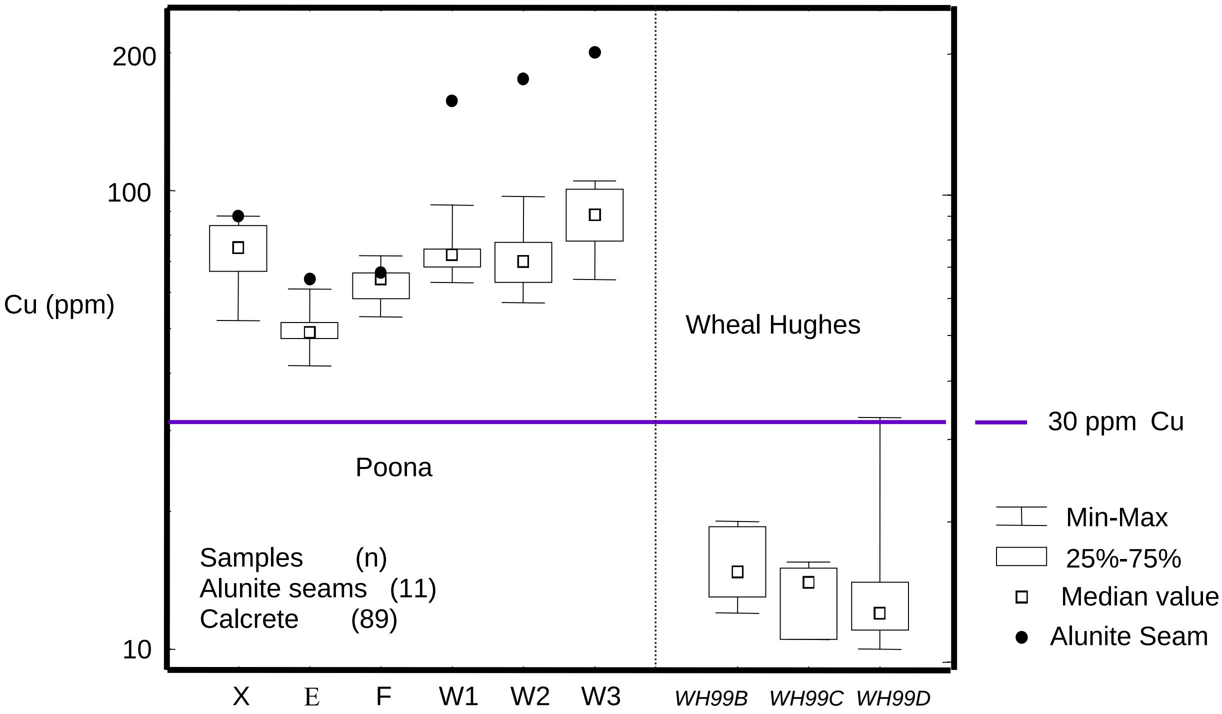

**Figure 1.** Box and whisker plots of Cu content in near surface calcrete and alunite samples from pit sections at Poona and Wheal Hughes mines highlighting the difference in Cu dispersion for the two deposits relative to the regional anomaly threshold of 30 ppm Cu, after Hartley (2000).

The question to be answered is why Cu ions are effectively transported into Hindmarsh Clay at Poona but not at Wheal Hughes. The presence of a weathered remnant of Cambrian sandstone at Wheal Hughes is an obvious difference between the two sites and has been suggested as a barrier to upward dispersion of metal ions into the clay (Hartley 2000, Keeling *et al.* 2003). Simply raising the water table would by itself be unlikely to produce the observed differences. The sandstone, though silicified in places, is also fractured and highly weathered and appears unlikely to be a barrier to hydraulic flow. Capillarity is the mechanism preferred by Jack (1917) to explain similar Cu dispersion observed at other localities in the district. However, depth to the water table and Cu source at Poona at around 15 m below the base of Pleistocene clay is significantly large, and ion diffusion through the vadose zone has been suggested as an alternative mechanism.

## CAPILLARITY

Fluid is present throughout weathered rock and sediment in the unsaturated zone above the water table. Fluid pressures in this zone are negative with respect to local atmospheric pressure and the water is held under tension and is not free to flow as it does below the water table. Water molecules at the water table are subject to an upward attraction due to surface tension of the air-water interface and attraction of the liquid to "wet" mineral surfaces (Fetter 2001). This effect is known as capillarity. Where the capillary fringe extends into the zone of evapotranspiration, the loss of water results in effective pumping of water and contained solutes from the water table to the near surface.

Capillary rise is a function of surface tension, fluid specific weights, contact angle (α) with the solid surface and pore diameter. For a cylinder of diameter *d*, capillary rise is described by the equation:

$$h_c = \frac{4\sigma Cos(\alpha)}{d\rho g} \qquad (1)$$

Where: $h_c$ = height of capillary rise, $\sigma$ = surface tension of fluid, α = contact or wetting angle of fluid with cylinder wall, *d* = diameter of cylinder, *ρ* = density of fluid, *g* = gravitational constant.

An estimate of capillary rise in a soil or sediment can be made by substitution of values for pure water at 20°C, having surface tension at about $7.3 \times 10^{-2}$ N/m, $\rho = 1$ and $g = 9.81 \times 10^{3}$ N/m$^3$. Water in contact with silicate minerals has a wetting angle (α) close to zero so that Cos (α) = 1, which reduces Equation 1 to:

$$h_{c(m)} \approx \frac{0.03}{d_{eff\,(mm)}} \qquad (2)$$

Where $h_c$ = capillary rise in metres and *deff* is the effective pore diameter in millimetres.

The height of capillary rise is inversely related to effective pore diameter, which in turn is governed by grain size and grain size distribution (i.e., texture) in a sediment or porous weathered bedrock. Theoretical values of capillary rise in sediments are given in Table 1. This provides an order of magnitude estimate of capillary rise and is sufficient to demonstrate that advective transport of solutes in solution by this mechanism over significant distances is restricted to silt-sized particles or finer with effective pore diameters < 10 µm and preferably < 4 µm (fine silt). Pore diameters observed by scanning electron microscopy of weathered Moonta Porphyry and clay sediments at Poona and Wheal Hughes are certainly within the range 4 - < 0.1 µm. These observations do not provide information on the degree of interconnection. The Cambrian sandstone at Wheal Hughes has not been examined but fracture porosity and inter-grain pores are likely to give rise to substantially larger effective pore diameters.

**Table 1:** Theoretical Height of Capillary Rise in Sediments

| Sediment | Grain diameter (mm) | Effective Pore diam (mm) | Capillary Rise (metres) |
|---|---|---|---|
| Fine gravel | 5 | 2 | 0.015 |
| Coarse sand | 0.5 | 0.2 | 0.15 |
| Medium sand | 0. 3 | 0.12 | 0.25 |
| Fine sand | 0.15 | 0.06 | 0.50 |
| Very fine sand | 0.075 | 0.03 | 1.0 |
| Coarse Silt | 0.025 | 0.01 | 3.0 |
| Fine Silt | 0.008 | 0.004 | 7.5 |
| Coarse Clay | 0.002 | 0.0008 | 37.5 |
| Fine Clay | 0.0002 | 0.00008 | 375.0? |

The hydraulic and biological properties of soil pores, summarised in Table 2, highlight two related factors that limit hydraulic transport in very fine pores: low hydraulic conductivity; and, high negative pore pressure. At < 0.2 µm effective diameter, hydraulic flow is negligible and water is held increasingly as hydroscopic water close to the surface of mineral grains. At high negative pore pressures of around pF 4.5 water approaches boiling point and boiling or the release of gases would disrupt the surface tension with continued water movement only in the vapour phase. Under semiarid to arid conditions, high evaporation rates and increased osmotic suction due to high salt content in soils will contribute additional water potential or suction that may transport water in micropores over greater vertical distances than predicted by capillarity alone. This effect is observed in trees such as Douglas fir, where evaporation from the leaves generates an atmospheric suction that can lift water to 110 m in xylem capillaries of diameter capable of capillary rise alone of < 1 m (Koch *et al.* 2004).

**Table 2:** Significance of pore size in physio-chemical and biological activity, modified from Blum (2002). pF is a measure of negative pressure or suction and is defined as the log of the height of an equivalent column of water measured in cm.

| Pore Size (mm diam) | Hydraulic conductivity Water retention in pF | Biological Conditions |
|---|---|---|
| Macropores > 0.05 mm | Excellent, gravity flow, free draining<br>0-1.8 pF | Large plant roots |
| Mesopores<br>0.03-0.05 mm | Good: some water retained after gravity draining<br>1.8-2.0 pF | Accommodates fungi and root hairs |
| Micropores<br>0.005-0.03 mm | Moderate capillarity flow<br>2.0-2.8 pF | Accommodates bacteria and other microbes |
| Ultra-micropores<br>0.0002-0.005 mm | Low capillarity flow<br>2.8-4.2 pF | Bacteria 0.5-3 µm, but space too small and not used by most microbes |
| Cryptopores or nanopores<br>< 0.0002 mm | Very low to negligible<br>> 4.2 pF<br>Water retained against plant root extraction forces | Too small for bacteria, no space for plant roots or soil organisms. Reaction with organic chemical by-products only |

Preliminary calculations for Poona indicate that a hydraulic flux of the order of 0.84 mm/year over a 100 ka would be required to generate a nodule of atacamite with around 600 gms Cu, formed at 15 m above the water table. The 100 ka time frame equates to the cumulative high sea level stands since deposition of the Hindmarsh Clay. For a 750 ka period the flux required would be 0.11 mm/year. Calculated flux rates for silty clay, using van Genuchten's model for unsaturated hydraulic conductivity, range from 5.11 - 0.019 mm/year for capillary diameters with pore pressures 2.7 – 4.2 pF (Tanji & Kielen 2003). Upward water fluxes in thick vadose zones in arid and semiarid environments have been modelled based on long term moisture potential measurements at sites in Texas and Nevada. Values of ~0.03 mm/year and ~0.05 mm/year were reported (Scanlon 2003). These data suggest that capillarity alone may be insufficient to account for the accumulation of Cu in Hindmarsh Clay. Given the very slow flux rates, ion diffusion is also a possibility.

## DIFFUSION

At very slow fluid flow rates, diffusion can be a more important mechanism than advection for dispersion of solutes. The rate of diffusion of a solute through water is described by Fick's law. Fick's Law needs to be modified for porous media where diffusion cannot proceed as fast as it can in water, simply because ions must travel around mineral grains, may diffuse into blocked pores and may be absorbed onto mineral surfaces. In this case the effective diffusion coefficient $D_e$ is used, where:

$$D_e = D_0 \tau$$

Where $D_o$ is the diffusion coefficient in water and $\tau$ is an empirical coefficient for tortuosity. Tortuosity cannot be readily measured in the field and is usually determined by reference to laboratory experiment. Fick's Law of diffusion in a porous medium becomes:

$$J_m = -\phi D_e \frac{\partial C}{\partial x} \qquad (3)$$

Where: $J_m$ = mass flux of solute per unit area per time, $\o$ = porosity, $D_e$ = effective diffusion coefficient (area/time), $\frac{\partial C}{\partial x}$ = concentration gradient (mass/volume/distance)

For $CuSO_4$, $Cu^{2+}$ is the rate limiting diffusing ion having a diffusion rate at 18°C of $5.88 \times 10^{-6}$ $cm^2 sec^{-1}$. For assumptions of initial concentration of 200 ppm Cu, tortuosity = 0.1 and porosity = 30%, the diffusion flux can be recalculated at 4.86 mm/year. This rate is significantly faster than capillarity in fine pores but as diffusion operates in all directions the effect is always to dilute the initial concentration. In order to accumulate sufficient Cu to form a nodule of atacamite with 600 gms Cu, a time period of the order of 9.0 Ma would be required, unless some means of focussing the diffusing ions was achieved. Even if this were possible, could the concentration gradient be maintained to drive the diffusion rate?

## FURTHER INVESTIGATION

The Poona and Wheal Hughes mine sites provide a unique opportunity to explore potential mechanisms for Cu dispersion through the unsaturated zone into sediments deposited over an already weathered mineralised host. Marked differences in Cu dispersion recorded at the two sites are yet to be fully explained and offer the tantalising possibility of new insights into the principal driver of metal ion dispersion in the vadose zone over geological timeframes of several hundred thousand years. Under a predominantly semiarid to arid climatic regime, factors of regolith composition and texture, landscape position, Pleistocene climate and sea-level variation all modify vadose zone hydrology that could affect metal ion dispersion. The significance of understanding which are the main drivers is illustrated in the Moonta situation where surface geochemistry is least effective in areas of sandstone cover providing an opportunity for new discoveries by mapping out the extent of sandstone and applying more appropriate techniques to these under-explored areas.

Investigations, in addition to further field work and sampling to confirm the distribution of Cu in key sections, are recommended including:

- Determine the distribution and composition of salts down the profile. Chloride especially has been used as a tracer of soil-moisture flux variation over time on the assumption that input is derived predominantly from atmosphere at a fairly constant rate and is moved downward, largely by advection. Any anomalous distribution would require explanation. Deuterium and oxygen isotopes have also been used to trace water movement in the unsaturated zone (Barnes & Allison 1988);
- Modelling the hydrological changes. The long time frame and slow flux rates mean that these processes are difficult to determine from laboratory experiments alone. Hydrological modelling software is available that can integrate a wide range of variables over geological time frames and can test various scenarios (e.g., MODFLOW (USGS), HYDRUS-1D, HYDRUS-2D (Colorado School of Mines)). Input parameters that may need to determined in the laboratory or field include: texture characterisation, moisture contents, pore water chemistry, total and matrix potential, and soil water retention curves for Hindmarsh Clay and weathered bedrock;
- Dating alunite samples (K-Ar or Ar-Ar) from both Pleistocene clay and weathered porphyry at the Poona open pit will assist in understanding the role of sulphate ions in the dispersion process.

## REFERENCES

BARNES C.J. & ALLISON G.B. 1988. Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. *Journal of Hydrology* **100**, 143-176.

BLUM W.E.H. 2002. Soil pore space as communication channel between the goesphere, the atmosphere and the biosphere. *17th World Congress of Soil Science*, 14-21 August 2002, Thailand.

FETTER C.W. 2001. *Applied Hydrology 4th Edition*. Prentice-Hall, New Jersey.

HARTLEY K.L. 2000. *Regolith studies of the Moonta copper mines, Yorke Peninsula, South Australia*. University of Melbourne, B.Sc. Honours thesis, unpublished.

JACK R.L. 1917. The geology of the Moonta and Wallaroo Mining District. *South Australia. Geological Survey Bulletin* **6**, 135 pp.

KEELING J.L., MAUGER A.M., SCOTT K.M. & HARTLEY K. 2003. Alteration mineralogy and acid sulphate weathering at Moonta copper mines. *In:* ROACH, I.C. ed. *Advances in Regolith*. CRC LEME, pp. 230-233.

KOCH G.W., SILLETT S.C., JENNINGS G.M. & DAVIS S.D. 2004. The limits to tree height. *Letters to Nature, Nature* **428**, 851-854, 22 April 2004.

MAUGER A.J., KEELING J.L., LUONG L. & SCOTT K.M. 1997. Poona Copper Mine, Moonta South Australia: investigation of alteration mineralogy using short wave infrared analysis. *South Australia. Department of Primary Industries and Resources.* **Report Book 97/51**, unpublished.

MAZZUCCHELLI R.H., CHAPPLE B.E.E. & LYNCH J.E. 1980. Northern Yorke Peninsula Cu, Gawler Block, S.A. *Journal of Geochemical Exploration* **12**, 203-207.

SCANLON B.R., KEESE K., REEDY R.C., SIMUNEK J. & ANDRASKI B.J. 2003. Variations in flow and transport in thick desert vadose zones in response to palaeoclimatic forcing (0-90 kyr): field measurements, modeling and uncertainties. *Water Resources Research* **39(7)**,1179-1196.

SOKOLOFF V.P. 1948. Geochemical reconnaissance in the Wallaroo mining district, South Australia. *South Australia. Mining Review, Adelaide* **88**, 32-71.

TANJI K.L. & KIELEN N.C. 2003 Agricultural drainage water management in arid and semi-arid areas. *FAO Irrigation and Drainage Paper 61*. Food and Agriculture Organization of the United Nations, Rome.

ZANG W. 2003. MAITLAND SPECIAL map sheet. *South Australia. Geological Survey. Geological Atlas 1:250 000 Series*, sheet SI53-12 & portion SI53-16.