

## MINERALOGY OF THE OXIDISED ZONE AT THE NEW COBAR OREBODY

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The “signature” for geochemical dispersion in the supergene environment for “Cobar-style” mineralisation is not well understood. Such an understanding would be germane to the development of exploration models that could be applied to deeply weathered terrane in the Cobar region. It would in turn rest on an understanding of the oxidized zone mineralogy that forms above the water table and although this is known in the most general terms, no recent systematic study of oxidized mineralogy in the region has been undertaken. The current open cut mining operation associated with the New Cobar orebody has provided an unparalleled opportunity to study the oxidized zone of Cobar-style deposits. The deposit is located in the central west of New South Wales, approximately 3 km south of the township of Cobar and is one of a number of north-south trending, structurally controlled, gold and base metal deposits in the area, including the New Occidental and Peak mines to the south, and the CSA and Elura mines to the north. An extensive study of the mineralogy of the oxidized zone at New Cobar has now been carried out. New Cobar is primarily a gold-copper deposit carrying minor lead, zinc, bismuth and other base metals in minor to trace amounts. Mineralisation is contained wholly within the Devonian age Great Cobar Slate formation and forms an elongated lens associated with a steeply dipping, second order splay from the Great Chesney fault (Stegman & Pocock 1996).

The study has identified a large suite of copper and lead minerals, a significant proportion of which have not been previously reported from the Cobar mining area. Minerals identified to date are summarized in Table 1.

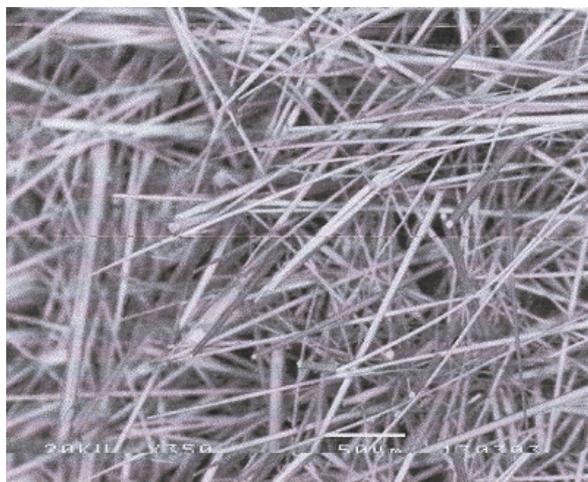
**Table 1:** Minerals found in the oxidized zone of the New Cobar deposit.

Acanthite	Ag <sub>2</sub> S
Agardite-(Nd)*	Cu <sub>6</sub> (Nd,LREE,Al)(AsO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> .3H <sub>2</sub> O
Arsenopyrite	FeAsS
Atacamite	Cu <sub>2</sub> (OH) <sub>3</sub> Cl
Azurite	Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>
Barite	BaSO <sub>4</sub>
Bayldonite	Cu <sub>3</sub> Pb(AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>
Berzelianite	Cu <sub>1.8</sub> Se
Bismutite	Bi <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>
Cassiterite	SnO <sub>2</sub>
Chenevixite	Cu <sub>2</sub> Fe <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>4</sub> .H <sub>2</sub> O
Chalcocite	Cu <sub>2</sub> S
Chalcopyrite	CuFeS <sub>2</sub>
Chlorargyrite (bromian)	Ag(Cl,Br)
Chrysocolla	CuSiO <sub>3</sub> .nH <sub>2</sub> O
Covellite	CuS
Cuprite	Cu <sub>2</sub> O
Duftite	PbCuAsO <sub>4</sub> (OH)
Gartrellite	PbCuFe(AsO <sub>4</sub> ) <sub>2</sub> (OH).H <sub>2</sub> O
Iodargyrite	AgI
Malachite	Cu <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub>
Mandarinoite	Fe <sub>2</sub> Se <sub>3</sub> O <sub>9</sub> .6H <sub>2</sub> O
Mimetite	Pb <sub>5</sub> (AsO <sub>4</sub> ) <sub>3</sub> Cl
Olivenite	Cu <sub>2</sub> AsO <sub>4</sub> (OH)
Philipsbornite	PbAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> .H <sub>2</sub> O
Plumbogummite	PbAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> .H <sub>2</sub> O
Segnitite	PbFe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> .H <sub>2</sub> O
Ungemachite	K <sub>3</sub> Na <sub>8</sub> Fe(SO <sub>4</sub> ) <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O
Wulfenite	PbMoO <sub>4</sub>

\*Descriptive name only. Agardite-(Nd) has not yet been accepted as a separate mineral species by the IMA.

In the top levels of the orebody, which is exposed at surface, extensive leaching has led to the development of a quartz-rich hematite-goethite gossan. This contains, *inter alia*, remnant resistate minerals, such as cassiterite, and secondary barite, jarosite, clays and gibbsite. An azurite/malachite/cuprite assemblage dominates the copper mineralogy of the upper levels of the oxidized zone and these species have infiltrated the country rock away from the central mineralised lode. Azurite and malachite form the bulk of the copper ore in the oxidized zone, occurring together in massive form, often filling fracture spaces in siliceous, brecciated lode material. Malachite is also found as dense “mats” of acicular crystals up to 10 mm long amongst gossanous material and on fracture faces. Azurite is found as earthy fracture fill and as crystalline material in tight vugs; it is frequently associated with intergrowths of malachite. While not as common as the copper carbonates, cuprite is seen in nearly all parts of the oxidized zone. It occurs most frequently as small, glassy, red patches amongst malachite and as a soft red/brown powder associated with secondary copper sulfides. Cuprite has also been identified as a late-stage mineral in the arsenate assemblages (*vide infra*), occurring as small, dark red to black, octahedral crystals. The rare minerals ungemachite, mandarinoite and wulfenite were all detected in waxy orange/green coatings in samples from the 235 RL. The coatings were also found to contain malachite and iodargyrite, while elsewhere in the same material covellite veinlets were found to contain minor amounts of the rare copper selenide berzelianite. Energy dispersive X-ray analysis of material from the same level identified small quantities of the minerals plumbogummite and acanthite, together with considerable amounts of cassiterite.

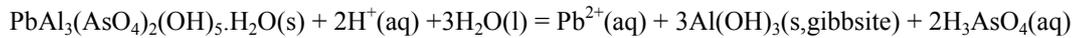
A significant copper/lead arsenate mineral assemblage has been identified from below 225 RL, in the central mineralised zone of the deposit. Of the eight individual arsenate minerals identified, seven have not been reported from the Cobar region previously. All of the arsenate mineralisation is confined to heavily weathered, quartz-rich lode material, often showing small patches of partially oxidized arsenopyrite. Segnitite is the most common arsenate mineral, occurring as powdery yellow coatings and occasionally as very small yellow to brown euhedral crystals. Philipsbornite, the aluminium analogue of segnitite, has also been identified in the deposit as yellow to green powdery coatings on quartz. Almost as common as segnitite is chenevixite, which occurs in dull, khaki green masses, often investing hematite. Chenevixite is also occasionally seen as very small, pale green plates and rarely as shiny mamillary coatings on goethite; it is the first arsenate to form. Olivenite occurs in the deposit as olive green, bladed crystals and is almost exclusively found in association with chenevixite. Bayldonite and duftite are found together in this arsenate assemblage, with duftite being the paragenetically later phase. Bayldonite generally forms as vitreous, grass green, flattened octahedral crystals, with poorly defined crystal faces. Less commonly it forms a dull green coating with individual crystals not discernable. Duftite is only slightly darker in colour than bayldonite but the two are easily separated due to the fact that duftite forms pyramidal crystals with very well defined, triangular crystal faces. Gartrellite, which occurs in bright yellow-green powdery masses, appears to have formed around the same time as bayldonite. Mimetite is one of the last arsenates to form as off-white to yellow hexagonal prisms up to 10 mm long. Agardite-(Nd) is usually encountered in small quantities wherever other arsenate minerals have formed. The mineral occasionally forms small, flat sprays, but is more commonly seen as masses of randomly oriented, sky blue needles sitting on and around quartz, azurite and bayldonite. It is also often seen in close association with olivenite, chenevixite, segnitite, and arsenopyrite. SEM images of agardite-(Nd) show that the needles are elongated hexagonal prisms that rarely exceed 2 mm in length and range from 2-10  $\mu\text{m}$  in width (Figure 1). The mineral is the last to form in the assemblage and is always found as a coating on other arsenates as well as on azurite and hematite. The neodymium-rich variety of agardite has not as yet been officially been accepted as a new mineral species by the International Mineralogical Association (IMA), and thus the name “agardite-(Nd)” is used only in a descriptive sense.



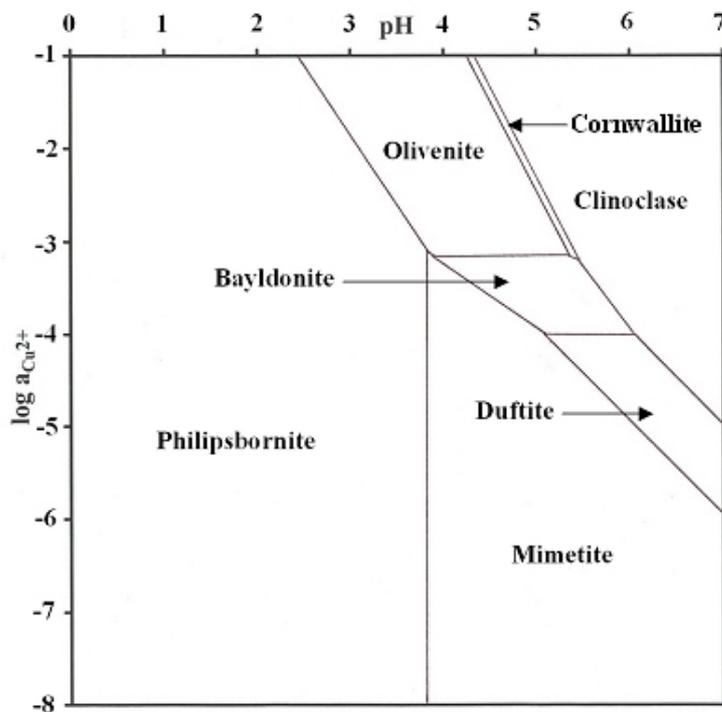
**Figure 1:** Agardite-(Nd) crystals perched, in this case, on chenevixite and quartz.

The existence of jarosite-alunite supergroup members of the crandallite-arsenocrandallite groups is a particular feature of the arsenic-rich assemblage of the New Cobar oxidized zone. In order to assess their modes of formation, we have used the published stability constant data of Schwab *et al.* (1993) for philipsbornite. Data are reported for a temperature of 333 K for members of stoichiometry  $\text{MAl}_3(\text{AsO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$  with  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ,

and Pb, as well as for a number of phosphate analogues. Stability constants for the latter are given for both 298 and 333 K. There is little difference in the calculated free energies of formation of the phases at the two temperatures. The stability constant for philipsbornite at 333K was corrected to 298K using the Clausius-Clapeyron equation, on the basis that the dependence on enthalpy for the phosphate and arsenate analogues is approximately equal, in line with observations concerning the very small differences (approx. 5 kJ mol<sup>-1</sup>) between  $\Delta fG^0$  values at the two temperatures for all examples given. Substitution of values of  $\Delta fG^0$  for the constituent species in the equation



(taken from Robie & Hemingway (1995) and a value for  $\Delta fG^0(\text{H}_3\text{AsO}_4, \text{aq}, 298.2\text{K})$  calculated from the stability constant data of Martell & Smith (1982) for arsenic acid and its conjugate anions in conjunction with a free energy value (Barner & Scheuerman 1978) for aqueous  $\text{AsO}_4^{3-}$ ) yields a value of  $-4361.2 \text{ kJ mol}^{-1}$  for  $\Delta fG^0(\text{philipsbornite}, \text{s}, 298.2\text{K})$ . Appropriate modifications to the phase diagram of Williams (1990) so as to include philipsbornite, together with mimetite, in relation to the copper and copper-lead arsenate minerals found at New Cobar (Figure 2), show that the lead-rich arsenate assemblage was developed at pH values between 3 and 5. Figure 2 is constructed for a  $\text{Pb}^{2+}$  activity of  $10^{-8}$  (in concentration terms, approximately 2 ppb). Even at such a low activity, the stability fields of the mixed Cu-Pb minerals encroach quite markedly on those containing copper alone. Olivenite must have crystallized under conditions of negligible Pb ion activities and it is noted that olivenite has not been seen directly associated with the lead arsenates. Furthermore, no cornwallite or clinoclase has been detected at New Cobar, in line with the conclusion that the secondary Pb-Cu suite formed under acidic conditions. Contributions from more than one cycle of secondary arsenate mineralisation are evident from paragenetic relationships. Mimetite is the last Pb-bearing arsenate to form in some specimens, but pseudomorphs and endomorphs of bayldonite and duftite after mimetite have been recovered from material from the 205 RL. This is evidence too of a subtle interplay of Pb and Cu ion activities in conjunction with varying chloride activities. The latter is probably contributed by groundwater, either by cyclical inundation or capillary action. These results explain why negligible cerussite is found in the assemblage, the system being too acidic. We note in passing that at New Cobar cerussite has been detected in only very minor amounts in a single powder X-ray trace of a total of some 150 samples. It is evident that, in this deposit, sufficient arsenate was available from the oxidation of arsenopyrite to fully account for the



**Figure 2:** Stability diagram calculated at 298.2 K for the main Cu(II) and Pb(II) arsenate minerals. Boundaries are calculated for activities of  $\text{Pb}^{2+}(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  equal to  $10^{-8}$  and  $10^{-3}$ , respectively. Higher chloride activities serve to make the stability fields of bayldonite and duftite vanish, with respect to the encroachment of that of mimetite.

amount of lead released during the oxidation of galena and other Pb-bearing sulfosalts. This pattern of mineralisation is reflected in the Spotted Leopard deposit, some 6 km north of Cobar, and situated between the Great Cobar and the CSA mines. Philipsbornite is present in gangue from the dump and presumably this is the material tentatively identified as corkite by Rayner (1969). However, later pyromorphite,  $\text{Pb}_3(\text{PO}_4)_3\text{Cl}$ , rather than mimetite, is associated with the philipsbornite in this case. Thus it is evident that separate P- and As-rich solutions were involved in the development of the oxidized Pb assemblage in this instance. No cerussite was found in samples taken from the dump.

The conspicuous absence of cerussite,  $\text{PbCO}_3$ , in the oxidized zone of New Cobar and at Spotted Leopard is noteworthy. Little carbonate is present in the primary gangue at New Cobar and stable isotope measurements in-

dicating a significant biological contribution to carbonate in the oxidized zone. The lead arsenate phases are comparatively insoluble and Pb is dispersed in the oxidized zone to a far more limited extent than is Cu. Secondary New Cobar mineralisation has further parallels with related material at the Elura mine, except for the fact that in the latter deposit cerussite was common. In this case, insufficient arsenate was available to fix all of the lead and it is likely that the cerussite and mimetite mineralising events at Elura were not simultaneous. Modelling of the chemistry of the lead-copper arsenate assemblage, in contrast to the malachite-azurite assemblage, indicates potential applications for exploration geochemistry in the region.

Finally, the occurrence of agardite-(Nd) in the arsenate assemblage could be further used to delineate the geochemical conditions prevailing at the time the mineralised suite was formed. Unfortunately, no thermochemical data for this phase are available although experiments are in progress to determine a stability constant for agardite-(Y), as an archetype for the group. Since naturally occurring agardite in the New Cobar deposit is rather sparse in its distribution, we have been forced to resort to synthesizing the mineral. A further advantage to this approach is that pure end-member compositions can be achieved. Fortunately, a simple hydrothermal method has proven to be effective and samples of the pure end-members agardite-(Y), -(La), -(Ce), -(Pr), -(Nd), -(Sm), and -(Eu) have been synthesised. A plot of refined  $a$  cell constants for the series against the 9-coordinate radius of the REEs gives a straight line in harmony with the lanthanide contraction. Mixite is the  $\text{Bi}^{3+}$  analogue of agardite, and this can be prepared by an analogous method. The plot can be used to estimate the hitherto unknown effective ionic radius of 9-coordinate  $\text{Bi}^{3+}$  and a value of 115 pm is obtained. However, mixite has not been observed at New Cobar, and the only secondary bismuth mineral detected in the deposit is bismutite.

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