SUPERGENE GEOCHEMISTRY OF THE ENDEAVOR ORE BODY, COBAR, NSW, AND RELATIONSHIPS TO OTHER DEPOSITS IN THE COBAR BASIN

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INTRODUCTION

The Endeavor lead-zinc-silver deposit (previously called the Elura deposit) is located approximately 45 kilometres NNW of Cobar and is currently the largest operating mine in the Cobar Basin. The deposit was discovered in 1974 and is presently being mined via underground methods. Limited mining at the base of the oxidized zone occurred during the mid 1980s and early 1990s, with ore from this zone containing very high grades of silver along with appreciable lead, copper and gold (Schmidt 1990). As with the majority of deposits in the Cobar Basin, the nature of the supergene mineralogy at this deposit is not well understood, although several publications have appeared concerning it (Chapman & Scott 2005, Scott 1987, 1994, Scott & Taylor 1987, 1989, Taylor *et al.* 1984). The present study has identified an extensive suite of secondary minerals, many exotic, and many which have not previously been reported from the deposit. A thorough investigation of the assemblage is a vital first step in modelling the chemistry of the supergene zone. This in turn can lead to a better understanding of the formation of geochemical anomalies associated with “Cobar style” mineral deposits, and the chemical mechanisms responsible for them. Initial modelling of the deposit suggests that the supergene zone shows many similarities to that of the New Cobar Au-Cu deposit (McKinnon 2003, Leverett *et al.* 2003), and other deposits in the Cobar Basin.

PRIMARY MINERALISATION

A note on the primary mineralogy is warranted as it directly affects observations made concerning the supergene zone. Schmidt (1990) notes that the sulfides present, in decreasing order of abundance, are pyrite > sphalerite > pyrrhotite > galena > arsenopyrite > chalcopyrite > tetrahedrite, with several very minor phases, including enargite and tennantite. With the exception of tennantite, all have been observed in the present study, along with minor bornite and primary chalcocite. A notable difference with respect to other deposits in the Cobar Basin is the predominance of Pb, Zn and Ag in the ore, with the other deposits tending to be more Cu-Au rich (Stegman & Pocock 1996). The location of silver in primary ore has not been discussed in the open literature, although Lawrie & Hinman (1998) refer to silver-rich tetrahedrite being present. Not surprisingly, microprobe analyses have shown that silver is present in very large amounts in the tetrahedrite, although contents do not reach the levels associated with the phase freibergite. Analyses of tetrahedrite grains from core in the southernmost ore zone give an average 19.33 wt. % Ag, and a derived formula based on a total of 13 S+Se atoms of $(Cu_{6.85}Ag_{3.19})(Fe_{1.36}Zn_{0.67})(Sb_{3.98}As_{0.07})(S_{12.97}Se_{0.03})$. This confirms that the high grades of silver in the supergene enriched zone are a result of the oxidation and subsequent enrichment from the weathering tetrahedrite, and minor primary acanthite. Despite the large amount of Hg associated with silver in the supergene enriched zone, no Hg was detected in the tetrahedrite. Element mapping of primary ore minerals shows that Hg is almost exclusively associated with galena. It may be included in the lattice at low concentrations (< 200 ppm) or be present as sub-microscopic inclusions of cinnabar. In any event, the levels of mercury are low in absolute terms. The observation of secondary antimony minerals in the supergene is also consistent with the weathering of tetrahedrite, although antimony has been analysed in arsenopyrite at levels of up to 2.5 wt. %.

SUPERGENE MINERALOGY

Taylor *et al.* (1984) described the general features of the supergene zone and its mineralogy. The southernmost ore body is completely oxidized to a depth of 103 m, whereas host rock is weathered to 84 m. Partial weathering of wall and host rocks (structurally controlled) has been observed at depths of up to 153 m. Apart from chemically resistant phases, the gossan is dominated by kaolinite, goethite and hematite. Residual cassiterite is prominent in many of the samples examined in the present study, as noted by other workers (Scott & Taylor 1989, Taylor *et al.* 1984). Not all of the Sn is present as cassiterite, however; remnant stannite was identified during the course of this study in supergene enriched sulfide ore from the 1 Drill Level. Studies of the supergene enriched zone (Scott 1987, Scott & Taylor 1987,1989) identified some of the more common secondary minerals present in the deposit, as well as several exotic species such as lead oxy- and hydroxychlorides (Scott 1994). The present study is based on samples collected from the 1 Drill Level in the early 1990s and material sampled from diamond drill holes that passed through the oxidised zone of the ore body. Mineral phases were identified using powder X-ray diffraction in conjunction with

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SEM/EDAX and electron microprobe analyses. Minerals identified here are listed in Table 1, along with those reported by others.

Table 1: Supergene mineralogy of the Endeavor deposit. Minerals identified in this study are highlighted in bold script. Gangue species such as goethite, hematite, quartz, clays and the like are omitted.

Acanthite	Ag_2S	**Eugenite**	Ag_9Hg_2 to $Ag_{11}Hg_2$
Alunite	$KAl_3(SO_4)_2(OH)_6$	**Galena**	PbS
Anglesite	$PbSO_4$	**Gypsum**	$CaSO_4.2H_2O$
Argentojarosite	$AgFe_3(SO_4)_2(OH)_6$	**Hidalgoite**	$PbAl_3AsO_4SO_4(OH)_6$
Barite	$BaSO_4$	**Imiterite**	Ag_2HgS_2
Beudantite	$PbFe_3AsO_4SO_4(OH)_6$	Lanarkite	Pb_2OSO_4
Blixite	$Pb_2Cl(OH)_3$	Laurionite	$PbOHCl$
Bornite	Cu_5FeS_4	**Luanheite**	Ag_3Hg
Brochantite	$Cu_4SO_4(OH)_6$	**Malachite**	$Cu_2CO_3(OH)_2$
Cassiterite*	SnO_2	Marcasite	FeS_2
Cerussite	$PbCO_3$	Mendipite	$Pb_3O_2Cl_2$
Chalcanthite	$CuSO_4.5H_2O$	**Mimetite**	$Pb_5(AsO_4)_3Cl$
Chalcocite	Cu_2S	Nadorite	$PbSbO_2Cl$
Chalcopyrite*	$CuFeS_2$	**Philipsbornite**	$PbAl_3H(AsO_4)_2(OH)_6$
Chlorargyrite	$AgCl$	**Plumbojarosite**	$Pb_{0.5}Fe_3(SO_4)_2(OH)_6$
Chursinite	$(Hg_2)_3(AsO_4)_2$	**Pyrite**	FeS_2
Copper	Cu	**Roxbyite**	Cu_9S_5
Coronadite	$PbMn_8O_{16}$	**Silver**	Ag
Covellite	CuS	**Sphalerite***	ZnS
Dervillite	Ag_2AsS_2	**Spionkopite**	$Cu_{39}S_{28}$
Digenite	Cu_9S_5	**Stannite***	Cu_4FeSnS_8
Dyscrasite	Ag_3Sb	**Stibiconite**	Sb_3O_6OH
Electrum	(Au,Ag,Hg)	Tripuhyite	$(Fe,Sb)O_2$
Enargite	Cu_3AsS_4	**Uraninite***	UO_2
Epsomite	$MgSO_4.7H_2O$	**Yarrowite**	Cu_9S_8

*Probable remnant primary phases

The presence of large quantities of native silver at the base of oxidation is noteworthy. Microprobe analyses reveal that at least two generations of native silver are present, with one generation being Hg-poor and the other containing between 10-34 wt. % Hg. Consistent analyses revealed the presence of luanheite, eugenite, and mercurian silver (amalgam). The occurrence of the very rare minerals imiterite and chursinite further attest to the large amount of mercury in the system. Secondary acanthite occurs frequently as black coatings on native silver, and less often in large pods associated with imiterite and beudantite. Chlorargyrite is developed preferentially on low-Hg native silver, with some of the chlorargyrite containing significant Br. The supergene enriched silver assemblage is consistent with the weathering (and subsequent enrichment) of silver from tetrahedrite, as is the formation of the secondary antimony minerals stibiconite, tripuhyite and nadorite. The secondary copper sulfides covellite and chalcocite, along with lesser enargite and dervillite are encountered in the lowest section of the oxidised zone as black/grey powdery masses. Diginite, roxbyite, yarrowite and spionkopite have also been identified, sometimes in significant quantities, with some being markedly enriched in Ag. The zone is also marked by the presence of cerussite, often coated by a thin layer of beudantite or brochantite, and frequently associated with massive anglesite. Minor replacement of anglesite by blixite, lanarkite, laurionite and mendipite has been reported (Scott 1994). Mimetite is the most common and widespread lead mineral, occurring at the base of the oxidized zone, and for tens of metres up into the gossan. It occurs in a variety of habits ranging from large prismatic crystals to massive material associated with native silver, and shows multiple overgrowths in cut section. The alunite-jarosite group of minerals is well represented in the deposit, with beudantite, hidalgoite and plumbojarosite commonly occurring in close association with mimetite. Light grey massive argentojarosite is associated with acanthite and native silver.

OXIDIZED ZONE GEOCHEMISTRY

The occurrence of most minerals in the oxidized zone can be described using appropriated stability field diagrams. Figure 1 refers to Cu(II) and Pb(II) arsenates at 298.2K. In this case, philipsbornite is used as a proxy for all alunite-jarosite type minerals, as thermodynamic data are not available for beudantite or hidalgoite. The diagram clearly illustrates that in acidic environments, and with all but high activities of Cu^{2+}, mimetite and philipsbornite dominate the Cu-Pb-As-Cl system. Any increase in the activity of Cl^- will also serve to enlarge the stability field for mimetite. This is reflected in the persistence of mimetite throughout the oxidized zone of the Endeavor deposit. The presence of alunite-jarosite type minerals throughout the supergene zone is also indicative of a comparatively low pH, as is the presence of the sulfate minerals anglesite and chalcanthite (Williams 1990). The supergene enriched zone is still chemically active with chalcanthite-saturated pore waters being associated with the weathering front. Although siderite is present in the gangue, it is pH neutral in its weathering reactions and does not serve to raise the pH. A limestone unit deep in the system (Lawrie & Hinman 1998) does not influence the oxidized zone. The presence of cerussite, however, which cannot form at a low pH, indicates that at least three separate mineralising events took place, an initial acidic event associated with the preliminary oxidation of sulfides, a high chloride activity "overprint", and a subsequent carbonate event after much of the acid had been neutralised. The first is typified by jarosite-group species, anglesite and lanarkite, and this was followed by multiple generations of mimetite with arsenate being derived mainly from the oxidation of arsenopyrite. Other minor chlorides formed at this stage as well. These observations confirm those of Scott (1994) with respect to high acidity being a feature of the early stages of oxidation of the deposit. Cerussite could only have been a stable phase when acidity had been considerably reduced and arsenate essentially exhausted in mineralising solutions.

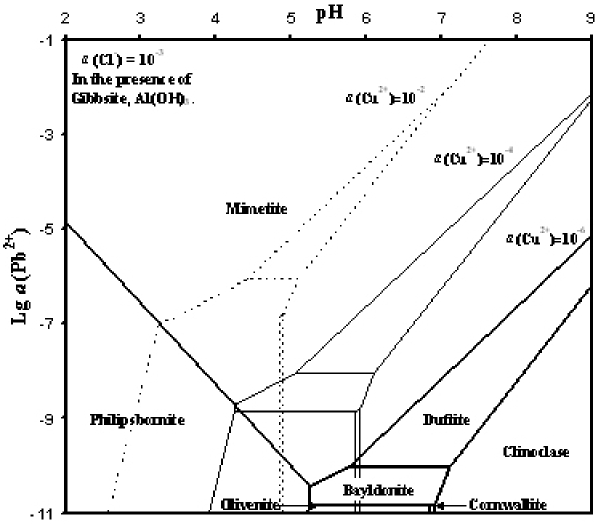

Figure 1: Stability field diagram for Cu(II) and Pb(II) arsenates at 298.2K in the presence of gibbsite, with activity of Cl^- = 10^{-3} and activity of Cu^{2+} as indicated.

The development of multiple stages in the formation of oxidized zones have been identified as a feature of deposits in the Cobar Basin. The oxidized zone of the New Cobar deposit (McKinnon 2003, Leverett *et al.* 2003) shares many similarities with the Endeavor deposit. It contains significant mimetite along with philipsbornite and its iron analogue, segnitite. Although cerussite is rare, malachite and azurite are prominent, but formed after the arsenate minerals had crystallized. The presence of bayldonite, $Cu_3Pb(AsO_4)_2(OH)_2$, duftite, $CuPbAsO_4(OH)$, and olivenite, $Cu_2AsO_4(OH)$, all of which are absent in the Endeavor deposit, is a result of a higher copper activity and a slightly less acidic pH regime. The absence of any significant cerussite, and the dominance of malachite and azurite, suggests that there was enough arsenic to fix much of the lead but not all of the copper. At the Endeavor mine, however, insufficient arsenic is available to fix all of the lead, with phases such as anglesite and cerussite forming as well. At Mineral Hill, to the south of Cobar, malachite, azurite and cerussite are common, as is pyromorphite (the phosphate analogue of mimetite) and phosphatian members of the alunite-jarosite group. The oxidized zone of the May Day deposit carries mimetite and beudantite, along with copper, lead and zinc carbonates. Mimetite and hidalgoite are the main Pb-bearing phases in the Cobar-Lyell deposit contains, along with copper and lead carbonates. Pyromorphite and beudantite are present in dump material at the Spotted Leopard shaft, south of the CSA mine, together with minor malachite. In all cases, Pb-As(P) mineralisation was emplaced first under more acid conditions than those that prevailed when base metal carbonates were subsequently emplaced.

METAL DISPERSION IN *IN SITU* REGOLITH

Chemical dispersion of metals away from an oxidized ore body is dependent on the minerals present and the chemistry of interacting solutions. Chemical modelling of the New Cobar ore body (McKinnon 2003, Leverett *et al.* 2003) showed that it is possible to predict the extent to which base metals will be dispersed, under various geochemical conditions. The presence of significant arsenate led to a secondary Pb assemblage that is much more insoluble in aqueous solution than the dominant Cu-carbonate assemblage. Thus the chemical basis of the differential dispersion of Pb and Cu was established. Similarly, extensive development of mimetite and Pb-bearing members of the jarosite supergroup in the Endeavor deposit has served to fix much Pb (and As), even under acid weathering conditions, while no such insoluble Zn phases formed. Little Cu is present at Endeavor. Thus an analogously restricted Pb(As) geochemical anomaly is predicted in this case as well and this appears to be born out by other workers (Taylor *et al.* 1984). In other deposits that have been examined, similar secondary Pb mineralization has been encountered, except for the presence of pyromorphite and cerussite in certain cases. As far as the former is concerned, the phosphate has solubility characteristics akin to those of mimetite. Cerussite is more soluble (certainly in acid solution) but is much more stable than smithsonite ($ZnCO_3$) and the copper carbonates in the oxidized zone. Thus, as far as geochemical anomaly development in *in situ* regolith is concerned, anomalous Pb and As is expected to be confined to the immediate environment of mineralized zones in this setting, and elsewhere in the Cobar Basin. Cu will be dispersed more widely, and because of the acid regime attending the early development of oxidized assemblages in the deposits of the Cobar Basin that have been examined, Zn will be extensively leached. Smithsonite has been encountered only in minor amounts at the May Day and Tharsis deposits. These observations should be of use in target selection as long as this would involve samples taken from *in situ* weathered material. An additional geochemical guide to the proximity of mineralization is Sn, given that cassiterite is chemically unreactive and present in most of the deposits in the region.

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