CHEMICAL MINERALOGY OF SUPERGE/NE
COPPER DEPOSITS OF THE CLONCURRY
DISTRICT, NORTH-WEST QUEENSLAND

A thesis submitted in partial fulfillment of the requirements for the degree
of Master of Science with Honours in the University of Western Sydney

by James Leslie Sharpe ASTC(Mech. Eng.) (STC)

November, 1998
PLEASE NOTE

The greatest amount of care has been taken while scanning this thesis,

and the best possible result has been obtained.
I declare that the work in this thesis has not been submitted to any other University for any other degree. I further declare that the thesis represents my own work, except where that of others is acknowledged.

[Signature]

James Sharpe
To my wife, Marie, I thank for her patience and support, without which I could not have completed this thesis.
ACKNOWLEDGEMENTS

I wish to thank Cloncurry Mining Company N.L. for permission to study the deposits at the Great Australia and Monakoff mines and to thank the staff, in particular Jim and Annette Heape for their support in locating many of the small mines in the district and Brett Tulloch and Grahame Pratt for their advice in relation to the Great Australia.

Murchison Resources are thanked for their permission to study the Mt. Cuthbert group and Majestic Resources N.L. for permission to study in the White Range. Arimco Mining Pty. Limited kindly arranged visits to Mt. Elliott and Selwyn.

In this endeavour I was helped on many occasions by the people of Cloncurry. In particular, I am grateful to Joe Vipen who guided us in remote areas when maps proved inadequate.

Foremost, I wish to thank my supervisor, Prof. Peter Williams, not only for his guidance, but for providing me with a wider insight into the science of mineralogy.
The following papers have been written in support of this thesis:


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Summary

The research described in this thesis has led to an understanding of the geochemical conditions controlling the formation, paragenesis and distribution of oxide zone copper species in the Eastern Fold Belt of the Mt. Isa Inlier. This area is also known as the Cloncurry Complex.

The regional geology and genesis of the copper deposits is reviewed and the deposits of particular interest to the study are described. Oxidation of pyrite and chalcopyrite by oxygen-bearing groundwater and the sources and mechanisms by which anions are carried by groundwater to reaction sites to form secondary copper species are discussed.

Physical and chemical conditions control the development of particular species. Equilibrium phase diagrams have been constructed to represent the stability fields for copper sulfate, phosphate, chloride, carbonate, nitrate, arsenate and silicate species. Where stability field data have not previously been published, thermodynamic data have been used to calculate stability limits. Stability data for the rare copper(I) chloride, nantokite, is of particular note as it provides an explanation for the extreme rarity of this mineral. Nantokite is abundant in the lower oxide zone of the Great Australia mine. An explanation for the relative abundance and spatial distribution of the basic copper phosphates is also provided.

Stability field data supported by observations made on deposits in the Cloncurry district and elsewhere provides a basis for assessing the paragenesis and distribution of secondary copper species in this and similar environments. This is discussed and illustrated using the Great Australia mine as a model.
List of minerals

All copper minerals referred to in this study are included in this list. Other common species are dealt with in the text.

Primary minerals

Pyrite \( \text{FeS}_2 \)
Chalcopyrite \( \text{CuFeS}_2 \)
Arsenopyrite \( \text{FeAsS} \)
Cobaltite \( \text{CoAsS} \)
Bismuthinite \( \text{Bi}_2\text{S}_3 \)

Secondary copper minerals

Copper \( \text{Cu} \)
Cuprite \( \text{Cu}_2\text{O} \) \( \text{(chalcolithite is a variety of cuprite)} \)
Tenorite \( \text{CuO} \)
Brochantite \( \text{Cu}_4\text{(SO}_4\text{)}_2\text{H}_2\text{O} \)
Antlerite \( \text{Cu}_4\text{(SO}_4\text{)}_2\text{H}_2\text{O} \)
Chalcanthite \( \text{CuSO}_4\cdot\text{H}_2\text{O} \)
Malachite \( \text{Cu}_2\text{(CO}_3\text{)}_2\text{(OH)}_2 \)
Azurite \( \text{Cu}_2\text{(CO}_3\text{)}_2\text{(OH)}_2 \)
Cornetite \( \text{Cu}_2\text{(PO}_4\text{)}\text{(OH)}_4 \)
Pseudomalachite \( \text{Cu}_2\text{(PO}_4\text{)}\text{(OH)}_4 \)
Libethenite \( \text{Cu}_2\text{(PO}_4\text{)}\text{(OH)}_4 \)
Hentschelite \( \text{CuFe}_2\text{(PO}_4\text{)}\text{(OH)}_6 \)
List of minerals (cont.)

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<td>Metatorbernite</td>
<td>Cu(UO₂)₆(PO₄)₂·8H₂O</td>
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**Other secondary minerals**

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<td>Wupatkiite</td>
<td>(Co,Mg,Ni)Al$_2$(SO$_4$)$_4$.22H$_2$O</td>
</tr>
<tr>
<td>Autunite</td>
<td>Ca(UO$_2$)$_2$(PO$_4$)$_2$.10-12H$_2$O</td>
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<td>Phurcalite</td>
<td>Ca$_2$(UO$_2$)$_3$(PO$_4$)$_2$(OH)$_4$.4H$_2$O</td>
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<tr>
<td>Beyerite</td>
<td>(Ca,Pb)Bi$_2$(CO$_3$)$_2$O$_2$</td>
</tr>
</tbody>
</table>
1. Introduction

1.1 General Description

The Cloncurry district of north-west Queensland lies in the transition zone between the wet tropics and arid inland of northern Australia (Fig. 1-1). The area is semi-arid with a mean annual rainfall of 430 mm, most of this falling between November and March and with summer daytime temperatures often exceeding 40° C. The vegetation is generally sparse, dominated by *Spinifex* and scattered low eucalypt.

![Location map - Cloncurry district.](image)

Fig. 1-1. Location map - Cloncurry district.

Just 117 kilometres from the industrial giant of Mount Isa (Fig. 1-2), Cloncurry has remained primarily a gouger’s field for nearly 100 years. However, with new technology a new era of mining has commenced, bringing new life to this pioneering town.

1.2 Historical Background

The products of the intense geological processes which occurred in the region were utilized long before Europeans arrived on the scene in their search for pastures and minerals.
Cloncurry landscape
Fig. 1-2. Map showing the Mt. Isa - Cloncurry region.
(from North Queensland, Department of Lands, Queensland, 1990).
The Kalkadoons and Mitakoodi, independent and fierce aboriginal tribes whose extensive tribal areas covered much of the Cloncurry mining district, used and traded tools and other artefacts manufactured from chert, quartzite and other rocks and minerals. Paint pigment was won from the outcrops of copper ore deposits.

The first Europeans known to have traversed the area were members of the ill-fated Burke and Wills expedition, but they made but brief reference to the area in their records. They crossed several rivers, one river of which Burke named in honour of Lady Cloncurry.

Two or three parties searching for survivors of Burke’s expedition crossed the area. It was one the search parties, John M’Kinlay’s, which first noted the presence of copper mineralisation. The country must have been in good condition when he noted “There is an abundance of water in many of the minor as well as the main creeks, mussels in all. Magnificent pastures all around, and lots of game, a specimen of copper picked up in one of the creeks: a great abundance of quartz and mica strewn everywhere.”

As in some of the other great Australian mining fields, it was men whose prime interest was in finding new pastures who discovered and developed the wealth below the ground. One such man was Ernest Henry.

Ernest Henry was born at Harrington, Cumberland County, England on the first of May, 1837. He was in turn ship’s cadet, soldier, explorer and pastoralist. In his search for new grazing land he collected samples, which he believed to contain copper, from an outcrop near Fort Constantine on the Cloncurry River about 30 km north of where the town of Cloncurry is now situated. The samples were tested at the nearest assay office at Peak Downs and found to be an oxide of iron.
This disappointment did not deter Henry and in May, 1867, he discovered and named the Great Australia mine. He had found malachite stains and on further investigation discovered native copper in the outcrop.

Despite the obstacles before him, isolation, searing summer temperatures and the hurdle of high transportation costs, Henry searched for and found additional deposits, which became the Crusader and Dobbyn mines. Unable to raise finance in Britain, he used his own resources to hire a Cornish mining captain and 30 miners to work the Great Australia. However, profits were marginal as the ore had to be carted by dray to Normanton and then shipped to Wales for smelting. Consequently the Great Australia was only worked when copper prices were high. This did not stop Ernest Henry. With the assistance of local aborigines he went on to stake out the Argylla (known in modern times as the Blockade), and Mount Oxide mines.

Henry was fortunate in that, on the basis of an enthusiastic report on the Cloncurry mineral field by a reputable consultant geologist, Dr. J.R. Robertson, a group of Scottish investors purchased the Great Australia and floated the Cloncurry Mining and Smelting Company. However, the Great Australia failed to produce profits and after operating from 1884 to 1889 it closed again. At the same time as Henry was pursuing copper, gold was found in the Selwyn Ranges to the south of Cloncurry. Although some 10,000 ounces were recorded as being produced, gold production was intermittent, but it did have the effect of attracting more miners to the field. In the meantime, another separate revival of mining was underway with the bonanza discoveries of Broken Hill and Mount Lyell. Promoters seeking new fields became interested in the discoveries to the south near Selwyn. Mines were established at Kuridala and Mount Elliott. High copper prices following the outbreak of
World War I, and the luxury of a new railway, resulted in a boom period for Cloncurry with additional deposits being developed including Mount Cuthbert, Dobbyn, Argylla, Crusader, Mount Oxide, Trekalano, and the re-opening of the Great Australia. However, at the end of the war copper prices slumped and although the Cloncurry mining companies struggled to survive, they eventually withdrew, leaving the field to small operators, referred to by Geoffrey Blainey as the “Cloncurry gougers.”

Today, Cloncurry is experiencing a revival of its fortunes as a mining centre. Old mines are being re-opened and new deposits are being discovered. The Great Australia has been brought into production as an open cut with metal recovery based on new technology. New underground mines have been developed at Selwyn and Mount Elliott. To the north-east of Cloncurry a huge copper deposit is being exposed by open cut methods. Appropriately, it is named Ernest Henry.

The rich history of Cloncurry is matched only by the diversity of the district’s minerals. Rare minerals of copper, cobalt and uranium have been found. The purpose of this study is to not only seek species not previously recorded, but to expand on the present knowledge relating to the formation of secondary copper species occurring in the Cloncurry district. It is these species that have been at the forefront of the development of the Cloncurry mineral field.

1.3 References


2. Regional Geology - An Overview

2.1 The Mt. Isa Inlier

The geology of the Mt. Isa Inlier has been studied in detail by a number of authors including Shepherd,\(^1\) Carter,\(^2\) Blake,\(^3\) Williams\(^4\) and Wyborn.\(^5\) Therefore, it is not intended that the regional geology will be described in detail except where it relates to the formation of copper deposits.

The Mt. Isa Inlier (Fig. 2-1)\(^4\) consists of two Proterozoic units divided by an older, north trending, basement structure composed mainly of igneous rocks. It occupies an area of 64,000 km\(^2\) and forms part of the Australian Precambrian Shield.\(^2\) To the northwest it adjoins the McArthur Basin.

![Diagram of the Mt. Isa Inlier and McArthur Basin showing the main tectonic divisions.](image)

Fig. 2-1. The Mt. Isa Inlier and McArthur Basin showing the main tectonic divisions.\(^4\)
2.2 The Western Succession

The Western Succession of the Mt. Isa Inlier contains the huge Century zinc deposit situated at Lawn Hill and the Mt. Isa lead and copper ore bodies. Another large ore body, Esperanza, has recently been explored and mining has commenced. It is in the same geological structure as the existing Gunpowder mine. The Western Succession has a less complex history of folding and shearing than the eastern part of the Mt. Isa Inlier, which is referred to as the Eastern Fold Belt.

2.3 The Eastern Fold Belt

Recently, considerable interest has been shown in the Eastern Fold belt (Figs. 2-2), following the discovery of the huge Ernest Henry copper - gold deposit to the north-east of Cloncurry. This has resulted in a better understanding of the genesis of the mineral deposits in this area, particularly from the work of Wyborn.

This Lower Proterozoic basin consists of old acidic lavas overlain by interbedded sediments and basalt with widespread basic igneous intrusions of various ages. Two major orogenic phases associated with extensive granite emplacement resulted in extensive north-west trending folding and widespread faulting of the Lower Proterozoic strata. Regional metamorphism has led to the extensive development of schists, quartzites and amphibolites.

2.4 Genesis of the Copper Deposits

With few exceptions, the copper deposits of the Eastern Fold Belt are localised by faults. Often deposits occur where faults or shears are intersected by cross-faults or tension gashes.
Fig. 2-2. Eastern Fold Belt of the Mt. Isa Inlier showing geology and important deposits (after Williams).
Extensive brecciation in these locations provided the conduit for the injection of mineral bearing fluids. The ore body of the Great Australia mine is typical of this mode of occurrence. The source of the mineralisation is a matter of some contention amongst geologists, but there is an increasing amount of evidence pointing to a hydrothermal origin. The Eastern Fold Belt has extensive underlying plutons of the Naraku and Williams Batholiths. Wyborn and Perkins et al. have shown that a close time and spatial relationship exists between these intrusives and associated copper, cobalt, tungsten and gold mineralisation.

Mineralogical observations noted during field work support the view that the deposits are of hydrothermal origin. High temperature minerals were often found. For example, at the Brilliant deposit, wolframite, scheelite and fluorite occur, indicators of high temperature magmatic origin. Also, molybdenite, a mineral most often associated with acid intrusives, is widespread.

In 1972, Wilson stated *A great majority of the copper deposits in the Cloncurry-Mt. Isa region are the result of hydrothermal activity related to dolerite and granite intrusions, metamorphism and structural deformation.*

*Copper in dolerite occurs as blebs of chalcopryite, and as an important constituent of late-stage hydrothermal fluids which formed mineralised quartz-calcite veins.*

Recently Wyborn noted that *As deposits can occur up to 3 km from the granite boundary, migration paths are always along major fracture zones and faults.*

Also *In the area surrounding the Williams and Naraku Batholiths Au and Cu*
mineralisation is predominantly hosted by reduced (C-or Fe\(^{2+}\)-rich) rocks, including banded iron formations, mafic volcanics, magnetite bearing felsic volcanics, earlier more mafic magnetite-bearing phases of the granite itself (rare), carbon bearing rocks, sulfide-bearing shales and magnetite-bearing skarns which more commonly replace silicate, rather than carbonate rocks.

Erosion and peneplanation has resulted in the exposure of many of these lodes and the burial of others such as Ernest Henry. Where the lode is above the water table, the process of weathering and chemical reaction with groundwater altered the primary minerals producing a range of secondary copper species and often increasing copper and gold grades. It was these lodes that attracted the early prospectors. The physical and chemical conditions which control the formation of particular copper species are discussed in Chapters 4 and 5.

2.5 References


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3. The Copper Deposits of the Cloncurry District

3.1 Overview

It has been estimated that there are approximately 2,000 copper deposits within the Mt. Isa Inlier, the majority being within the Eastern Fold Belt. Most, if not all, would have been prospected at some time, and about 800 have produced over one tonne of copper.¹ Not all important deposits are discussed in detail as some, particularly those being mined underground, are not readily accessible for the required mineralogical field studies. The deposits described below are those of particular relevance to the mineralogy to be discussed in Chapter 5. A short description of other deposits inspected during the fieldwork is provided in Appendix I.

In this and later chapters, the geographic region of the Eastern Fold Belt will be referred to as the Cloncurry district as it approximates the area within the Cloncurry Shire boundary (Fig. 3-1).²

3.2 The Great Australia

This deposit is situated 2 km south from the township of Cloncurry. The most recent phase of mining commenced with the first blast on the 23rd of November, 1995, with the objective of mining approximately 1.5 million tonnes from the main pit and 0.6 million tonnes from the nearby Paddock Lode, with a grade of 1.5% copper. All of this resource was within the oxide zone.³ LME grade A copper, (99.9% purity), is produced at the mine by a solvent extraction- electrowinning (SX-EW) process.
Fig. 3-1
CLONCURRY DISTRICT
showing copper and cobalt deposits referred to in the text.

Cloncurry Shire boundary

Town or locality

Mineral deposit

Mt. Isa

Cloncurry

Kuridala

0 50 100 km

NORTH
Fig. 3-2. Mining on bench 3, Great Australia mine, Dec. 1995.

Fig 3-3. Main Lode shear looking north, Great Australia mine.
FIG. 3-4
PLAN - MAIN AND B TANGYE LODGES
GREAT AUSTRALIA MINE
Mining operations ceased early in 1998, after most of the proven oxide resource at the Great Australia and Paddock Lodes had been mined. Figure 3-2 illustrates mining on Bench 2 at the Main Lode, Great Australia during December, 1995. Figure 3-3 is a view of the Main Lode shear.

The mineralisation is localised by the Main Lode shear trending NNW and dipping to the west at approximately 50°, and the intersecting vertical B Tangye shear which trends NE (Fig. 3-4). The western side of the Main Lode shear consists of metasediments whilst to the east there is metabasalt which contacts the Corella and Gilded Rose breccia. These carbonate rich formations are intruded by the Naraku Granite.⁴

Primary mineralisation consists of pyrite and chalcopyrite in association with magnetite, dolomite and calcite in quartz veins. Gold, lead and zinc values are low. Anomalous cobalt values have been noted in the drill core,⁵ but no cobaltite or arsenopyrite has been detected, indicating that cobalt is probably held within the pyrite lattice. This has been confirmed by microprobe analysis of minerals in drill core (P. A. Williams, pers. com.). Cobalt has been identified in the black manganese wad found in the oxide zone.⁶

The oxide zone of this deposit has a depth of approximately 60 m and it is from the study of the secondary copper mineralisation in this zone that most data has been obtained.

3.3 The Monakoff

The Monakoff deposit, 23 km ENE of Cloncurry, has been explored intermittently since 1954. A shaft on the lode indicates that some ore has been produced in the past. Cloncurry Mining N.L., after further exploration, added this deposit to their tenements with the object of treating the ore at the Great Australia leach plant.
Fig. 3-5. Monakoff deposit - section through lode.
The ore proved difficult to leach and the deposit was abandoned after the deposit was partially mined. The deposit contained 0.25 million tonnes having a grade of 1.8% copper.\textsuperscript{3}

The mineralisation occurs in a narrow, 60 m long, E-W trending, sub-vertical banded iron formation (BIF), with a depth of oxidation of 20 m. A shear zone exists within the BIF (Fig. 3-5), probably because the BIF was the least competent formation to resist the stress induced during folding. Primary mineralisation in quartz veins has been injected into this shear. Pyrite, chalcopyrite, sphalerite and minor galena were present in a gangue of fluorite, quartz and barite. No secondary zinc or lead minerals were found in the oxide zone. Anomalous cobalt and uranium values have been noted.\textsuperscript{5}

The main copper minerals present in the oxide zone were malachite, azurite and chrysocolla, with minor amounts of cuprite, brochantite, antlerite, pseudomalachite, libethenite and metatorbernite. It is probable that small amounts of native copper and tenorite are also present. A micro amount of the rare copper nitrate, gerhardtite, was found in a specimen of massive cuprite. Autunite and the rare uranium mineral phuralite were also found.

3.4 The Lorena Gold Mine

The Lorena is a small gold mine 13 km east of Cloncurry currently being mined to a depth of approximately 15 m by open cut methods. In addition to gold, the mineralisation includes pyrite, chalcopyrite, arsenopyrite, cobaltite and native bismuth. The lodes occur within a quartz breccia in two parallel subvertical shears. The secondary copper arsenate conichalcite is common in a shallow hematite gossan. Minor amounts of olivenite, pseudomalachite, malachite, azurite and chrysocolla were noted.

A pink efflorescent mineral was found in the eastern shear. This was identified as
wupatkiite, a hydrous cobalt aluminium sulfate of the halotrichite group, found only once previously at a deposit in Arizona.  

3.5 The Mt. Cuthbert Group

This group includes the Mt. Cuthbert, Warwick Castle and Crusader deposits which are being mined as open cuts by Murchison Resources, whose tenements include the Dobbyn deposit. They are situated on a line of mineralised country running from Mt. Cuthbert, 14 km NW of Kajabbi to Dobbyn, 25 km to the north. Early this century underground mines were operating at Mt. Cuthbert and Dobbyn, which at the time were connected by rail to Cloncurry. Mining ceased with a fall in copper prices and the mines closed in 1920. A new operation is now in progress to mine all four deposits and recover the copper by SX-EW technology.

The Mt. Cuthbert deposit occurs in a 90 m wide, northerly trending, vertical shear zone in metabasalt and rotten schists. Malachite veins up to 4 cm thick in siliceous hematite gossan are common. The quartz lode breccia has chrysocolla filling many of the fractures. Minor native copper, chalcolite, brochantite, pseudomalachite and, at the surface, a little libethenite were also noted. This deposit is still being mined (Fig. 3-6).

The Warwick Castle deposit was inspected prior to the commencement of the current phase of mining. At that time there was an old shallow open cut. A notable feature was an abundance of libethenite in joints and fractures. The second inspection was made after the pit had been mined to a depth of 20 m. Only one small specimen of libethenite micro-crystals could be found at this level. Copper mineralisation was predominantly felted acicular masses of malachite with azurite and pseudomalachite and minor chrysocolla and chalcolite. This is a small deposit in an E-W shear in metasediments and metabasalt. The lode is bounded by two parallel quartz veins having an overall width of 5 m and a strike of 100 m. Mining of the
Fig. 3-6. The open cut at Mt. Cuthbert with the old smelter stacks in the background.

Fig. 3-7. The Crusader lode looking south showing kaolinisation.
oxide zone has been completed.

The Crusader deposit is within an E-W shear in metasediments, mudstones, shales and quartzite. The lode is in vein quartz and a hematite-quartz gossan which is heavily kaolinised (Fig. 3-7). Veins of malachite up to 4 cm thick occur in fractures. An interesting form of *chalcotrichite* was found on quartzite. It had the appearance of being painted onto the surface of the rock.

Minor copper minerals included chrysocolla, brochantite and pseudomalachite. A few sulfides, pyrite and chalcopyrite, were found, having been protected from further reaction by massive quartz.

### 3.6 Mt. Cobalt

Although Mt. Cobalt is not regarded as a copper deposit, it deserves mention because a number of relative rare copper minerals have been found in the old dumps and prospecting pits. The deposit is most famous for the superb erythrite specimens that have been obtained by collectors over many years. Beyer *et al.* have recorded the rare copper arsenates agardite, clinoclase, cobaltaustinite, lavendulan and olivenite, as well as the more common species conichalcite. The lodes are contained within a north trending shear along a contact between metadolerite and a quartz-mica schist.

### 3.7 The Desolation

The Desolation is a series of small prospecting pits on a copper lode which has both high cobalt and arsenic contents. It is situated on the southern end of a belt of copper-cobalt mineralised exploration tenements in the White Range known collectively as Greenmount. Copper minerals collected at this site were malachite, azurite, pseudomalachite, chrysocolla,
conichalcite, olivenite and clinocease, occurring in fractures and along bedding planes in metasediments. A small amount of erythrite was also found. If it is mined, this deposit will probably be found to contain a range of minerals similar to Mt. Cobalt\(^8\) and Dome Rock\(^9\) in South Australia.

3.8 References


5. S. Milner, Exploration Manager, Cloncurry Mining Company N.L. (pers.com.)


4. Development of the Secondary Zone

4.1 Oxidation of primary sulfides

The Great Australia has a relatively simple assemblage of primary sulfides, consisting of pyrite and chalcopyrite. Well formed crystals of djurleite and chalcocite in calcite and quartz were found on the ROM pad, but it is not precisely known as to where in the pit these occurred and the area believed to be the source is now under water. They are of secondary origin. Other copper deposits in the district are similar or have associated arsenopyrite, cobaltite, pyrrhotite or small amounts of other base metal sulfides. Sulfides are oxidised by oxygen derived from the atmosphere, and delivered to the reaction site by groundwater.

The mechanism by which groundwater conveys oxygen is discussed in detail by Williams.¹ The rate at which oxidation of sulfides will occur will depend on physical factors such as permeability of the strata and the enclosing gangue, depth of the water table, rainfall and erosion rates, and in shear hosted lodes, degree of fracturing, in which case the process is less dependent on the lithology of the overlying strata. The rate of oxidation also depends on the species present and their relative ratio. The oxidation of pyrite provides a supply of sulfurous acid which in turn is oxidised to sulfuric acid, accelerating the oxidation of chalcopyrite.² The overall reaction for pyrite is

\[
\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (1)
\]

and for chalcopyrite

\[
\text{CuFeS}_2 + 4\text{O}_2 \rightleftharpoons \text{Fe}^{2+} + 2\text{SO}_4^{2-} + \text{Cu}^{2+} \quad (2)
\]
Krauskopf's sums up the result,

the weathering of sulfides may be described by a variety of equations, all of them only an approximate representation of a complex natural process. The net results are (1) to get the metal ion into solution or in the form of an insoluble compound stable under surface conditions, (2) to convert the sulfur to sulfate ion, and (3) to produce relatively acid solutions.

4.2 Oxide zone development

Most outcropping or near surface deposits will have an oxide zone. Some oxide zones are quite deep, notable examples being Tsumeb where a large shear allowed groundwater to be transported below an extensive zone of sulfide mineralisation, and at Bisbee, where a very deep water table and cavernous limestone allowed groundwater to percolate to great depth. Deposits with a well developed oxide zone are usually found where (1) the region has low or restricted seasonal rainfall, (2) the water table is not close to the surface, and (3) the rate of erosion is low. The presence and relative mass of reactive rocks, e.g. limestone, by reason of their buffering effect, will also effect the extent of the oxide zone.

4.3 Anions

Whilst the mineralogy of the secondary copper minerals of the Cloncurry district is discussed in detail in Chapter 5, it is worthwhile, at this point, to discuss the source of the anions which go to form the many species found in the oxide zone. In some cases this will be apparent from previous discussion, e.g. sulfate ion which is derived from the oxidising sulfides. Other anions have to be derived from elsewhere.

In some cases, atmospheric CO₂ dissolved in rainwater to form carbonic acid
accounts for the supply of carbonate anion to form stains and stringers of malachite in outcrops. However, the major source of carbonate anion is deeper in the deposit where acids, primarily sulfurous and sulfuric, from oxidation of sulfides, reacts with carbonates in the gangue or wallrock. Therefore it should not be unexpected that malachite and azurite are encountered at all depths above the watertable.

The copper phosphates pseudomalachite and libethenite are more widespread than has previously been recognised.\(^4\) There is a plentiful supply of phosphate ion, \(\text{HPO}_4^{2-}\), from the weathering of apatite species; e.g., fluorapatite, \(\text{Ca}_5(\text{PO}_4)_3\text{F}\) is a common accessory mineral in igneous rocks. At the Mt. Elliott mine apatite occurs commonly within the primary ore body.

The oxidation of arsenopyrite and in some cases cobaltite provides the arsenate ion for the precipitation of the copper arsenates. The arsenic bearing sulfides appear to be the only source of this anion.

Saline brines are common in vadose, i.e., deep circulating, groundwater, particularly in semi-arid environments, and this is the case at Cloncurry. Therefore, a ready supply of chloride ion is available to form such species as nantokite.

Except for the caliche deposits of Chile,\(^5\) there is very little published on the source of nitrate related to mineral deposits. Nitrogen cycling in organic systems is well understood and an organic origin is possible for the Andean deposits. However, an alternative and more probable source is from electrical disturbances in thunderstorms, which produce annually approximately 10 million tonnes of nitrogen as nitrate.\(^6\) The basic copper nitrate, gerhardtite, occurs in the Cloncurry district. It has only been recorded from arid areas with sparse vegetation and, at all locations, it is of very limited distribution and is only found within massive cuprite.
FIG. 4-1
TYPICAL OXIDE ZONE IN SHEAR SHOWING MAJOR ION FLUXES

- nitrate from rainwater
- original surface
- metasediments
- oxygen enriched groundwater
- leached zone
- phosphate ex. apatite
- silicate from weathering rock-forming minerals
- schist
- limestone
- oxide zone
- carbonate from limestone
- circulating groundwater containing chloride
- supergene enriched zone
- oxidising primary sulfides
- sulfate
- 
- 
- 

metabasalt

SO$_4^{2-}$ from weathering sulfides

Cu$^+$

water table (fluctuating)
The ubiquitous copper silicate chrysocolla is a product of the reaction of silicic acid with other copper species or as a precipitate from ionic solution of these reactants. Silicic acid is a product of the weathering of silicate rock forming minerals, e.g., feldspar, usually in an acidic environment resulting from the oxidation of pyrite. The presence of kaolin is an indicator as to the extent of oxidation and acid bleaching that has occurred. Although chrysocolla is often associated with quartz, the latter, because of its inert nature, does not provide silicate anion. The presence of hydroxyl anion should not be overlooked as it extends the range of secondary species by way of basic salts. The overall process is shown in Fig. 4-1.

4.4 References


5. Secondary Copper Minerals

5.1 Native Copper

Copper occurs in a number of mines in the Cloncurry district. However, it is not commonly found on the dumps of abandoned mines. This is not an indication of the absence of native copper in the outcrops but a mark of the thoroughness of the gougers of past years, who would have been careful to bag and despatch the richest ore. Historical records often refer to the presence of native copper at the surface. Williams\(^1\) points out that copper ions are readily reduced in aqueous solution. Garrels \textit{et al.}\(^2\) note that native copper is more likely to be precipitated under feebly reducing or oxidizing conditions while cuprite and tenorite require increasingly higher pH, respectively, as can be demonstrated by Eh-pH stability relationships (Fig 5-1).

At the Great Australia mine three distinct modes of occurrence have been noted. Throughout the shears containing the lodes and at all depths in the oxide zone it is common to find masses of highly siliceous yellowish-brown goethite. Frequently this siliceous gossan is rich in native copper and cuprite as kernels and disseminated masses (Fig. 5-2). No tenorite was found in this context.

Later stage secondary silica has invaded goethite gossan forming a dense siliceous mass resistant to weathering and further reaction. The paragenesis can be determined from the occasional vugh where the silica has formed delicate crystalline linings over copper- cuprite-rich goethite. As depth increases, notably from Bench 10 to Bench 16, native copper becomes more abundant, usually as pods and stringers within cuprite, which between these benches is the major ore mineral. Cuprite occurs as vein fillings in brecciated quartz and hematite. On rare occasions the veins are completely filled with native copper and where a
vein opened into a vugh dendritic native copper studded with cuprite crystals to 8 mm has been found (Fig. 5-3). All the material here is highly silicified, both in the Main and B Tangye Lodes.

![Graph](image)

**Fig. 5-1** Simplified diagram of redox potential - pH for copper and copper oxides in association with hematite and goethite (after [2]). Depending upon the availability of sulfur, various copper and copper-iron sulfides are formed under conditions below the Cu + Fe₂O₃ boundary.

Native copper also occurs as nodules with a cuprite rind. Masses 20 cm across have been recovered. Often these nodules have an outer rind of siliceous tenorite followed by chrysocolla or malachite. The nodules were found on near surface Benches 2, 3 and 5.
Fig. 5-2. Native copper and cuprite in siliceous goethite.
Great Australia mine, Cloncurry. FOV 10 mm.

Fig. 5-3. Native copper and cuprite. Bench 25,
Great Australia mine, Cloncurry.
Cuprite crystal is 6 x 6 mm.
Using the Great Australia as a model it can be reasoned that the distribution of native copper follows a predictable pattern for this environment. Native copper found in the outcrop or near surface is the remains of native copper formed at depth as conditions become increasingly reducing at lower pH. The remnant copper is found either within quartz veins or highly siliceous goethite where it has been physically protected from oxidation, or as slugs or nodules of such a mass that only the first one or two centimetres has been further reacted.

As depth increases and the present water table is approached there is a marked increase in native copper and associated cuprite, and they become the dominant copper minerals. Laterally there appears to be little redistribution of native copper outside the shear zones holding the original sulfide orebodies.

Enrichment of orebodies by native copper and cuprite as the water table is approached is known to occur in other major deposits in arid regions. This observation is discussed at some length by Emmons. Other open cuts in the study area were not of sufficient size or depth to make similar observations.

5.2 Oxides

Cuprite, Cu$_2$O, is one of the most abundant copper minerals and is the main constituent of the ore at the Great Australia mine. It is often associated with native copper as the conditions favourable for the development of cuprite parallel that of the native element, as discussed above. Cuprite is also formed by the oxidation of native copper. It is common to find nodules of cuprite with cores of native copper varying in size from barely discernible to being the greater proportion of the mass. At the Great Australia mine, as depth increased, cuprite became the dominant ore mineral, forming veins within a quartz breccia. The vein filling often gave way to a cuprite-hematite-goethite association and to a lesser extent native copper. As with native copper, the cuprite is held tightly within the original lode horizon.
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Numerous small vughs occur, frequently lined with lustrous cubic, octahedral or combined crystal forms of cuprite up to 8 mm across, occasionally with dendritic or sub-crystalline native copper. Some cuprite shows unusual deep etching on the crystal faces (Fig. 5-4). This has the appearance of preferential corrosion along structural planes. Rarely, other species such as atacamite occur within cuprite vughs. The best development of crystalline cuprite occurred within the Main Lode between Benches 15 and 16, ca 50 m depth. It was here that the uncommon extremely acicular variety of cuprite, chalcoltrichite (Fig. 5-5), occurred in many of the vughs. In the B Tangye lode a microcrystalline form of chalcoltrichite was found which gave the substrate a pink painted appearance. Elsewhere in the lode chalcoltrichite was rare.

*Chalcoltrichite* is a capillary form of cuprite where both cubic and octahedral crystals are greatly extended. The fibres can be extremely fine. An SEM photograph (Fig. 5-6) shows chalcoltrichite from the Great Australia mine at x1000. The finest fibre in the field of view has a thickness of approximately 0.6 microns.

Cuprite of varying quality can be found on most mine dumps in the region where an appreciable amount of ore has been won. The variety known as "tile ore" is relatively common. This is a mixture of cuprite and hematite or goethite varying in colour from yellowish to brick red to almost black.

Tenorite, CuO, is also relatively common in the Cloncurry district, but is far less abundant than cuprite. It is variable in appearance from dark steely grey to black and sometimes earthy, and when siliceous it has the appearance of pitch. In the field tenorite can usually be distinguished in hand specimens from common black manganese wad by its less intense black colour.
Fig. 5-4. Cuprite crystal showing corrosion along grain boundaries. Great Australia mine, Cloncurry. FOV 4 mm.

Fig. 5-5. Chalcotrichite on goethite. Great Australia mine, Cloncurry. FOV 10 mm.
Fig. 5-6. SEM photograph of chalcotrichite fibres. 
The finest fibre is 0.6 microns across. 
Bench 16, Main Lode, Great Australia mine.

Fig. 5-7. Chrysocolla and tenorite (black) rind on a cuprite core. 
Great Australia mine, Cloncurry. FOV 25 mm.
Whilst tenorite could be found on many mine dumps it was observed that at the Great Australia mine it occurred from the surface down to bench 5, either in rounded masses up to approximately 300 mm in diameter and coated with microcrystalline malachite and more rarely brochantite, or forming a rind around a cuprite core (Fig. 5-7). This often had a further rind of chrysocolla and/or malachite. Dana describes similar mixtures of tenorite, chrysocolla and malachite having a pitchy appearance from Bisbee, Arizona, called melanochalcite, melaconite or copper pitch ore. Excellent examples of this association are to be found in the outcrop of the Mount McCabe mine in the White Range, 40 kms south of Cloncurry.

Schwartz examined specimens of “tenorite” from various locations in the U.S.A. and concluded that all were mixtures of tenorite and manganese or iron oxides and that the material most closely approaching copper oxide was to be found in the siliceous black rind around cuprite referred to previously. This was found to contain 66.6% Cu, but as a complete analysis was not given this could also include some malachite and chrysocolla into which these black rinds grade.

Schwartz also refers to a brownish manganese bearing variety occurring as concentric shells or nodules. Similar specimens were found on Benches 3 to 5 within the Main Lode at the Great Australia mine, in nodules as large as footballs.

Short states that the massive variety, the more common, is melaconite; and the prismatic variety, tenorite. Melaconite commonly has more or less chemically combined manganese oxide and silica. If it contains more than about 5 per cent of either of these two components, the mineral is known as “copper pitch ore”.

No examples of the “prismatic variety” were found during field work in the Cloncurry district. Melaconite is no longer recognised as a mineral species.
Fig. 5-8  Relative stabilities of copper, cuprite and tenorite with $p(CO_2) = 10^{-3.5}$ (after Williams').

Fig. 5-9  Stability field diagram calculated as for Fig. 5-8, but with $p(CO_2) = 10^{-4.36}$ (after Williams').
Field observations indicate that the tenorite found in the Cloncurry district is the result of oxidation of cuprite under near surface conditions. For tenorite to be formed in preference to native copper or cuprite, conditions of relatively higher pH or redox potential and the absence of most other ions would be required (Fig. 5-1). Williams¹ has shown that where the copper carbonates malachite and azurite are crystallizing in association with copper oxides, with increasing partial pressure of CO₂, tenorite tends to form malachite (Figs. 5-8 and 5-9), the reaction being (Eqn. 1).

\[2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Cu}_2\text{CO}_3(\text{OH})_2\]  

(1)

The required partial pressure of CO₂ to bring this about could occur in the context of an oxidizing sulfide ore body with circulating ground water in wall rock containing calcite and dolomite. However, near the surface groundwater charged with O₂(g) and CO₂(g), and subsequently depleted in the latter via reaction to form malachite, may then effect the transformation of cuprite to tenorite.

5.3 Sulfates

Brochantite, Cu₄(SO₄)(OH)₆, occurs at most of the deposits currently being mined, but not in large quantities. It usually occurs as sporadic small sprays of elongated prismatic crystals to 2 mm in vughs in cuprite or quartz and very often is in association with malachite and atacamite. In the field it may be distinguished from malachite by its bluish green colour and slightly pearly lustre.

Two other forms of brochantite were recorded from the Great Australia mine. The first occurred near the surface on Bench 2 where brochantite formed tabular striated crystals on the surface of pseudomalachite and malachite coating goethite (Fig. 5-10).
Fig. 5-10. Tabular brochantite crystals on malachite. Bench 2, Main Lode, Great Australia mine, Cloncurry. Specimen A5. FOV 10 mm.

Fig. 5-11. Antlerite crystals. Monakoff mine, Cloncurry. Specimen MK3. FOV 10 mm.
A similar form of brochantite was reported from the Propriety Mine, Broken Hill. Another form found at the Great Australia mine consisted of fine acicular brochantite crystals 1 to 2 mm long on a crystalline coating of malachite over massive tenorite. Excellent examples of the tabular form were found at the Monakoff mine and as a drusy crystalline crust at the Lady Fanny mine.

Although sporadic in distribution in the Cloncurry district it is widespread and at the Great Australia mine is persistent within the oxide zone in agreement with the statement by Emmons that brochantite is relatively stable. This does not appear to be the case at other Australian copper fields, only three minor occurrences having been reported in South Australia. Nor was brochantite recorded at Girilambone or Northparkes mines, both of which have been the subject of earlier field work. Brochantite has been collected by the author at the Redbank mine in the Northern Territory. This is close to the Queensland border and is near the northern margin of Mount Isa Basin.

Antlerite, Cu₃(SO₄)(OH)₄, is a relatively rare mineral except at a few localities such as Chuquicamata, Chile, where it was generally the principal ore mineral during the early mining period, and at the type locality, the Antler mine in Arizona.

Antlerite has been collected from the Monakoff mine. Specimens have been analysed by powder X-ray diffraction methods and found to be either antlerite or a mixture of brochantite and antlerite with the latter predominating. As there was no apparent difference in the appearance of hand specimens it seems that the brochantite has in some instances partially replaced the antlerite rather than it being a case of co-deposition which would have resulted in the formation of distinct brochantite crystals. The antlerite occurs as vein filling in the iron rich sandstone which forms the banded iron formation (BIF) of the Monakoff mine. Occasionally, a few deep green crystals, stout, tabular and showing light striations, form
within the veins as radiating aggregates (Fig. 5-11).

The stability relationship at 25°C and higher between antlerite, brochantite and tenorite has been established by Williams' (Fig. 5-12), from which it is apparent that compared with brochantite, antlerite forms at higher sulfate ion activity and/or lower pH. Williams also found that antlerite was metastable relative to brochantite at 25°C, and that to produce antlerite in the laboratory it was necessary to increase the temperature of the reaction solution to about 35°C; large crystals of antlerite can only be formed at higher temperatures. Bandy observed the connection between high acidity associated with sulfate activity and the formation of antlerite at Chuquicamata where brochantite is uncommon except in the north-west sector of the lode, associated with gypsum and in what Bandy described as a low acid area. Rapid oxidation of pyritic ore, an exothermic reaction releasing sulfate and hydrogen ions will provide the conditions for the formation of antlerite.

![Stability field diagram](image)

*Fig. 5-12. Stability field diagram for the system CuO-SO$_3$-H$_2$O at 25°C (after [1]).*
Fig. 5-13. Malachite in an unusual form. Bench 7, Main Lode, Great Australia mine, Cloncurry. FOV 20 mm.

Fig. 5-14. Malachite replacing cuprite on siliceous goethite matrix. Great Australia mine, Cloncurry. FOV 15 mm.
These observations and the stability field diagram provide the data to explain why antlerite and brochantite occur at the Monakoff but only the latter has been found at the Great Australia mine. At the Great Australia occasional pods of carbonate rock can be found within the lode which is bounded on the S-E side by the Corrella limestone, thus providing a buffer against excess acidity, and with \( \text{Ca}^{2+} \) ions reacting to reduce sulfate activity by forming gypsum. On the other hand, carbonate rocks are virtually absent from the Monakoff mine.

No other copper sulfates were observed. Chalcanthite has not been found even as a post mining mineral suggesting that the low pH necessary for the formation of chalcanthite combined with relatively high sulfate ion activity is rarely to be found in the Cloncurry mineral field.

5.4 Carbonates

It is certain that malachite, \( \text{Cu}_2(\text{CO}_3)(\text{OH})_2 \), is present at all the copper deposits in the Cloncurry district. It would be an unusual deposit that did not have malachite in the outcrop resulting from contact of copper mineralisation with atmospheric carbon dioxide. On the other hand, azurite, \( \text{Cu}_2(\text{CO}_3)_2(\text{OH})_2 \), is abundant at some deposits, scarce at many and absent in others. Limestone is common in many of the formations in the Cloncurry district and both dolomite and calcite are present as gangue with the primary sulfides thus providing a ready source of carbonate anion or higher \( p(\text{CO}_3) \) values in the oxide zone environment.

Malachite is the main ore mineral in the upper levels of the operating open cut mines. It occurs as stains, impregnations, coatings, veins and in vughs as linings of acicular crystals or as reniform crusts often showing rhythmic banding. Very often these bands will consist of alternating layers of malachite and pseudomalachite, \( \text{Cu}_6(\text{PO}_4)_3(\text{OH})_4 \), on a matrix of goethite. Whilst this latter form of mineralisation could be found throughout the Great Australia lode,
it was best developed in the outcrop. Another unusual wafer-like form was found at the Great Australia (Fig. 5-13), possibly as the result of evaporation in ponds akin to the calcite formations of similar appearance found in limestone caves.

Malachite rarely forms distinct crystals. Occasionally cuprite vughs contained small dark green prismatic crystals often associated with atacamite, $\text{Cu}_2\text{Cl}($OH$)_2$. When malachite forms in quartz or goethite vughs at depth it is common for the malachite to be in fine acicular crystals having a felt-like appearance. Larger crystals are rare. However, during the field studies several specimens were collected from the dump at the Canteen mine in the Soldiers Cap group, which contained slender acicular prisms of malachite to 10 mm. Attractive specimens of malachite crystals coated with finely crystalline secondary quartz are common at several deposits.

An uncommon form encountered at both the Great Australia and Duck Creek deposits consisted of very fine felted masses of silvery green fibres. They were not recognised as malachite until analysed by XRD. The silvery appearance is possibly an optical effect resulting from the extreme fineness of the fibres.

Field observations indicate that this ubiquitous mineral is most developed near the surface and around the periphery of the lodes. At depth and tightly within the lode cuprite dominates and malachite is a minor component. However, malachite is widespread and is prominent as vein filling and stains in the wall and surrounding country rock. On the near surface benches at the Crusader mine, 45 km north of Kajabbi, compact botryoidal malachite veins up to four centimetres thick are being mined. Occasionally, near the surface malachite is found coating or replacing cuprite. A cuprite crystal partially replaced by malachite is shown in Fig. 5-14.

Azurite is common in the Cloncurry district but is not as abundant as malachite nor
can it be assumed that it is present at all deposits. At the Great Australia mine the occurrence of azurite is very sporadic. It occurred in the old workings and was encountered deep in the B Tangye Lode near the junction with the Main Lode. Overall, very little has been encountered during current mining. Azurite was a major component of the ore at the Wee McGregor and Inkerman mines. It occurs as earthy masses, filling or coating fractures and occasionally as small crystals lining vughs and fractures, or “starburst” aggregates of slender prisms.

Azurite crystals found in the Cloncurry district are commonly nucleated on a manganese oxide surface which often forms over quartz and other gangue minerals. This association is rarely observed with malachite despite the greater abundance of the latter.

The stability relationship between azurite and malachite has been examined in detail by Williams who has pointed out that malachite is the stable carbonate at the normal partial pressure of CO₂ in the atmosphere (approx. 10⁻³.₅ atmospheres) and that the partial pressure at which both are in equilibrium at 298.2 K can be derived from equation (2).

\[
3\text{Cu}_2\text{CO}_3\text{(OH)}_2(s) + \text{CO}_2(g) \rightleftharpoons 2\text{Cu}_2\text{(CO}_3\text{)}_2\text{(OH)}_2(s) + \text{H}_2\text{O(l)}
\]  

(2)

Thus at equilibrium \( p(\text{CO}_2) \) is \( 10^{-1.36} \) atmospheres and at pressures below this malachite will form. A partial pressure in excess of this is unlikely to develop near the surface unless there is considerable chemical or biological activity within a relatively impervious structure. Such a situation is more likely to be found at depth as a reaction front reaches carbonate rock.

It has been observed that when azurite is formed at depth it is often preceded by a layer of malachite. This can be readily explained in terms of the slow rates typical of geochemical reactions and the rate at which the reaction front approaches the reactive rocks. This would be a function of the rate of erosion of the surface which in a semi-arid environment and geologically old and stable structures is slow in the extreme. Thus the
initial pressure in the vugh or fracture may be below the equilibrium pressure for malachite-azurite with the result that malachite forms first, but as acidic groundwater derived from oxidising sulfides reaches and reacts with carbonaceous minerals in the lode or wallrock to increase the pressure of CO₂, azurite forms (Fig 5-15). Schwartz⁵ examined 150 oxidized copper ore specimens from the south-west of the U.S.A. and concluded that most commonly where azurite and malachite were associated, the malachite precipitated first. Very good examples of this paragenesis resulting from the variation of the partial pressure of CO₂ were found in the Copper Queen mine, Bisbee, Arizona.¹² At this deposit part of the lode is formed within a massive cavernous limestone containing not only calcite stalactites, but stalactites composed of alternating bands of malachite and azurite. Once again, the carbonate deposition commenced with malachite.

While it is clear that this sequence of events must occur, it is extremely rare to find pseudomorphs of azurite after malachite whilst the reverse is relatively common. The explanation of this probably relates to the time scales involved and the greater opportunity for malachite to replace azurite as eventually partial pressures of CO₂ must fall to lower values, when malachite is stable.

The relationship of the copper carbonates with tenorite is worthy of examination. The relative stability diagram¹ for the carbonates and the boundary with tenorite derived from equations (3) and (4).

\[
2\text{CuO(s)} + \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{Cu}_2\text{CO}_3(\text{OH})_2 \quad (3)
\]

\[
3\text{CuO(s)} + 2\text{CO}_2(\text{g}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{Cu}_3(\text{CO}_3)_2(\text{OH})_2 \quad (4)
\]

is shown in Fig. 5-16. It is apparent that azurite cannot exist at equilibrium with tenorite, a fact observed in the field. Nodules of cuprite with a rind of tenorite referred to previously,
have an outer rind of either chrysocolla or malachite, never of azurite. In the study area these nodules have only been found near the surface.

![Stability field diagram for calcite, azurite, malachite, and tenorite](image)

**Fig. 5-16** Stability field diagram for calcite, azurite, malachite, and tenorite with $a(Ca^2+) = 10^{-3}$ and $p(CO_3) = 10^{-5}$ (broken lines) and $10^0$ (full lines) respectively, after [1].

### 5.5 Phosphates

Phosphate mineralisation has long been known in the Mt. Isa Block, particularly with respect to uranium bearing phases. Metatorbernite, $\text{Cu}_4(\text{UO}_2)_2(\text{PO}_4)_2\cdot8\text{H}_2\text{O}$, occurs as minute to 0.5 mm emerald green, square, thin transparent plates on manganese oxide coatings in the BIF of the Monakhoff mine. Associated uranium mineralisation includes autunite, $\text{Ca}_2(\text{UO}_2)_2(\text{PO}_4)_2\cdot10\cdot12\text{H}_2\text{O}$, and the rare mineral phuralite, $\text{Ca}_2(\text{UO}_2)_2(\text{PO}_4)_2(\text{OH})_4\cdot4\text{H}_2\text{O}$. 

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Fig. 5-15. Malachite with later azurite. Bench 11. Main lode, Great Australia mine, Cloncurry. FOV 10 mm.

Fig. 5-17. Pseudomalachite hemispheres on chrysocolla. Mt. Glorious deposit, Cloncurry. Specimen is 12 x 8 mm.
Metatorbernite was the ore once worked for uranium at the Milo mine, where it occurs as minute flakes in a kaolinitic clay. Although the groundwater at the Great Australia has anomalous uranium values, no uranium mineralisation has been found. The extensive granites of the district have probably been the source of the uranium.

The copper phosphates, particularly pseudomalachite, $\text{Cu}_3(\text{PO}_4)_2(\text{OH})_4$, are more widespread than is generally realised. However, it has been only the result of this study that the very widespread nature of secondary copper phosphate mineralisation in the region has been revealed. Frequently the presence of pseudomalachite in a deposit has not been recognised because, as the name implies, it has been confused with malachite. This can have commercial implications if the recovery process involves acid leaching as whilst malachite leaches rapidly, pseudomalachite reacts comparatively slowly. Pseudomalachite can be found at the operating mines and on most of the old dumps of any size in the Cloncurry district. Libethenite, $\text{Cu}_3(\text{PO}_4)(\text{OH})_5$, is also widespread but usually sparse within any particular deposit. The third copper phosphate, cornetite, $\text{Cu}_3(\text{PO}_4)(\text{OH})_3$, is relatively rare, having been recorded from only two deposits in the district.

Pseudomalachite most commonly occurs as reniform or botryoidal linings to vughs in goethite. Particularly noteworthy are rhythmically banded, botryoidal malachite - pseudomalachite composites comprised of individual layers up to a few tenths of a millimetre thick that have been recovered from the upper sections of the Main Lode at the Great Australia mine. In the Main Lode outcrop, these composites had weathered such that malachite had been removed to leave shells of thin pseudomalachite crusts. These casts were most common just below the outcrop in the gossan. Similar rhythmic banding involving the minerals was noted in the upper oxide zone of the Warwick Castle lode, north of Kajabbi.

Thermodynamic data for libethenite, pseudomalachite and cornetite have been
evaluated by Magalhães et al.,\textsuperscript{14} and their equilibrium relationships with malachite and azurite have been assessed. In general, equilibrium routes from the phosphates to the carbonates are restricted in kind. Routes are limited to pseudomalachite— and cornetite—azurite transformations, and to cornetite—malachite transformations. Unusually, malachite—pseudomalachite \textit{assemblages} cannot form directly, one mineral from the other, under natural conditions. Intermediate steps involving azurite or cornetite are necessary, thus making malachite—pseudomalachite \textit{assemblages} quite stable under appropriate conditions. This appears to be the case with the deposits mentioned above in that the rhythmically banded malachite—pseudomalachite material would simply reflect the fluctuating availability of H$_2$PO$_4$(aq) or HPO$_4^{2-}$(aq) in mineralizing solutions. When more phosphate was present, pseudomalachite would form for solubility reasons (although perhaps \textit{via} a thin and subsequently pseudomorphed layer of cornetite). Weathering of malachite—pseudomalachite to leave the phosphate mineral as thin casts probably represents the result of similar solubility differences to those mentioned above, as well as to the fact that pseudomalachite dissolves reversibly in weakly acid solutions much more slowly than does malachite.\textsuperscript{15}

Another common habit noted at a number of deposits is for pseudomalachite to form as bluish green coatings or clots over malachite. Pseudomalachite often forms on chrysocolla, (Cu,Al)$_2$H$_2$Si$_2$O$_5$(OH)$_4$.nH$_2$O, as translucent clots or rounded balls. The best examples of the latter have been found at the Mount Glorious mine, 8 km west of Cloncurry (Fig. 5-17). Similar occurrences have been observed over the entire district. At Mt. Cuthbert, near Kajabbi, pseudomalachite is associated with malachite and minor libethenite and brochantite and at the Crusader it is found with malachite and brochantite. Pseudomalachite and libethenite occur at the Monakoff mine. These deposits are being mined. On the dumps at the Inkerman both pseudomalachite and libethenite are commonly found associated with
azure and malachite. The same association is found at the Young Australia hosted in a graphitic schist. At the Lorena gold mine both phosphates are associated with olivenite, \( \text{Cu}_3(\text{AsO}_4)(\text{OH})_2 \) and conichalcite, \( \text{CaCu}(\text{AsO}_4)(\text{OH})_2 \). Pseudomalachite is found in the dumps of the Blockade group, Soldiers Cap, Mt. Cobalt and White Range areas and Wee McGregor and Lady Jenny deposits associated with malachite and chrysocolla. Collecting from old dumps has limitations, but this does serve to demonstrate the widespread occurrence of pseudomalachite.

The rare occurrence of cornetite, confined to the Great Australia Main Lode outcrop, is related to the fact that it may only form under somewhat more unusual chemical conditions (relatively high pH and copper and relatively low phosphate ion activities) than its more common congeners pseudomalachite and libethenite (Magalhães et al., op. cit.). That there was considerable variation in these parameters is evidenced by the fact that all three occurred in all possible crystallization orders in the outcrop of the Main Lode at the Great Australia.

Microcrystalline, sharp prismatic cornetite, deep blue in colour (Fig. 5-18), was found with later, bladed, light olive-green libethenite. Also, cornetite may be observed to be both coated by pseudomalachite, and forming on the latter. However, it is possible that the occurrence in this setting of cornetite is related to pH effects since the outcrop was in the vicinity of carbonate rocks of the Corella formation. An equilibrium pH-activity diagram indicating these relationships (Magalhães et al., op. cit.) is shown in Figure 5-19. The only other deposit in the Mount Isa Block at which cornetite has been found is the Blockade mine, 70 km WNW of Cloncurry. The zone containing the cornetite has been mined out but a specimen in the author’s collection has bright blue prismatic microcrystals of cornetite on a 3 mm thick layer of malachite. In places the malachite is covered with a crust of dark green translucent pseudomalachite. Libethenite has not been reported from the Blockade.
A separate, but remarkable, observation in many deposits that have been examined is the zoning of the secondary copper phosphates in the supergene profile. In particular, libethenite is always found near the top of the oxidized zone. Kaolinization of hosting metadolerites immediately underneath the dipping orebodies at the Great Australia is associated with sulfuric acid generation as the result of the oxidation of pyrite. Secondary phosphate mineralization was extensive. Pseudomalachite and libethenite were present in the outcrop of the Great Australia Main Lode and libethenite was found near the surface in vughs in ferruginous quartz and associated with pseudomalachite and cornetite near the surface in a small pod of altered tuffs. As mining of the oxide zone proceeded abundant libethenite was found in and immediately beneath the silicified gossan of the Main Lode, particularly towards the northern end of the main open cut. Aggregates of acicular and bladed crystals to 10 mm were scattered over joints and fractures and in vughs in ferruginous lode quartz and in silicified gossan, sometimes accompanied by turquoise. However, all traces of libethenite had vanished at a depth of about 15 m. Pseudomalachite, as crystal aggregates or bunches, coating vughs in friable gossan and as banded botryoidal material associated with malachite persisted to the base of bench 11 (ca 35 m from surface) in the Main Lode. Little phosphate mineralization was noted in the intersecting B Tangye Lode.

In other deposits in the Mt. Isa Block, the same zoning is evident. At the Warwick Castle, libethenite as prismatic and platy crystals to 8 mm liberally coated shattered lode quartz and joints in altered metabasalts in the lode outcrop, associated with minor pseudomalachite, azurite and chrysocolla. In some cases, dark olive-green, prismatic crystals of libethenite had formed over an inflorescence of sub-crystalline blue-green pseudomalachite on a siliceous goethite-quartz breccia matrix (Fig. 5-20). Libethenite was confined to the near surface (<10 m) zone, with pseudomalachite as crystal clots and rhythmically banded
aggregates with malachite persisting deeper than 30 m (190 RL bench). At the Hardway mine, near Mt. Isa, libethenite associated with pseudomalachite occurs in a kaolinized quartz-rich gossan at the surface and persisting to a depth of a few metres in a small open cut. Here the paragenetic sequence is the reverse of the above with the libethenite forming first, followed by a coating of blue-green pseudomalachite. There were a few minor exceptions indicating some fluctuation in conditions at the stability boundary. This should not be unexpected but points to the possibility of erroneous conclusions in determining paragenesis without a planned sampling program. Occasionally the libethenite has formed over a coating of pale blue chrysocolla. Most specimens show the libethenite as a sub-crystalline coating often giving way to typical isolated crystals around the margins of the coating. At the Desolation prospect, south of Cloncurry, libethenite and pseudomalachite occur in small pits within a metre of the surface, associated with malachite, chrysocolla and the secondary arsenates, olivenite, conichalcite, and clinoasite, Cu$_3$(AsO$_4$(OH)$_2$, the latter three minerals being the result of oxidation of arsenopyrite, cobaltite and chalcopyrite.

Elsewhere in Australia a similar distribution of copper phosphates has been observed. At Girilambone in north western New South Wales libethenite was confined to a zone 10 to 18 m from the surface. By way of contrast, pseudomalachite was a comparatively common secondary phase which extended through the libethenite zone to bench 28, approximately 90 m from the surface and a similar distribution has been described for the copper phosphates in the ore bodies at Northparkes where alteration and leaching of the hosting quartz monzonite porphyry has produced bleached, kaolinized zones from which all visible trace of mineralization are removed.
Fig. 5-18. Prismatic cornetite crystals. Outcrop, Great Australia mine, Cloncurry. FOV 4 mm.

Fig. 5-20. Inflorescence of pseudomalachite with prismatic libethenite crystals. Warwick Castle mine, Kajabbi district. FOV 3 mm.
Fig. 5-19 Stability field log $a$(Cu$^{2+}$) versus pH for the simpler Cu(II) minerals at 298.2 K (after [1]).

Fig. 5-21 Stability field log $a$(H$_2$PO$_4^-$) versus pH for the simpler Cu(II) minerals at 298.2 K.
Immediately beneath these zones pseudomalachite and libethenite occurred. Libethenite was limited to the top contact of the oxidized zones with pseudomalachite persisting to a few metres deeper and grading into malachite - azurite - cuprite - native copper - chalcosite assemblages.\textsuperscript{9}

All of these observations lend weight to the conclusion that libethenite generally occurs in the upper sections of the oxidized zone, with pseudomalachite further down. The reason for this is not readily apparent from an inspection of Figure 5-19, although it does explain the rarity of cornetite and the fact that it can only form under comparatively basic pH conditions. However, the figure can be recast in such a way that the observed zoning is easily understood, as shown in Figure 5-21. Constraints of pH are such that $\text{H}_2\text{PO}_4^{-}(\text{aq})$ is the predominant phosphate species in solution. The stability relationships between libethenite, pseudomalachite, cornetite and $\text{H}_2\text{PO}_4^{-}(\text{aq})$ have been determined using the following equations.

\begin{align*}
5\text{Cu}_2\text{(PO}_4\text{)}\text{(OH)}_2 + 3\text{H}_2\text{O} & \rightleftharpoons 2\text{Cu}_3\text{(PO}_4\text{)}\text{(OH)}_3 + \text{H}_2\text{PO}_4^{-} + \text{H}^+ \quad (5) \\
3\text{Cu}_3\text{(PO}_4\text{)}\text{(OH)}_3 + 3\text{H}_2\text{O} & \rightleftharpoons 5\text{Cu}_2\text{(PO}_4\text{)}\text{(OH)}_2 + \text{H}_2\text{PO}_4^{-} + \text{H}^+ \quad (6) \\
3\text{Cu}_2\text{(PO}_4\text{)}\text{(OH)} + 3\text{H}_2\text{O} & \rightleftharpoons 2\text{Cu}_3\text{(PO}_4\text{)}\text{(OH)}_3 + \text{H}_2\text{PO}_4^{-} + \text{H}^+ \quad (7)
\end{align*}

Calculations were carried out for the reactions at $T = 298.2$ K and $P = 10^5$ Pa using $\Delta f\text{G}^\circ$ values taken from the literature.\textsuperscript{17,18} The figure indicates that libethenite forms at most concentrated phosphate activities and pseudomalachite from solutions with lower amounts of dissolved phosphate, for a given copper ion activity.

In a classical study of the weathering of a gneiss, Goldich\textsuperscript{19} found that apatite, the source of phosphate for all the above species, was among the least stable minerals, together
with plagioclase, epidote, hornblende and sphene. Ollier\textsuperscript{20} noted that hydroxylapatite was most easily weathered and chloroapatite less so. Fluorapatite is fairly resistant to weathering and is a common detrital mineral. Thus the observed zoning may simply be accounted for by the intensity of weathering of the host rocks. Most intense weathering at the surface will lead to higher phosphate concentrations in solution, thus making the formation of libethenite more likely. As weathering intensity diminishes with depth, less phosphate will be available and pseudomalachite will dominate the secondary copper phosphates. This observation, together with appropriate pH control, serves to unify all of the occurrences of the secondary copper phosphates in the deposits examined. Finally, in this connection, Stumm and Morgan\textsuperscript{21} suggest that the formation of hydroxylapatite controls phosphate concentrations in groundwaters. Crane \textit{et al.}\textsuperscript{12} noted that at Northparkes, secondary hydroxylapatite is one of the last minerals to form in the oxidized zone. It is commonly found as hexagonal plates to 1 mm on pseudomalachite and chrysocolla endomorphs after libethenite. No copper minerals were observed to form after hydroxylapatite.

5.6 Arsenates.

During field work relatively few copper arsenates were found. However, there were a few deposits where arsenopyrite or cobaltite formed part of the primary ore thus providing the opportunity for the formation of secondary copper arsenates.

Conichalcite, CaCu(AsO$_4$)(OH), is by far the most common copper arsenate encountered. It is best represented at the Lorena gold mine where it is the predominant secondary copper mineral. The Lorena is a small but high grade gold deposit east of Cloncurry, containing as primary mineralisation pyrite, arsenopyrite, cobaltite, chalcopyrite, native bismuth and gold, and is the site from which was collected the rare mineral wupatkiite,
CoAl₂(SO₄)₄.22H₂O, recorded only once previously.\textsuperscript{22} Most of the conichalcite at the Lorena is in the form of grass green crusts but occasionally spheres with a radially fibrous structure can be found on a matrix of ferruginous quartz and goethite (Fig. 5-22). At the Poiseidon mine, conichalcite occurs as dull yellowish-green coatings and globules in chert. Similar conichalcite can also be found at Mt. Cobalt and at the Desolation mine in the White Range.

Clinoclase, Cu₃(AsO₄)(OH)₆, was found as scattered, rosettes of dark indigo blue crystals to 0.5 mm (Fig. 5-23), associated with conchalcite and olivenite, Cu₃(AsO₄)(OH), at the Desolation mine. Minute crystals of clinoclase were found at the Poseidon mine and one minor occurrence has been reported from Mount Cobalt.\textsuperscript{21} In the Australian context, clinoclase must be regarded as a rare mineral, the only locality of note for this mineral being Dome Rock in South Australia; even there it is not common.\textsuperscript{24}

Olivenite is also of restricted occurrence in the Cloncurry district. It has been found at both the Desolation and Lorena mines as radiating groups of slender prismatic crystals to 1 mm, varying in colour from olive green to almost golden brown. Day and Beyer\textsuperscript{23} collected olivenite from the Mount Cobalt deposit, which was pink at the crystal terminations due to inclusions of erythrite, Co₃(AsO₄)₂.8H₂O, a common mineral at Mt. Cobalt.

Whilst it could be expected that the copper arsenates would have a similar species distribution to their phosphate analogues, this is not so, particularly in the presence of calcium. In the Cloncurry district there is an abundant source of calcium from either decomposing granite or carbonate rocks. The area occupied by conichalcite in the stability field increases dramatically with increasing calcium ion activity\textsuperscript{1} (Fig. 5-24), requiring a much higher activity of copper to precipitate olivenite or clinoclase in preference to conichalcite; hence the relative rarity of the former in this district is readily apparent.
Fig. 5-22. Radial aggregates of conichalcite on gossan.
Lorena gold mine, Cloncurry. FOV 6 mm.

Fig. 5-23. Clinoclase crystals with malachite lining fractures in metasediments. Desolation prospect,
White Range. Crystals are 2 mm long.
Olivenite and clinooclase at the Desolation occur together with pseudomalachite and malachite. With respect to the former, a superimposition of the relevant stability field diagrams for the phosphate and arsenate systems \(^1,^{14,17}\) serves to limit the solution conditions that applied when this assemblage formed.

It ought to be noted that intensive searches have failed to uncover any cornubite, \(\text{Cu}_4(\text{AsO}_4)_2(\text{OH})_6\), or its dimorph, cornwallite, which is of the same composition as pseudomalachite but with arsenate in place of phosphate. The stability field for cornubite is very small compared to that of olivenite or clinooclase, and to that of pseudomalachite versus libethenite or cornetite in the corresponding phosphate system.\(^1\) It may also be that when cornubite or cornwallite have formed, they have subsequently been replaced by the more common secondary arsenates as solution conditions have changed.

![Graph](image)

**Fig. 5-24** Effect of \(\text{Ca}^{2+}\) (aq) on the stability field for copper arsenates. Calcium activities are \(10^{-3}\) (firm line) and \(10^{-4}\) (broken line) (After [1]).

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Two other rare copper arsenates have been reported from Mount Cobalt. They are cobaltaustinite, Ca(Co,Cu)(AsO$_4$)(OH)$_2$, as dull green crusts and globular coatings, and agardite, (REE,Ca)Cu$_6$(AsO$_4$)$_3$(OH)$_6$.3H$_2$O, as pale green to nearly white acicular crystals on mica schist with minor conichalcite.$^{23}$

5.7 Chlorides.

Chloride is the only halide reported in the copper mineralogy of the Cloncurry district. However, amongst the chlorides there is a number of rare and interesting species.

One of the rare minerals in this group, nantokite was first noted as a result of its alteration product, atacamite, CuCl(OH)$_2$, forming as pale green earthy crusts on specimens of cuprite and native copper from several of the lower benches in the Great Australia. XRD was used to identify the alteration product as it had been reported from other deposits as being paratacamite.$^7$ When these specimens were broken open and the fresh surface examined it was found that nantokite was present as colourless to white transparent to translucent flakes and masses superficially resembling quartz, and often showing a conchoidal fracture. The distinguishing features are a hardness of 2.5 and, because of the thixotropic properties of the mineral, its sectile nature, similar to that of candle wax. On exposure to the atmosphere it commences to oxidise and hydrate within a few days to form atacamite or its polymorph, paratacamite, changing to a pale green, crumbly powder. Nantokite was most commonly found in massive cuprite containing native copper (Fig. 5-25). Metallic copper in contact with aqueous chloride solutions will react to form nantokite. It is commonly found as a corrosion product on copper archeological artifacts.$^1$
Fig. 25. Nantokite with native copper and cuprite. 
(A) shows freshly exposed nantokite which is water clear, 
with conchoidal fracture surface. (B) shows in top RH corner 
white nantokite altering to green atacamite. Bench 16, Main 
Lode, Great Australia mine, Cloncurry. Cuprite crystal is 3 mm across.
The stability relationships between copper, nantokite, paratacamite and cuprite have been determined (Fig. 5-26) for a range of $a(\text{Cl}^-)$ using the following equations.

\[
\begin{align*}
\text{CuCl}_{(s)} + e^- & \rightarrow \text{Cu}_{(s)} + \text{Cl}^- \quad (8) \\
\text{Cu}_2\text{Cl(OH)}_2 + \text{Cl}^- + 2e^- + 3\text{H}^+ & \rightarrow 2\text{CuCl} + 3\text{H}_2\text{O} \quad (9) \\
\text{Cu}_2\text{Cl(OH)}_2 + 4e^- + 3\text{H}^+ & \rightarrow 2\text{Cu} + \text{Cl}^- + 3\text{H}_2\text{O} \quad (10) \\
\text{Cu}_2\text{Cl(OH)}_2 + 2e^- + \text{H}^+ & \rightarrow \text{Cu}_2\text{O} + \text{Cl}^- + 2\text{H}_2\text{O} \quad (11) \\
\text{Cu}_2\text{O} + 2e^- + 2\text{H}^+ & \rightarrow 2\text{Cu} + \text{H}_2\text{O} \quad (12) \\
\text{Cu}_2\text{O} + 2\text{Cl}^- + 2\text{H}^+ & \rightarrow 2\text{CuCl} + \text{H}_2\text{O} \quad (13)
\end{align*}
\]

Calculations were carried out for the reactions at $T = 298.2$ K and $P = 10^5$ Pa, using $\Delta f G^\circ$ data taken from the literature. The limits of the diagram have been extended beyond those found in nature, but attention is drawn to relative portions of the stability field. Native copper in contact with acidic saline groundwater can form nantokite as the required oxidation potential ($E_{\text{ox}}$) is well within the limits found in groundwater. Analysis of groundwater from ten exploratory drill holes on the mining lease gave a mean of 116 mg/l and a maximum of 218 mg/l, the latter approximating $\log a(\text{Cl}^-) = -1.2$. It was noted that nantokite was most abundant in cuprite containing native copper, commonly being found at the cuprite - native copper interface. This is in agreement with the predictions of the stability field diagram showing that nantokite is most likely to form as a result of saline groundwater reacting with native copper at low pH.

It is significant as well to note that, aside from the possible paratacamite to nantokite transformations (never reported in the literature, perhaps not being observed for kinetic reasons), it is possible to generate nantokite from cuprite at constant $a(\text{Cl}^-)$ and $E$, via a shift to more acid conditions. Such a situation would however, give rise to other phenomena which
are well known in the basic inorganic chemical literature.\textsuperscript{15} Cu\textsubscript{2}O disproportionates in acid, according to equation (14).

\[
\text{Cu}_2\text{O(s)} + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + \text{Cu}^0(\text{s}) + \text{H}_2\text{O(l)} \quad (14)
\]

This process is very fast and may serve to prevent, for mechanistic reasons, observations of the direct cuprite to nantokite transformation. Note again, however, that native copper is produced in (14).

In detailed studies of the Main Lode at the Great Australia, nantokite was not observed with cuprite alone, but always in association with native copper. For the most part, nantokite was found as an alteration product of native copper. It is significant that few nantokite specimens were found in the B Tangye Lode. In this lode very little native copper accompanied the cuprite. These observations bear out the fundamental chemistry mentioned above and suggest the main, if not sole, source of nantokite at the Great Australia is the result of the alteration of native copper.

The abundance of nantokite at the Great Australia is noteworthy. Nantokite altering to atacamite was first observed, but not recognised, in specimens from Cloncurry as early as 1887 when Lindon\textsuperscript{27} noted, \textit{I find that specimens of massive cuprite, or native copper changing to cuprite, from Cloncurry are very liable to be encrusted with malachite after keeping for a short time in the atmosphere of Brisbane}. In other localities it is a very rare mineral. Nantokite was first reported in 1867 from the Carmen Bajo mine a few kilometres west of Nantoko, Chile.\textsuperscript{28} The second report was made by Liversidge\textsuperscript{29} in 1894 regarding specimens found in a matrix of cuprite, associated with native copper (in line with the above discussion) and cerussite from the Broken Hill South mine. Bottrill\textsuperscript{7} has also reported nantokite from the South mine, as a coating on native copper. Crystals were not reported from
Fig. 5-26 Stability field diagram for nantokite, paratacamite, cuprite and native copper for \( a(CI) = 10^1, 10^6, 10^4 \) and \( 10^3 \) respectively at 298.2K.
Carmen Bajo or Broken Hill, nor have they been found in the specimens from Cloncurry. Small complex crystals to 6 mm have been reported from the Southwest mine, Bisbee, Arizona. At the Great Australia, however, a block of mineralisation \textit{ca} 4 m wide, more than 10 m deep and exposed in the open cut over a distance of 40 m contained significant amounts of nantokite. In all, its extent in the Main Lode must have been greater than the few exposed benches sampled in 1996 and 1997. It is concluded that this deposit contains the largest mass of nantokite in one deposit, so far, in the world.

Probably nantokite is quite widespread in small amounts but has not been recognised because of its superficial resemblance to quartz and the very rapid alteration when exposed. Conditions favourable for native copper to react with chloride rich groundwater to form nantokite as described above exist elsewhere in the Cloncurry mineral field. Nantokite was also identified in cuprite - native copper specimens collected from the Magpie and Wewak mines, supporting this conclusion.

Claringbullite, $\text{Cu}_3\text{Cl}_2(\text{OH})_{14}.\text{H}_2\text{O}$, is another very rare mineral. It was first found in the late 1960's, in a cuprite specimen from Bisbee, but the quantity was too small to carry out the necessary descriptive work. In 1973, this specimen together with two from the M'sesa mine, Katanga and Nchanga pit, Zambia, were submitted to the British Museum where they were X-rayed and found to be identical and were identified as a new species. The distinct characteristics of claringbullite make it easy to identify in the field. It is translucent, light sky blue in colour with a pearly lustre and a micaceous habit, and is usually found as flat plates, occasionally on edge and rarely as flat hexagonal crystals (Fig. 5-27). In all reported instances it has been found within cuprite with one or more associated minerals, brochantite, connellite, ideally $\text{Cu}_{19}\text{Cl}_4(\text{SO}_4)(\text{OH})_{32}.3\text{H}_2\text{O}$, atacamite or gerhardtite, $\text{Cu}_3(\text{NO}_3)(\text{OH})_3$. Williams' found that claringbullite could be isolated as a metastable
Fig. 5-27. Claringbullite crystal. Great Australia mine, Cloncurry. Crystal is 0.7 mm dia. Photo and specimen B. Beyer.

Fig. 5-29. Connellite crystals in vugh lined with secondary quartz. Bench 6, Tangye Lode, Great Australia mine, Cloncurry. FOV 6 mm.
intermediate from dilute aqueous CuCl₂ by reaction with NaOH, provided other anions were absent. Therefore, claringbullite would have formed after sulfate and nitrate ion species had been depleted in forming brochantite, gerhardtite and connellite. At the Great Australia mine claringbullite was found in massive cuprite on Bench 6 in the B Tangye Lode, associated with all the previously mentioned minerals, but not in the massive cuprite lodes which occurred deeper. No other occurrences have been recorded and all references²⁸,²⁹ indicate scant quantities of material being available. At the Great Australia the many specimens that have been recovered by collectors suggests that this mine may have been the world’s most prolific source of the mineral.

Atacamite, referred to previously, is found in the Cloncurry district but is not abundant, occurring as small crystal groups lining vughs, commonly in cuprite, and less frequently lining fractures in siliceous hematite. Soft, pale green atacamite, formed as an alteration product of nantokite is occasionally encountered in situ but this is likely to be a result of exposure following mining. Atacamite occurs as vertically striated, chisel ended, slender prisms, emerald to dark green in colour, commonly associated with brochantite. Atacamite is one of four polymorphs, the others being paratacamite, bottallackite and clinoatacamite.³² The two latter minerals are rare, and there is some uncertainty as to the abundance of paratacamite as it is probable that many specimens described as atacamite are paratacamite.³³

The stability diagram for eriochalcite, CuCl₂·2H₂O, atacamite, bottallackite and paratacamite (Fig. 5-28),¹ shows that atacamite and paratacamite occupy regions of moderate acidity likely to prevail in the copper lodes of the Cloncurry district. Williams¹ pointed out that atacamite and bottallackite are metastable with respect to paratacamite, and that

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paratacamite is the stable phase under ambient conditions, except that atacamite will persist metastably in the presence of high amounts of chloride ion in solution. This is in agreement with observations in the field. For example, localities in the Chilean copper belt, Copiapo and Chuquicamata, sources of fine atacamite specimens, have an acidic, chloride rich environment. As mentioned previously, the vadose water of the Great Australia is also chloride rich.

![Graph showing the relative stabilities of eriochalcite and paratacamite at 298.2 K. The corresponding boundaries between the former and atacamite and botallackite are shown with broken lines. After [1].](image)

Connellite was originally described in 1863 from a specimen found in the Wheal Providence mine, Cornwall. Although regarded as a rare mineral, it has been recorded from a number of localities in Arizona, Utah and California as well as Cornwall, Algeria and Africa. In Australia, connellite has been recorded from the Ediacara mine in the Flinders Ranges, and was first reported from the Great Australia in 1990 by Wallace and Pring.
Further specimens have been obtained during current mining on Bench 6 in the B Tangye Lode in massive cuprite - hematite boulders and associated with the species described previously. Connellite occurs as long, blue acicular to hair-like crystals to 2 cm (Fig. 5-29), and more rarely as very small, deep blue prismatic crystals. The latter were X-rayed as it was thought the darker mineral may have been buttgenbachite, Cu$_{19}$Cl$_4$(NO$_3$)$_2$(OH)$_3$$\cdot$2H$_2$O, which is isomorphous with connellite. However, connellite was confirmed by IR and EDAX methods. An SEM EDAX analysis gave strong signals for Cu, S and Cl. In the infrared, a spectrum recorded of a powdered sample using a transmittance FTIR spectrophotometer showed strong absorptions for SO$_4^{2-}$, and barely detectable absorptions for nitrate.

Although cuprite was more plentiful at depth, connellite was not found deeper in the lode. Instead, nantokite became more abundant, consistent with the stability field predictions (Figs. 5-30, 31 and 32), which show that connellite requires low acidity *e.g.*, pH > 5, whilst for the same activity of Cl, nantokite requires pH < 5. The stability field shown in Fig. 5-30 most closely represents the conditions within the cuprite lodes at the Great Australia, with CO$_2$ at ambient partial pressures of around 10$^{-3.5}$, as malachite, not tenorite, is a commonly associated mineral, not so much within the vughs, but as veins in breccia and films on cuprite boulders. Nantokite at depth is also entirely consistent with falling values of redox potential as the water table is approached.

There has been much interest in the so called "zeolite-like" structure of connellite and it has been suggested that it may form a complex solid-solution series with buttgenbachite, where the nitrate partially or completely replaces the sulphate ion. Buttgenbachite has been tentatively reported from the Great Australia. Microprobe analysis at the Museum of Victoria of a very small specimen similar to connellite, but a darker blue, indicated an absence of sulfur and the presence of chlorine and nitrogen. However the
specimen was too small for complete analysis. The only confirmed occurrence is at the type locality, Likasi, Katanga \(^{34}\) and Mashamba West, Shaba, Zaire. \(^{39}\) It is further noted here that numerical inconsistencies in the reported structures of both connellite and buttgenbachite, together with the attribution of an extremely unlikely coordination geometry for one of the copper atoms in the structure, suggests that structural redeterminations to evaluate this complex solid solution series would be highly desirable.

![Stability field diagram for the copper(II) halide minerals in the absence of CO\(_2\). The firm and broken lines are drawn for sulfate activities of 10\(^{-3}\) and 10\(^{-1}\) respectively, (after [36]).](image)

Fig. 5-30 Stability field diagram for the copper(II) halide minerals in the absence of CO\(_2\). The firm and broken lines are drawn for sulfate activities of 10\(^{-3}\) and 10\(^{-1}\) respectively, (after [36]).
Fig. 5-31 Effect on stabilities of the copper chlorides of CO$_2$(g). The firm line in the absence of CO$_2$, the broken line is for p(CO$_2$) = 10$^{-3.5}$, (after [36]).

Fig. 5-32 Redox-pH diagram for the copper minerals with activities of SO$_4^{2-}$ = 10$^{-5}$ and Cl$^-$ = 10$^{-1.75}$, (after [36]).
5.8 Nitrate

Gerhardtite, Cu₂(NO₃)(OH)₃, has been found at the Great Australia where it occurs within massive cuprite associated with connellite and claringbullite. A single specimen was also collected during field work at the Monakoff mine. Gerhardtite from the Great Australia was first reported by McColl in 1978⁴⁰ and was the subject of further analysis by Wallace and Pring³⁵ in 1990. The specimens had been collected from cuprite boulders in the dumps. During the current field work all specimens were found on Bench 6, B Tangye Lode, always as inclusions or within small vughs in massive cuprite which would have protected the gerhardtite from further alteration. It has not been found in the deeper and more acidic environment of the Main Lode due to gerhardtite being readily soluble in dilute acids.

Gerhardtite was first described in 1885⁴¹ from a specimen collected at the United Verde mine, Jerome, Arizona. It was not reported again until 1956⁴² from Likasi, Katanga, Zaire. At these locations also, gerhardtite was found in cuprite.

Crystals of gerhardtite from the Great Australia appear to be a very dark, almost black colour and occur as blades up to 1mm across. The mineral has good basal cleavage, with cleavage faces being either blue or green as gerhardtite is pleochroic; X = Y = green, Z = blue.⁴ There is a degree of chatoyancy in the blue colouration which is an aid to field identification (Fig. 5-33).

The conditions in which gerhardtite may be found are limited to arid environments where nitrates will not be consumed by vegetation (See Chapter 4), a relatively impervious host e.g. massive cuprite and non-acidic, copper rich fluids. The source of the nitrate is a matter of conjecture, i.e. from an organic origin or, more probably, from lightning generated during thunderstorms.⁴³
Fig. 5-33. Gerhardtite crystal which appears almost black, whilst the cleavage face shows a distinctive blue chatoyancy. Great Australia mine, Cloncurry. FOV 4 mm. Specimen and photo B. Beyer.
5.9 Silicates.

Chrysocolla, (Cu,Al)$_2$H$_2$Si$_2$O$_6$(OH)$_4$,$n$H$_2$O, is as common as malachite, being present at most deposits in the district. Chrysocolla is often found filling fractures and penetrating along bedding planes in the surrounding rocks or forming veins in quartz breccia. Some deposits, e.g., the Trafalgar, have a cap of chrysocolla as a result of less resistant rock forming minerals weathering and allowing chrysocolla to remain as a residual. Most chrysocolla is found around the top of the lode although exceptions are occasionally encountered. At a depth of 30 m at the Great Australia, a pod of reniform chrysocolla was found lining a vugh in friable goethite. Spectacular secondary silica was found at all depths, particularly in the Main Lode.

![Stability diagram for chrysocolla versus the copper carbonates](image)

Fig. 5-34 Stability diagram for chrysocolla versus the copper carbonates (after [9]).
In vughs or fractures, chrysocolla will form as blue or blue-green translucent to opaque, botryoidal linings. X-ray analysis of specimens from the Trafalgar indicates that malachite is frequently present as an impurity, (M. Crane, pers. comm.), which may be responsible in many instances for the green colour. Very often malachite and less often azurite and pseudomalachite form over chrysocolla. Occasionally pseudomorphs of chrysocolla after malachite after azurite are found. Stability parameters (Fig. 5-34)\(^9\) show that chrysocolla cannot directly replace azurite except under very restricted conditions as the solubility limit of silicic acid truncates the azurite - chrysocolla stability field leaving only a minute interface of these phases. Therefore, in a geological environment malachite must form as an intermediate phase. These pseudomorphs have been found at the Great Australia, Monakoff and Trafalgar mines. They are also known from other mineral fields.

Fig. 5 - 35 Stability field diagram for chrysocolla versus Cu(II) phosphates at 298.2 K, with log \(a(H_3PO_4)\) = -4.
The copper phosphates, particularly pseudomalachite, are frequently associated with chrysocolla. At the Great Australia, Hardway and Blockade mines scattered crystals of cornetite or libethenite and clots of pseudomalachite are found on coatings or linings of chrysocolla. Cornetite and libethenite form distinct crystals. No pseudomorphs of chrysocolla after either of these minerals were found. The stability relationship of this group for the geochemical conditions prevailing at Cloncurry, can be determined (Fig. 5-35) using the equations below.

\[
\begin{align*}
\text{Cu}_2(\text{PO}_4)(\text{OH}) + 2\text{H}_4\text{SiO}_4 & \rightleftharpoons 2\text{CuH}_2\text{SiO}_4 + \text{H}_2\text{PO}_4 + \text{H}_2\text{O} + \text{H}^+ \quad (11) \\
3\text{Cu}_2(\text{PO}_4)_2(\text{OH})_4 + 5\text{H}_4\text{SiO}_4 & \rightleftharpoons 5\text{CuH}_2\text{SiO}_4 + 4\text{H}_2\text{PO}_4 + 4\text{H}_2\text{O} + 2\text{H}^+ \quad (12) \\
\text{Cu}_3(\text{PO}_4)(\text{OH})_3 + 3\text{H}_4\text{SiO}_4 & \rightleftharpoons 3\text{CuH}_2\text{SiO}_4 + \text{H}_2\text{PO}_4 + 3\text{H}_2\text{O} + \text{H}^+ \quad (13)
\end{align*}
\]

and selecting a low phosphate activity, in this case \(a(\text{H}_2\text{PO}_4) = 10^{-4}\). Calculations were carried out for reactions at \(T = 298.2\) K and \(P = 10^5\) Pa, using \(\Delta fG^0\) data taken from the literature.\(^{18}\) With the activity of silica\(^9\) limited by saturation to \(10^{-7}\), it can be immediately seen that chrysocolla could not replace these copper phosphates.

As described previously, slugs of native copper at the Great Australia often have an outer rind of chrysocolla over inner rinds of cuprite and tenorite. The tenorite is very siliceous which has given rise to the term “black chrysocolla”. In 1908, Ball reported diopside from a number of locations including the Mount Wheeler mine in the Soldiers’ Cap group.\(^{44}\) However it may be that the term as used 90 years ago actually refers to chrysocolla. Dioptase has not been found during field work, nor has it been recently reported.
5.10 Paragenesis and Distribution

In this discussion on paragenesis, the Great Australia is used as the model, firstly because it is the only relatively large oxide zone deposit extensively mined by open cut methods during the period of field work, and secondly it is representative of the outcropping fault hosted copper lodes of the district. Other deposits are either too small or mining has not been sufficiently advanced to provide an overall assessment of the mineralogy. Examples from these deposits are described where relevant, however.

In assessing the paragenesis of secondary mineralisation it is necessary to consider not only the evidence revealed by examination of samples which may be representative of a particular part of the deposit, but also the geochemical processes that dictate the order of formation of the various species. In a natural system conditions of pH, oxidation potential, mix of species and presence of naturally occurring catalysts or nucleators e.g. manganese oxide, and deeper in a lode, temperature and pressure variants, serve to create local fluctuations. The most striking example of this is the cornetite- pseudomalachite- libethenite association at the Great Australia. It will also be evident from the chemistry discussed previously that often there is more than one route to the formation of a species.

During the study period it was possible to collect samples and make observations from the commencement of the new phase of mining, which except for an old shallow open cut, was at the surface, to a depth of about 60 m where mining ceased. This was unfortunate in that it was not possible to observe the transition from the cuprite to the chalcocite zone. A few specimens of chalcocite were found, mostly as small inclusions within quartz breccia, a few having alteration rims of tenorite or malachite, only one of cuprite. A small number of secondary chalcocite and djurleite crystals in a quartz and calcite gangue were also found.
Schwartz's states that cuprite is most often formed by direct oxidation of sulfides, especially chalcocite. Polished sections of chalcocite from the Campbell shaft, Bisbee, show chalcocite brecciated and being replaced by cuprite. Apart from one specimen, no evidence of this was observed at the Great Australia, but the current mining operation did not expose the supergene enriched zone to any significant extent.

It is evident that at the Great Australia, within the lode that was mined, native copper and cuprite were formed as a result of precipitation in the presence of iron oxides as described previously. Small fluctuations in pH or redox potential could result in either being formed, although most native copper occurs within cuprite, suggesting that the former was first to be precipitated. Also, a number of specimens of arborescent native copper have been found with well-developed cuprite crystals scattered over the surface. Large slugs of native copper with a surface rind of cuprite are occasionally found.

It has also been shown that nantokite is formed directly from alteration of native copper in the presence of saline ground water at relatively low pH and in the absence of oxygen, the latter having been consumed in forming cuprite. These are the first oxide zone species to form.

The frequent presence of brochantite was noteworthy, not only at the Great Australia, but elsewhere in the district, being found at most larger deposits and at all depths, but always tightly within the lode. This is consistent with the observation that the source of the sulfate ion is the oxidising sulfides of the ore body. Brochantite was not found on any native copper specimens, but was commonly associated with atacamite in cuprite vughs. Brochantite can form at a very late stage as shown by the presence of tabular brochantite crystals found on reniform malachite-pseudomalachite aggregates within 10 m of the surface. It was common to find brochantite on malachite but the reverse order of formation was never encountered.
The Main Lode at the Great Australia contained an extraordinary amount of nantokite and therefore it is probable that most atacamite was formed by reaction of nantokite with oxygen bearing vadose water. The rare chlorides claringbullite and connellite, together with the nitrate gerhardtite, were found in only one location; in hematite-cuprite boulders on Bench 6, B Tangye Lode. They occurred in small enclosed vughs in siliceous hematite-cuprite which appears to have sealed the contents from further reaction with groundwater external to the vughs. Brochantite, atacamite and to a lesser extent malachite were also present as later forming minerals. The first to form were connellite and gerhardtite which were often embedded in the cuprite, followed by claringbullite as the chloride rich solution was depleted of other anions. These vughs are another example of protection within an enclosed micro-environment.

Malachite is found at all depths, but as depth increased it was restricted to around the periphery of the lode reflecting the availability of two sources of CO\textsubscript{2}; atmospheric CO\textsubscript{2} in groundwater channelled down the shear and through permeable strata, and CO\textsubscript{2} generated by acidic vadose water reacting with carbonates in the gangue. At the same time as native copper and cuprite were being formed, copper carbonates were also being formed via reaction with cuprite. The replacement of cuprite by malachite is often observed, and in a few locations e.g., the intersection of the Main and B Tangye Lodes, azurite has been found, formed as a result of acidic vadose water reacting with intermittent pods of carbonates to develop CO\textsubscript{2}(g) at a partial pressure above 10\textsuperscript{-13}. As described previously, the majority of azurite specimens collected in the Cloncurry district have a base layer of malachite, formed before equilibrium CO\textsubscript{2} pressure was reached.

Both libethenite and pseudomalachite are present in the Main and B Tangye Lodes. The formation in the isolated pod of tuff of all three phosphates as previously
described is treated as a separate event. In the lodes most pseudomalachite and libethenite have been found separately, with only two samples from Bench 6 Main Lode showing both minerals and with pseudomalachite forming later than libethenite. It would not be prudent to base a general paragenesis on two samples when at other deposits, i.e., the Hardway and Warwick Castle, both orders of formation have been observed under similar conditions. However, pseudomalachite persists to greater depths and the geochemistry discussed previously has shown that libethenite will form as phosphate activity increases resulting from weathering of apatite species.  

In the pod containing cornelite, pseudomalachite and libethenite, all orders of formation were found. It is noteworthy that in some samples only cornelite and libethenite were found, indicating that locally there were extreme fluctuations in pH and/or copper or phosphate ion activities. However, most samples show cornelite forming first and others with cornelite alone, indicating a resultant order of formation in this isolated pod of cornelite-pseudomalachite-libethenite.

Chrysocolla is very common near the surface and around the periphery of the lode until the cuprite zone is reached where it becomes much less common. Although there is ample secondary silica in this deeper zone, it has not formed chrysocolla.

Figure 5-36 is a schematic assessment of the distribution of copper species within the oxide zone of the Great Australia mine. The paragenesis of these minerals is illustrated in Figure 5-37.
FIG. 5-36

DISTRIBUTION OF OXIDE ZONE COPPER MINERALS
GREAT AUSTRALIA MINE

GOSSAN

LEACHED ZONE

Major ore minerals
malachite
cuprite

Minor ore minerals
chrysocolla
pseudomalachite
tenorite
native copper

Minor associated minerals
libethenite
brochantite
atacamite
azurite

Rare minerals
nantokite
connellite
claringbullite
gerhardtite
cornelite

LIMIT OF MINING

WATER TABLE

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PARAGENESIS OF OXIDE ZONE COPPER MINERALS
GREAT AUSTRALIA MINE

EARLY
- copper
- nantokite
- cuprite

LATE
- tenorite
- atacamite
- brochantite
- malachite
- azurite
- pseudomalachite
- pseudomalachite
- libethenite
- connellite
- clarinbullite
- gerhardtite
- chrysocolla

CORNITITE POD
- chrysocolla
- cornetite
- pseudomalachite
- libethenite
5.11 References


24. P. Bayliss, L. J. Lawrence and D. Watson, *Rare copper arsenates from Dome Rock*, 89


6. DISCUSSION

6.1 The role of geochemical models in predicting the occurrence and distribution of mineral species in ore deposits

This study has shown that the occurrence of oxide zone copper minerals can be predicted in terms of frequency and spatial distribution once geochemical constraints, *i.e.*, pH, Eh and groundwater composition, are fixed. Stability field diagrams for many common species are to be found in the literature, or may be constructed from published thermodynamic data. From the known conditions the species most likely to form can be determined by reference to the relevant stability field(s) for the group(s) of species under consideration. In some instances stability phase data will also indicate species that will not form or only form *via* an intermediate phase. The approach also explains the apparent rarity of some species *e.g.*, cornwallite and corunbite compared with the more common conichalcite.

Although the list of known copper species is relatively long, there are only 13 species that are common or occur in significant quantities in the Cloncurry district. Therefore determination of the range of species present at a deposit in the district is not a formidable task.

The mining of oxide zone copper deposits has entered a new phase with modern SX-EW process replacing the inefficient cementation method for the treatment of these ores. Miners can now efficiently mine and process relatively small lodes as the plant can be scaled down to practically any production rate. However, initial leach rate will be determined by the
species present, which can impact on initial cash flow, a matter of critical importance to most companies.

The detection of a particular mineral in exploratory drill core may be a single random occurrence. From stability phase data for the species combined with ground water analysis it would be possible to predict whether the mineral is likely to be widespread in the deposit. In this regard, the presence in substantial quantities of the mineral nantokite is noteworthy. Whilst there is no available data on the effect this may have had on leach rates, and it is probable that it was not significant, it could have a bearing if other forms of concentration were used. For example, if the oxide ore was sulfidised and floated the concentrate may contain excessive chloride such as to incur toll penalties for smelting. This situation did occur with atacamite in the concentrate in at least one deposit in the region. Nantokite has been found at two other deposits in the district and almost certainly exists in others where native copper is present in the vicinity of oxidising sulfides and where saline groundwater occurs.

It would worthwhile to construct a geochemical model for supergene ore deposits whilst at the exploration stage as the process is not difficult. The geochemical model constructed for the Great Australia shows a remarkable correlation with data from the field study.
Appendix I

Mines of the Cloncurry District included in the study.

Appendix I is a brief description of the deposits inspected during the study. It is by no means a complete list of the deposits in the district. The most extensive survey is that of Ball, although it relates to mining prior to 1908. More recent reports are those by Brooks and Krosch et al.

Deposits are grouped by area to avoid repetition.

A. Deposits near Cloncurry township.

The Great Australia, Monakoff and Lorena deposits have been described in Chapter 3.

Mt. Glorious 8 km west of Cloncurry

This was a small gouger show first worked in the late 1960's and then for a short time about 1985. The lode is in a ferruginous gossan and quartzite with a massive central quartz vein. This vein has yielded unusual specimens of pseudomalachite, consisting of sheaves of parallel crystals which form botryoidal masses about one centimetre across, often on a matrix of sky blue chrysocolla. Fractures in the quartz are filled with malachite, chrysocolla and pseudomalachite. Brochantite, as small prismatic crystals, occurs in gossanous hematite.

The deposit is on the south side and close to the Barkly Highway and is readily accessible.

The Magpie

The Magpie is approximately 1.5 km south of Mt. Glorious and is accessed by the same track. It is one of a series of mines worked early in this century as a source of flux and
copper for the Hampden and then later for the Mt. Isa smelters. More recently it has been worked as both an open cut and underground operation, high grading for copper as a gouger operation supplying to Mt. Isa. Operations ceased in the late 1980’s. The copper mineralisation is primarily cuprite with native copper, tenorite, malachite and chrysocolla, which occur in siliceous goethite. A specimen of cuprite and native copper from the Magpie, in the author’s collection, was found to contain atacamite and nantokite. The deposit is in a north trending shear in metadolerite intruding the calc-silicate breccia of the Corella formation.

**Double Oxide, Chum**

15 km NW of Cloncurry

These adjacent leases are in schists and quartzite containing malachite, chrysocolla, cuprite and native copper. They have been worked intermittently since early this century as underground operations. The only mineralisation found on the surface was a little native copper. It appears that all the dump material has been removed for smelting.

**Fairfield**

16 km WNW of Cloncurry

This deposit has been mined by gougers by both open cut and underground methods with the ore being high-graded for smelting at Mt. Isa. The remaining dumps appear to contain workable grades of copper, and a small leach plant is being operated to recover copper from these dumps. The main copper minerals in the dumps are malachite and azurite, with minor pseudomalachite and chrysocolla. Ball reported chalcocite and malachite grading 30% Cu at grass, and stated that the relatively large gossanous goethite cap indicated that there would possibly be an increase of sulfides at depth.

**Poseidon**

15 km SW of Cloncurry

The Poseidon is a prospect near Marimo siding, southwest of Cloncurry. The small dump contains abundant conichalcite with chrysocolla, malachite, azurite and minor
pseudomalachite. The conichalcite occurs as typical yellowish-green micro-botryoidal crusts on quartzite.

**Eagle Hawke**

Ball\(^1\) reported that 6 tons of chalcocite ore was mined in 1906 from this deposit in Pumpkin Gully. Specimens of native copper with rims of cuprite, siliceous tenorite and chrysocolla, together with malachite and azurite were found in the dump. The lode is in siliceous ironstone.

**Crows Nest**

This small mine is nearby and similar to the Eagle Hawk. A little chalcopyrite was also found in the dump. A specimen of brochantite was also collected.

**Ernest Henry**

The Ernest Henry open cut mining operation, a joint venture of M.I.M. Holdings Limited and Savage Resources Limited, is the largest in the district. Mining of ore did not commence until late 1997. This copper-gold deposit has no surface outcrop and lies at a depth of 40 m beneath an alluvium cover. The deposit has only two zones, *i.e.* a zone of supergene enrichment extending to a depth of about 150 m below the surface and containing chalcocite, native copper, secondary bornite and chalcopyrite, and a primary zone containing chalcopyrite and pyrite. Gold and minor cobalt accompanies the sulfides. The total reserve as at June, 1996, was 127 mt. with a grade of copper at 1.1 % and gold at 0.55 gm/t.\(^6\)

**B. Mines at Duck Creek**

The Duck Creek area, contains a number of small deposits which have been intermittently worked for copper or gold and one has been worked for cobalt.
The Alone Hand

The Alone Hand is a small mine 3 km west of Marraba siding which has been mined on a small scale for copper, bismuth and gold. Total production from the mine is 2.8 tons of Cu, 0.51 tons of Bi and 32 oz of gold from 58 tons of ore raised between 1904 and 1936.

The orebody is in a north trending shear in metabasalt which has been altered locally to an epidote rich rock containing quartz and carbonates. A prominent quartz blow marks the outcrop which can be followed on the surface for 30 metres. Masses of chalcopyrite and bismuthinite up to 5 cm across occur in both quartz and carbonates consisting of calcite, ankerite and siderite. Secondary minerals include malachite in felted masses of acicular crystals to 1 cm, minor chrysocolla, pseudomalachite, cuprite, native copper and chalcocite, the latter replacing chalcopyrite.

The secondary bismuth minerals, bayerite\textsuperscript{7} and bismutite can be found in the dump. Bayerite, (Ca, Pb)Bi\textsubscript{2}(CO\textsubscript{3})\textsubscript{2}O\textsubscript{2} is a rare mineral that has been recorded on only five occasions. The earlier records show Pb substituting for Ca in the ratio of approximately 1:25. Bayerite from the Alone Hand contains no lead and is therefore the first recorded occurrence of the end member.

Success

The Success mine, situated west of Yoomoo siding, is one of only three mines in the district that have produced cobalt. This small mine was opened for copper but as depth of mining increased, cobalt as earthy black asbolan with erythrite developed in association with the copper. The shaft extends to a depth of approximately 35 metres. There is no dump remaining, the shaft now being used as a bore. Scattered traces of ore were found, mainly chalcopyrite.
Horseshoe

This small deposit two kilometres west of Marraba siding was being mined to supplement the ore at the Great Australia. The deposit is in a sheared metabasalt with a quartz-gossan lode containing chalocite and minor azurite. Rich chalocite with azurite, pseudomalachite and minor chrysocolla was found on the ROM pad.

New Dollar

The New Dollar is adjacent to the Horseshoe. These two parallel deposits trend 246°N. Malachite, chalocite and minor pseudomalachite occurs in shattered lode quartz, with more chrysocolla (at a greater depth) than was found in the Horseshoe. Chlorite is well developed in the shear with much chlorite-hematite rock with malachite stains.

Rainbow

The Rainbow is a very small mine near Mitakoodi siding. Jack reported the presence of sulphide of copper and antimony, which is probably chalcostibite. This grey ore was not found in the small dump. Thick veins of malachite and chrysocolla were found in an outcrop of quartz and schist. Ball states that a shaft was sunk to 20 feet.

A number of other deposits around Duck Creek were inspected, but yielded no notable specimen material. They included Red Arrow, Pioneer, Celestial, Chinaman, Highland Mary, Mountain Maid, Copper Express and Joker.

C. White Range

The White Range contains a major potential copper and cobalt resource along the valley floor known as Greenmount. This is currently being explored by Majestic Resources N. L. A number of small mines have been worked in this area. The Desolation has been described in Chapter 3. Others of interest are:

40 km south of Cloncurry
Mount McCabe

Mt. McCabe is a small mine perched on a spectacular peak of the range. It is notable for the well developed rinds of siliceous tenorite and chrysocolla around cuprite in a matrix of siliceous goethite. Ball describes the ore as black oxide of copper. Malachite was also found in the outcrop. The lode is in metabasalt and schists adjacent to a limestone member. The deposit has been worked up to 1990 as a gouger operation supplying to Mt. Isa.

Greenmount shaft

This is an old prospecting shaft on the present exploration lease. Chalcocite, malachite and chrysocolla in Marimo slate can be found on the dump.

Vulcan

This deposit at the southern end of the White Range has been mined and the ore treated by leaching. Remaining dumps have been removed and only traces of mineralisation can be seen.

Pete’s Prospect, Speculation

These deposits are near the Vulcan. Malachite, chrysocolla and pseudomalachite were found in the outcrops.

D. Soldiers Cap Group

The Soldiers Cap is a prominent mesa which can be seen from the Landsborough Highway. Gold has been mined at nearby Mt. Freda. A number of small copper mines are situated north of Soldiers Cap.

Mt. Norma

This is the largest of the copper mines in the vicinity. It was intermittently worked as an underground mine from around 1900, but it was not until 1968-1972 that any major work
took place with 6,564 tons of ore being raised to yield 458 tons of copper and 6,236 oz of silver. Production accelerated during 1972 and a further 254 tons of copper was won from 3,279 tons of ore. Workings consisted of a decline and drive approximately 60 m long and two small open cuts. The lode occurs in kaolinite and crushed quartz and brecciated siliceous sediments. The ore was mainly chalcocite, cuprite and malachite. A significant amount of libethenite and pseudomalachite was observed in the dumps.

Canteen

This small open cut at the base of the mesa is of interest in that crystals of malachite to 10 mm in length were found in vughs in siliceous goethite. Malachite rarely forms distinct crystals. Malachite, chrysocolla and pseudomalachite commonly occurs in the dumps.

Brilliant

Not strictly a member of the Soldiers Cap group, the Brilliant is a deposit approximately 10 km west of Mt. Norma and close to Snake Creek. Several small shafts have been sunk along a quartz outcrop. Copper minerals found in the dumps were malachite, chrysocolla, chalcopyrite and minor azurite. Also, wolframite, scheelite and cuproscheelite were found in a calcite-actinolite-quartz gangue.

E. Selwyn

In the Selwyn area, two major underground mines, accessed by declines, are operated by Arimco Mining Pty. Limited. They are Mt. Elliott, close to the abandoned township of Selwyn, and the Selwyn mine which is 18 km south of the old town.

Mt. Elliott

Two orebodies, parallel to each other are being worked at Mt. Elliott. The Main Lode is primary with sulfides, chalcopyrite, pyrite and pyrrhotite in a skarn containing calcite,
quartz, magnetite and hedenbergite. The other, the Corbould Lode, is supergene in part, with 
chalcocite and native copper the major ore minerals in some zones. Arborescent masses of 
native copper are relatively common, rarely enclosed within large crystals of gypsum.

The first shaft was sunk on Mt. Elliott in 1901. In 1906 the lease was purchased by a 
new company of English and French investors who erected a smelter and developed a major 
mine which operated until 1919. Up until 1920, 264,000 tons of ore had been mined to 
produce 24, 430 tons of copper and 33,890 oz. of gold.

Selwyn mine

Arimco are mining the Starra lode which consists almost entirely of black hematite 
containing chrysocolla and cuprite. The unique feature of this deposit is that much of the 
cuprite is the capillary variety, chalcotrichite.

Mt. Stewart, Victoria North

These open cuts are close to Selwyn mine. They have both been recently mined. The 
ore consists of malachite and chrysocolla in a black quartzite gangue, adjacent to a granite 
intrusion (Williams Granite).

F. Duchess area 80 km SSE of Mt. Isa

Lady Fanny

The Lady Fanny is 15 km NW of Duchess and near the Mt. Isa railway. The deposit 
has been worked intermittently since 1905 by two shafts and an open cut. The lode is in 
quartzite, volcanics and schists. The ore consisted of malachite, chrysocolla, chalcocite, 
tile ore and at the 150 ft. level, chalcopyrite. These minerals, as well as azurite, brochantite, 
pseudomalachite and covellite (on pyrite), were collected from the dumps.
G. Ballara area

Ballara in the Fountain Range was a small township once linked to the Cloncurry-Duchess railway, which serviced a number of mines in the district. From World War II to 1990, most deposits were worked as gouger operations supplying ore to Mt. Isa.

Wee McGregor

The Wee McGregor is one of the largest in this area. Ball reported that the outcrop ran for 1000 ft with 500 ft mineralised with copper. Malachite, cuprite and azurite occurs in kaolinised schists with quartz veins along a contact with microgranite. The author visited this open cut in 1990 when it was still being worked. At that time azurite was the major ore mineral. Most of the dumps have been removed, but a little azurite, malachite and pseudomalachite were found.

Trafalgar

The Trafalgar is notable for the extent of the chrysocolla cap on the lode. Malachite, azurite, pseudomalachite and libethenite were collected from the dumps.

Lady Jenny

A leach pad has been constructed on this site but there has been no recent mining activity. The outcrop shows earthy malachite and chrysocolla, with minor pseudomalachite.

Inkerman

The Inkerman was worked by small open cuts connected by an adit and a winze. The lode occurs in a quartz breccia within metavolcanics and schists, the ore minerals consisting of malachite, azurite, chrysocolla and chalcocite. Brochantite, libethenite and pseudomalachite also were found in the dumps.
H. Mary Kathleen area

Mount Lindsay

This mine is on the northern side of the Barkly Highway. The mine consisted of two shafts and an open cut which were worked intermittently from 1912 to 1963 when a bonanza lode of supergene enriched ore was discovered. Production for 1961-1964 was 2047 tons yielding 272 tons of copper. The lodes occur at the contact of the Wonga granite with volcanics. Mineralisation is in schists and siliceous goethite (jasper) and is primarily chrysocolla, malachite, azurite with minor pseudomalachite. Chalcocite and some native copper with chalcanthite was reported by Syvret. 10

I. Blockade group

The Blockade was previously called the Argylla. It was the second significant deposit claimed by Ernest Henry when in 1880 he was led to the outcrop by aborigines. To the north of the Blockade there are several other small mines or prospects.

Blockade

Although Henry’s comments indicates an extensive outcrop of copper mineralisation,11 up to 1972 only 13,600 tonnes were produced by underground mining. The mine was purchased by Mount Isa Mines Limited in 1971 and an opencut developed to supply cupriferous silica as flux. Mining was completed by 1990 and the mine sold. The remaining dumps and pit are now being leached and copper recovered by the cementation process.

The mineralisation is within ferruginous quartz veins and schists in two parallel shears separating metabasalt and rhyolite. At depth, the ore minerals were chalcopyrite and chalcocite. Malachite was reported as being the main ore mineral in the oxide zone.
Pseudomalachite, azurite and chrysocolla were found in the dumps. Cornetite has been reported.  

Other mines inspected were the IXL, Gosp, Iron Duke and Blue Star. Malachite, azurite, chrysocolla, pseudomalachite, chalcocite were collected from the dumps. They were small gougler operations.

**J. Brolga group**  
15 - 30 km WSW of Quamby

This group is to the west of Quamby. Two mines in the group were inspected.

**Native Companion**

This is a small deposit 15 km WSW of Quamby once worked from several shafts. The lode is in a pegmatite contact with tremolite and schists. Malachite, chrysocolla and chalcocite were collected from the dumps.

**Volga**

The Volga is another small mine a further 15 km to the west. Malachite, azurite, chrysocolla and chalcocite can be found in the dumps. The old shaft has been sunk in massive epidote, quartz and schist.

**K. Queen Sally**  
20 km SE of Kajabbi

The Queen Sally is one of the three mines in the district that produced cobalt. Two shafts have been sunk to 15 m in quartz breccia and schists. Heterogenite, (CoO(OH)), and erythrite with a little cobaltite appear to have been the main ore minerals. Minor amounts of conichalcite, malachite and azurite were found in the dumps.
Federal group

32 km WNW of Cloncurry

Federal

The Federal mine is on the old Mt. Isa road. It has been mined as an underground operation. The lode is in slates and chloritic schists, with mineralisation consisting of malachite, azurite and chalcocite.

Margaret

Malachite, chrysocolla, pseudomalachite and large masses of chalcocite within quartz breccia in iron rich sediments were noted.

References


Appendix II

Stability field diagrams — calculations

In instances where stability field data was not available from the literature, the
stability field was determined by calculation using thermodynamic data now published for
many minerals.

Example.

The stability field for nantokite - paratacamite - native copper - cuprite.

Refer Chapter 5, Chlorides. All reactions at 298.2 K.

(a) For the reaction \( \text{Cu}_2\text{O} + 2e^+ + 2\text{H}^+ \rightarrow 2\text{Cu} + \text{H}_2\text{O} \) (1)

\[
\Delta G^0 = \Sigma (\Delta fG^0) \text{ of products} - \Sigma (\Delta fG^0) \text{ reactants} \quad (2)
\]

Where \( \Delta G^0 \) = standard free energy of reaction
\( \Delta fG^0 \) = standard free energy of formation

From Woods et al. \(^1\)

\[
\begin{array}{c|c|c}
\text{copper} & \Delta fG^0 \text{ (kJmol}^{-1}\text{)} \\
\text{cuprite} & 0 & \text{by definition} \\
\text{water} & -146.4 \\
\end{array}
\]

Therefore \( \Delta G^0 = (-237.1) - (-146.4) \)

\[= -90.7 \text{ kJmol}^{-1} \]

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From Krauskopf\textsuperscript{2} \( \Delta G^0 = -nFE^0 \) \hspace{1cm} (3)

Where \( n \) = number of electrons
\( F \) = Faraday Constant
\( E^0 \) = Standard electrode potential

substituting values

\[-90.7 = -2 \times 96.68 \times E^0\]

from which \( E^0 = 0.4690 \) volts

Oxidation potential\textsuperscript{2} \( (E_v) \)
also from (2) \( E_v = E^0 - \frac{2.303 \times R \times T \times \log K}{n \times F} \) \hspace{1cm} (4)

Where \( R \) = gas constant
\( T \) = temperature K
\( K \) = equilibrium constant

\[ E_v = E^0 - \frac{0.0591 \times \log K}{n} \] \hspace{1cm} (5)

As \( K = \frac{[\text{Cu}] \times [\text{H}_2\text{O}]}{[\text{Cu}_2\text{O}] \times [\text{H}^+]^2} \)

\[ = \frac{1}{[\text{H}^+]^2} \]

As \( \text{pH} = - \log [\text{H}^+] \)

equation (5) may be written as

\[ E_v = 0.4690 - 0.0591 \times \text{pH} \] \hspace{1cm} (7)

When \( \text{pH} = 0 \), \( E_v = 0.4690 \) volts
When \( \text{pH} = 10 \), \( E_v = -0.1220 \) volts
As this is a linear relationship a stability field diagram for these species can be constructed as shown in Figure 1 below.

![Stability field diagram for Cu - Cu₂O](image)

Fig. 1. Stability field for Cu - Cu₂O at 298.2 K.

(b) for the reaction

\[
\text{Cu}_2\text{O} + 2\text{Cl}^- + 2\text{H}^+ \rightleftharpoons 2\text{Cu}^+\text{Cl} + \text{H}_2\text{O}
\]

\[
\Delta G^o = \Sigma (\Delta fG^o)_{\text{products}} - \Sigma (\Delta fG^o)_{\text{reactants}}
\]

From (1)

<table>
<thead>
<tr>
<th>Species</th>
<th>(\Delta fG^o) (kJmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>cuprite</td>
<td>-146.4</td>
</tr>
<tr>
<td>nantokite</td>
<td>-118.8</td>
</tr>
<tr>
<td>water</td>
<td>-237.1</td>
</tr>
<tr>
<td>chloride ion</td>
<td>-131.2</td>
</tr>
</tbody>
</table>

Therefore

\[
\Delta G^o = (2 \times 118.8 - 237.1) - (-146.4 - 2 \times 131.2) = -65.9 \text{ kJmol}^{-1}
\]

\[
\log K = \log \frac{1}{[\text{Cl}]^2 \times [\text{H}^+]^2} = -2 \times \log a_{\text{Cl}^-} + 2 \times \text{pH}
\]
\[ \log K = \frac{\Delta G^0}{2.303 \times R \times T} \]

\[ = \frac{-65.9}{-2.303 \times 8.3143 \times 10^{-3} \times 298.2} \]

\[ = 11.54 \]

Substituting 11.54 for log K in eqtn. 10

\[ 11.54 = -2 \times \log a_{\text{Cl}^-} + 2 \times \text{pH} \]

\[ \text{pH} = 5.77 + \log a_{\text{Cl}^-} \] (12)

As this is independent of oxidation potential, a series of co-ordinates can be plotted using values of \( E_v \) and pH likely to occur in nature.

<table>
<thead>
<tr>
<th>e.g.</th>
<th>Log ( a_{\text{Cl}^-} )</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.77</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>5.77</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>4.77</td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>3.77</td>
<td></td>
</tr>
</tbody>
</table>

This relationship can be plotted as shown in Fig. 2.

![Graph](image)

Fig. 2. Cuprite - nantokite. pH versus \( \log a_{\text{Cl}^-} \)
(c) For the reaction \[ \text{CuCl}(s) + e^- \rightarrow \text{Cu}(s) + \text{Cl}^- \] (13)

\[ \Delta G^\circ = \Sigma (\Delta fG^\circ) \text{ of products} - \Sigma (\Delta fG^\circ) \text{reactants} \]

\[ = (-131.2) - (-118.8) \]

\[ = 12.4 \text{ kJmol}^{-1} \]

from eqtn. 3

\[ E^0 = \frac{\Delta G^\circ}{n \times F} \] (14)

\[ = \frac{-12.4}{-1 \times 96.68} \]

\[ = 0.128 \text{ volts} \]

from eqtn. 4

\[ E_v = E^0 - \frac{0.0591 \times \log K}{n} \] (15)

also

\[ K = \frac{[\text{Cu}(s)] \times [\text{Cl}^-]}{[\text{CuCl}(s)]} \]

Solids = 1

\[ = [\text{Cl}^-] \] (16)

therefore,

\[ \log K = \log a_{\text{Cl}^-} \]

substituting \( \log (a_{\text{Cl}^-}) \) for \( \log K \) in eqtn. 15,

\[ E_v = E^0 - 0.0591 \times \log a_{\text{Cl}^-} \]

\[ = 0.128 - 0.591 \times \log a_{\text{Cl}^-} \]

This relationship is independent of pH. The value of oxidation potential for a range of activity of chloride ion can be calculated and plotted as shown in Figure 3.
<table>
<thead>
<tr>
<th>Log $a_{\text{Cl}^-}$</th>
<th>$E_v$ volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.069</td>
</tr>
<tr>
<td>0</td>
<td>0.128</td>
</tr>
<tr>
<td>-1</td>
<td>0.187</td>
</tr>
<tr>
<td>-2</td>
<td>0.246</td>
</tr>
</tbody>
</table>

![Graph showing pH vs. $E_v$ and log $a_{\text{Cl}^-}$](image)

Fig. 3. Native copper - nantokite. Oxidation potential versus log $a_{\text{Cl}^-}$.

The process is repeated for nantokite - paratacamite, native copper - paratacamite and cuprite - paratacamite relationships to complete Fig. 5-26, Chapter 5.

**References**
