CHEMICAL MINERALOGY OF THE OXIDIZED ZONES OF THE E22, E26 AND E27 ORE BODIES AT NORTHPARKES, NEW SOUTH WALES

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INTRODUCTION

A number of porphyry copper-gold deposits at Northparkes in central New South Wales are associated with finger-like intrusions of 430-440 Ma quartz-monzonite porphyries, which intrude Ordovician age Goonumbla volcanics (Heithersay *et al.* 1990). Major primary minerals are pyrite, bornite and chalcopyrite, together with economically significant native gold. Both primary and secondary ores from three bodies, E22, E27 and E26 North (E26) have been worked for copper and gold since 1994. The three deposits are covered by a mixture of clays, some of which are *in situ* weathering products, and transported overburden (Arundell 2004, Heithersay *et al.* 1990). The region has experienced prolonged and episodic weathering. Two significant weathering events have been identified, one in the Carboniferous and a subsequent event in the Cenozoic (O'Sullivan *et al.* 2000, Pillans *et al.* 1999). As a result, the E22, E26 and E27 deposits display well-developed oxidized zones, with intense leaching of the upper sections (Crane *et al.* 1998, McLean *et al.* 2004). The base of oxidation extends to 80 m from surface, with strong kaolinization from approximately 5 to 45 m below surface. Upper oxidized zones are dominated by the secondary Cu(II) phosphate minerals libethenite (Cu_2PO_4OH) and pseudomalachite ($Cu_5(PO_4)_2(OH)_4$) and, uniquely to E26, sampleite ($NaCaCu_5(PO_4)_4Cl.5H_2O$). Beneath the phosphates a zone dominated by malachite ($Cu_2CO_3(OH)_2$), azurite ($Cu_3(CO_3)_2(OH)_2$) and chrysocolla ($CuSiO_3.nH_2O$) gives way at depth to a thin native copper-cuprite (Cu_2O)-chalcocite (Cu_2S) supergene enriched zone. E26 is exceptional in that the formation of the secondary Cu(II) carbonates was preceded by extensive precipitation of atacamite ($Cu_2Cl(OH)_3$), this being reflected by the compositions of present ground waters (McLean *et al.* 2004); those associated with E26 are much more saline (NaCl). We have reconstructed the solution conditions associated with the development of these assemblages to better understand the dispersion of copper. In order to model the environment of phosphate mineral deposition in E26 a stability constant for sampleite at 298K has been measured.

SOLUTION STUDIES

Pure sampleite was synthesized by hydrothermal methods. The mineral was equilibrated with aqueous 10^{-3} mol dm^{-3} HCl plus 0.1 mol dm^{-3} NaCl at 298.2K; the solubility of sampleite under these conditions is $1.22 \pm 0.03 \times 10^{-4}$ mol dm^{-3} with a pH of 4.550 ± 0.001. Species distribution calculations and correction for activity coefficients gave a value of $\Delta fG°$ at 298.2K of -6342.8 ± 7.4 kJ mol^{-1}.

GEOCHEMISTRY OF DEVELOPMENT OF THE OXIDIZED ZONES

The oxidized zones at Northparkes developed as a result of a series of discontinuous events. Secondary Cu(II) phosphates are present in the upper sections of all three oxidized zones and represent an early phase of mineralization. Conditions under which libethenite and pseudomalachite form have been explored previously (Crane *et al*. 2001). Figure 1 is a stability field diagram for the secondary phosphates at 298.2 K. Libethenite, common to all three oxidized zones at Northparkes, can only form with elevated activities of dissolved phosphate species and at rather low pH values. In order to mobilize sufficient phosphate, mineralizing solutions must be acidic enough to dissolve accessory fluorapatite; acidity is associated with oxidation of sulfides and the hydrolysis of Fe(III) ions. As protons are consumed by reaction with feldspars to give mainly kaolinite, leached copper and phosphate will react to form libethenite and pseudomalachite in turn. Additional evidence for the neutralization of acidic phosphate-bearing solutions with time is found in the crystallization of late secondary hydroxylapatite (Crane *et al.* 1998). In conjunction with these phenomena, extensive crystallization of sampleite in the oxidized zone of E26 took place. For this to occur, *both* elevated phosphate and chloride activities are necessary. The rarity of sampleite is thus seen as a consequence of the rather unusual solution conditions required for its crystallization. Fluorapatite dissolves incongruently to form fluorite (Misra 1999). Based on thermodynamic data of Robie & Hemingway (1995) for the reaction $2Ca_5(PO_4)_3F(s) + 12H^+(aq) \leftrightarrows CaF_2(s) + 9Ca^{2+}(aq) + 6H_2PO_4^-(aq)$, by ignoring activity coefficients, $\lg [H_2PO_4^-] = -0.551 - 0.8$ pH at 298.2K when Ca^{2+} is derived solely from fluorapatite. For pH =3, 4, 5 and 6, $\lg [H_2PO_4^-]$ = -2.95, -3.75, -4.55 and -5.35, respectively. To preclude formation of atacamite, $a(H_2PO_4^-)$ would need to be of the order of 10^{-5} and the pH thus less than 5.

Table 1: Ground water analyses (concentrations in mol dm^{-3} except for pH) for E22 and E26.[a]

Sample number	**E26P118**	**E26P119**	**E22P157**
pH	7.25	6.85	7.80
carbonate	neg[b]	neg	neg
bicarbonate	0.0034	0.0044	0.0034
chloride	0.3255	0.3458	0.0265
sulfate	0.0364	0.0394	0.0059
potassium	0.0005	0.0005	0.0002
sodium	0.2693	0.2845	0.0154
calcium	0.0188	0.0245	0.0047
magnesium	0.0442	0.0457	0.0082
$\Sigma(+)$	0.3958	0.4252	0.0415
$\Sigma(-)$	0.4018	0.4290	0.0416
I	0.50	0.54	0.06
$\gamma^{\pm}$	0.737	0.726	0.806
$\gamma^{2\pm}$	0.295	0.278	0.432
lg $a(Cl^-)$	-0.62	-0.60	-1.67
lg $a(Ca^{2+})$	-2.26	-2.17	-2.70

[a] Analytical data originally reported in ppm; rounding of concentration data refers only to the last quoted digit. [b] Not detectable.

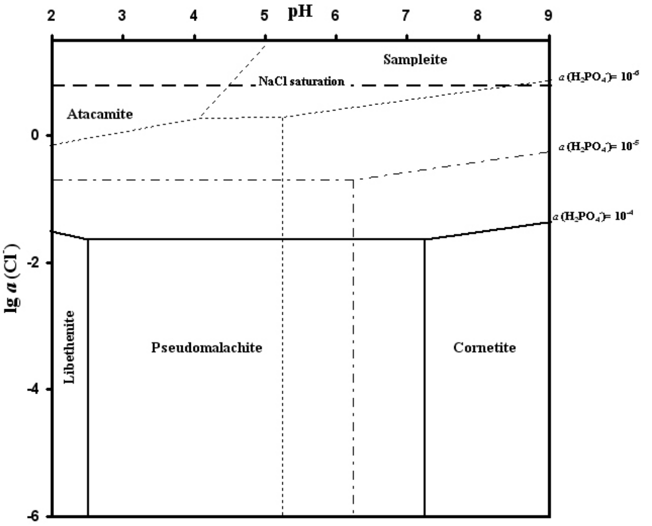

Figure 1: Stability field diagram for the phosphate minerals at 298.2K. The diagram was constructed using a value for $a(Na^+)$ equal to that of the chloride ion, and 10 times that of

For libethenite to form, as observed in the zone of sampleite crystallization, the pH must have locally fallen below 3 with an Cl^- activity on the order of 0.1. However, a more realistic set of solution parameters can be deduced on the basis of current ground water geochemistry. It is apparent that present day ground water compositions reflect mineralogical differences in the oxidized copper assemblages at Northparkes. Table 1 lists data for three high-quality analyses of ground waters associated with E22 and E26. It is particularly noteworthy that the two samples from E26 have chloride concentrations of more than one order of magnitude greater than the sample from E22. Use of Ca^{2+} activities calculated from the data for the acid dissolution of fluorapatite gives (E26P118) lg a $(H_2PO_4^-) = -3.86$, -5.86, -7.86 and -9.86 for pH 3, 4, 5 and 6, respectively. Corresponding values for sample E26P119 are lg a $(H_2PO_4^-) = -3.73$, -5.73, -7.73 and -9.73, for the same pH conditions. Corrections for activity coefficients give values of lg $a(Cl^-)$ of -0.62 and -0.60 for E26 and -1.67 for E22 (Table 1). Reference to Figure 2 indicates that an $a(H_2PO_4^-)$ of less than 10^{-5} in the presence of suitable amounts of Na^+ and Ca^{2+} will cause the crystallization of sampleite, whereas for the E22 case, $a(H_2PO_4^-)$ must be somewhat greater than 10^{-4}. This higher value was not achieved and sampleite is absent from both E22 and E27. Calculations fix the pH of mineralizing solutions in E26 during the phosphate phase at between 3 and 4. This low pH regime is quite consistent with the oxidation of sulfides in a poorly buffered environment and serves to explain other features of the deposits at Northparkes. Leaching of the upper oxidized zones is extensive and the phosphate minerals are not accompanied by any other Cu(II) phases to any significant extent, because the latter are simply too soluble at low pH. To illustrate this phenomenon, reference is made to equilibrium conditions between sampleite and pseudomalachite. Use of the data of Table 1 gives for E26 lg a $(H_2PO_4^-) \cong -4$, and pH $\cong 3.1$; in turn, $a(Cu^{2+})$ is about 0.03. Inspection of the data of Table 1 for this level of dissolved copper indicates a deficiency in anion concentrations and the question is what would make this up. It is possible to deduce this, with a somewhat surprising outcome. First, extra chloride would be a component, now incorporated in subsequent atacamite mineralization. More significant, however, would be sulfate released during the oxidation of sulfides. As protons reacted with Ca-rich plagioclase, the overall exchange process involves protons for calcium ions. A feature of the profiles at Northparkes is the pervasive development of gypsum at a level somewhat below the water table (Heithersay *et al.* 1990). This then is seen as a natural consequence of the weathering of both sulfides and host rock silicates during the development of the supergene sequence.

As aqueous phosphate activities fell (with an accompanying and necessary rise in pH), solution conditions evolved to be consistent with those associated with the continuing formation of pseudomalachite and, with the essential exhaustion of available phosphate, atacamite. Thus, the development of atacamite and secondary copper carbonate mineralization in E26 are seen as later, separate events. Pseudomorphs of atacamite, chrysocolla and, more rarely, pseudomalachite after sampleite noted in the oxidized zone of E26 (McLean *et al.* 2004) lend further support to the evolution of oxidizing conditions with time. Atacamite deposition in E26 took place after the phosphate suite had developed and was emplaced higher in the oxidized zone than still later secondary copper carbonates. Development of atacamite is thus seen as a natural consequence of a second mineralization event, resulting from available dissolved phosphate species being essentially exhausted, and a rise in pH as protons reacted with feldspars and the like. The development of atacamite versus malachite or azurite is dictated by the rising pH of mineralizing solutions and increasing partial pressure of $CO_2(g)$. Figure 2 illustrates relationships between atacamite, malachite and brochantite at 298.2 K, at a $p(CO_2)$ value of $10^{-1.36}$, corresponding to equilibrium conditions for malachite and azurite. Atacamite progressively encroaches on the stability fields of the other species as $a(Cl^-)$ increases. With respect to E26, for a value of lg $a(Cl^-) = -0.6$ (Table 1), brochantite can only form when $a(SO_4^{2-})$ is greater than $10^{-1.4}$. This is consistent with the fact that brochantite is very rare in E26 (McLean *et al.* 2004). As $p(CO_2)$ increased from, say, $10^{-3.5}$ (atmospheric) to 10^{-1} conditions pass progressively from those that would give rise to atacamite to those associated with malachite and azurite formation in turn. This simple geochemical picture serves to explain how all of the major Cu(II) minerals developed in E26 (and E22 and E27); in addition, it illustrates why phases common in other settings are not seen.

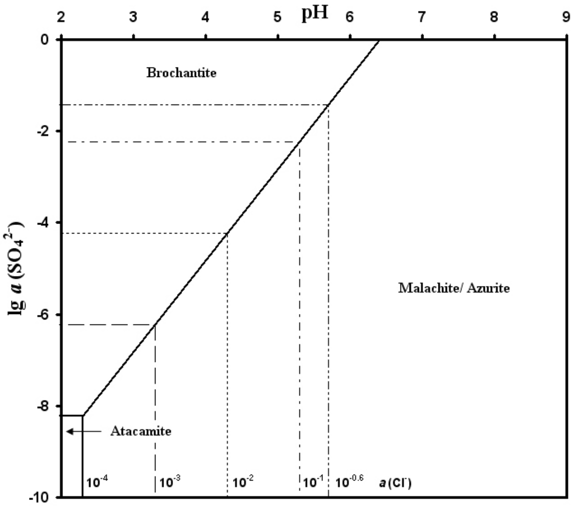

Figure 2: Stability field diagram for atacamite versus brochantite and malachite/azurite ($p(CO_2 = 10^{-1.36})$ at 298.2K.

GEOCHEMICAL DISPERSION OF COPPER

Leverett *et al.* (2004) described a method for estimating the extent of element mobility in ground waters at the New Cobar deposit, based on a reconstruction of ground water compositions. In adapting this to Northparkes, present day ground water compositions are taken as proxies as far as major cations and anions are concerned; this must be the case with respect to current metal mobilization in any event. First, as outlined above, major Cu mobilization attended the secondary phosphate event. Attention is now focused on subsequent chloride and carbonate mineralization. The approach is to use the ground water composition to calculate a total dissolved copper load in equilibrium with atacamite, malachite and azurite at given pH and $p(CO_2)$ values. Stability constant data for dissolved carbonate species, $CuHCO_3^+$, $CuCO_3°$, $Cu(CO_3)_2^{2-}$, $CuCl^+$ and $CuSO_4°$, together with malachite and azurite were taken from the literature (Martell & Smith 1982, Smith & Martell 1976, 1989, Williams 1990; Zirino & Yamamoto 1972). Corrections to activities were made in the usual way and total copper concentrations summed. At $pCO_2 = 10^{-3.5}$ and pH = 5, atacamite is stable with respect to E26 ground waters and malachite for E22. Total dissolved copper concentrations for the two E26 and the E22 ground water analyses are 3.66×10^{-3}, 3.74×10^{-3} and 4.07×10^{-2}, respectively. At $pCO_2 = 10^{-1.36}$ and pH = 7, when azurite is stable in all cases, total dissolved copper concentrations for the two E26 and the E22 ground water analyses are 3.29×10^{-6}, 3.33×10^{-6} and 2.89×10^{-6}, respectively. There is little evidence for increased total copper in solution as a result of elevated Cl^- activities associated with E26. More copper is in solution associated with malachite at lower pH values (E22), as expected, and greater dispersion will have taken place under conditions where lower Cl^- activities prevailed and atacamite could not form. This result seems counter-intuitive at first glance, but simply reflects solubility relationships for the carbonate minerals; acid reacts with carbonate and significant amounts of malachite and azurite can only form at higher pH values. However, copper dispersion from all three deposits (E22. E26 and E27) was most pronounced during the phosphate mineralizing event. In E22 (and presumably in E27) copper dispersion was greater than in E26 until approximately neutral pH was attained. Subsequently, there has been negligible difference in the relative extent of copper mobility. Taken together, these facts indicate that the copper geochemical signature of weathering Northparkes-style mineralization is independent of ground water salinity.

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REFERENCES

ARUNDELL M.C. 2004. Northparkes Cu-Au mines, central NSW. *In:* BUTT C.R.M., CORNELIUS M., SCOTT K.M. & ROBERTSON I.D.M. eds. *Regolith Expression of Australian Ore Systems*. CRC LEME, Perth, 3 pp. Available on-line at http://crcleme.org.au/.

CRANE M.J., SHARPE J.L. & WILLIAMS P.A. 1998. The mineralogy of the oxidized zones of the E22 and E27 orebodies at Northparkes, New South Wales. *Australian Journal of Mineralogy* **4**, 1-8.

CRANE M.J., SHARPE J.L. & WILLIAMS P.A. 2001. Formation of chrysocolla and secondary copper phosphate in the highly weathered supergene zones of some Australian deposits. *Records of the Australian Museum* **53**, 49-56.

HEITHERSAY P.S., O'NEILL W.J., VAN DER HELDER P., MOORE C.R. & HARBON P.G. 1990. Goonumbla porphyry copper district – Endeavour 26 North, Endeavour 22 and Endeavour 27 copper-gold deposits. *In:* HUGHES F.E. ed. *Geology of the Mineral Deposits of Australia and Papua New Guinea*. The Australasian Institute of Mining and Metallurgy, 1385-1398.

LEVERETT P., MCKINNON A.R. & WILLIAMS P.A. 2004. A supergene exploration model for Cobar style deposits. *In:* MCQUEEN K.G. & SCOTT K.M. eds. *Exploration Field Workshop Cobar Region 2004, Proceedings*. CRC LEME, Perth, 46-50.

MARTELL A.E. & SMITH R.M. 1982. *Critical Stability Constants. Volume 5: First Supplement*. Plenum Press, New York.

MCLEAN A.L., CHAPMAN J., SHARPE J.L. & WILLIAMS P.A. 2004. The mineralogy of the oxidized zone of the E26 ore body at Northparkes, New South Wales. *Australian Journal of Mineralogy* **10**, 53-58.

MISRA D.N. 1999. Interaction of citric or hydrochloric acid with calcium fluorapatite: precipitation of calcium fluoride. *Journal of Colloid and Interface Science* **220**, 387-391.

O'SULLIVAN P.B., GIBSON D.L., KOHN B.P., PILLANS B. & PAIN C.F. 2000. Long-term landscape evolution of the Northparkes region of the Lachlan Fold Belt, Australia: constraints from fission track and paleomagnetic data. *Journal of Geology* **108**, 1-16.

PILLANS B., TONUI E. & IDNURM M. 1999. Paleomagnetic dating of weathered regolith. *In:* TAYLOR G. & PAIN C. eds. *New Approaches to an Old Continent*. Proceedings of the Regolith 98 Conference, Kalgoorlie, May 1998. CRC LEME, Perth, pp. 237-242.

ROBIE R.A. & HEMINGWAY B.S. 1995. Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10^5 Pascals) pressure and at higher temperatures. *United States Geological Survey Bulletin* **2131**.

SMITH R.M. & MARTELL A.E. 1976. *Critical Stability Constants. Volume 4: Inorganic Complexes*. Plenum Press, New York.

SMITH R.M. & MARTELL A.E. 1989 *Critical Stability Constants. Volume 6: Second Supplement*. Plenum Press, New York.

WILLIAMS P.A. 1990. *Oxide Zone Geochemistry*. Ellis Horwood, Chichester.

ZIRINO A. & YAMAMOTO S. 1972. A pH-dependent model for the chemical speciation of copper, zinc, cadmium and lead in seawater. *Limnology and Oceanography* **17**, 661-671.