CHAPTER ONE
INTRODUCTION

Since the development of mining and smelting techniques in antiquity, the identification and exploitation of anomalous concentrations of elements (usually metals) has been important to the development of civilization. An ore is usually defined as an anomalous concentration of elements that can be economically exploited (Edwards and Atkinson, 1985). As technology has changed over time, the nature and kinds of ore which are defined as economic has also changed, although the overall nature of base metal ore deposits is remarkably similar both in chemistry and mineralogy (Williams, 1990).

In this work a metallic ore is simply taken as an anomalously high concentration of metallic elements that may or may not have at some time been economically exploited. Depending on the conditions under which individual species form, these metallic elements usually combine with other elements to form a wide range of minerals. Metallic ore deposits containing lead, copper and zinc usually combine with sulfur to form sulfide-type orebodies. These orebodies form under similar environmental conditions often referred to as the primary environment (Williams, 1990). The primary environment is characterised by more or less elevated temperatures and pressures compared to ambient conditions, low oxygen concentrations and highly reduced sulfur species. Within the top few hundred metres of the earth’s surface, temperatures and pressures vary little from ambient conditions, oxygen is abundant and water is freely available. This is known as the secondary environment. Under these conditions, sulfur forms stable highly oxidised species such as sulfate and a completely different set of stable mineral species exist.

A combination of these two environments is often found in base metal sulfide ore deposits that occur at or close to the Earth’s surface. Most minerals that formed in the
primary zone are unstable when exposed to the new physical and chemical conditions close to the Earth’s surface and break down to form new phases which are stable in this environment. With time only the most chemically stable minerals such as quartz remain.

The secondary environment is frequently zoned, both chemically and mineralogically, with depth. This is reflected in Figure 1.1, the classic oxidised base metal deposit profile. This diagram should be treated only as an ideal representation as not all these zones are present in all weathered deposits. The thickness of these zones can vary greatly and complex geological and hydrological factors can alter this somewhat simplistic profile (Andrew, 1980; Williams, 1990).

The secondary zone, which is also termed the supergene zone, generally extends from the Earth’s surface (the gossan) to just below the water table (a zone of secondary enrichment for some elements).

![Figure 1.1](image)

**Figure 1.1** An idealised profile of a metallic sulfide orebody outcropping at surface (after Williams, 1990).
Minerals such as sulfides that are unstable in oxygenated environments react with water, oxygen and atmospheric CO₂ at ambient conditions. Apart from releasing various metal ions into the groundwater, the chemical reactions dramatically affect circulating groundwater geochemistry (particularly pH). This has further implications in the evolution of oxide zone geochemistry. For example, pyrite FeS₂, a common accessory mineral in most sulfide deposits, reacts with water and oxygen as follows

$$2\text{FeS}_2(\text{aq}) + 7\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{Fe}^{2+}(\text{aq}) + 4\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq})$$

to release iron(II), sulfate and hydrogen ions. The release of hydrogen ions results in a significant decrease in the pH of the circulating groundwaters and it should be noted that this reaction represents an overall stoichiometry, not the detailed reactions which take place. Subsequent oxidation of Fe²⁺ and hydrolysis leads to the formation of goethite, FeOOH, and other iron(III) oxyhydroxides according to the following overall equations, thus

$$4\text{Fe}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightleftharpoons 4\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$

$$\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{FeOOH}(\text{s}) + 3\text{H}^+(\text{aq})$$

releasing more H⁺(aq) and further decreasing pH. In many deposits, the sulfide orebody has undergone intense weathering leaving only these iron(III) oxyhydroxides, manganese oxides and other chemically resistant minerals in what is termed the gossan. The famous Broken Hill lead-zinc-silver deposit, Australia, owes its name to the 2.5 kilometre long resistant ridge of iron and manganese oxide gossan that capped an extraordinarily rich oxide zone. This was the result of well over 5 million years (possibly as much as 100 million years) of weathering that resulted in the removal of at least 20% of the original sulfide ore (Birch, 1999). As the primary minerals break down, their chemical components are transported via groundwater down the supergene zone profile, which in most cases acts as a freely draining column, to the water table. Below the gossan, a
leached zone dominated by clays and other weathering products is often present depending on the nature of the primary minerals and intensity of weathering (Andrew, 1980). Primary feldspars and micas react with H⁺(aq) to form clays. For example, a typical mass balance for the formation of kaolinite is given below

$$2KAlSi_3O_8(s) + 2H^+(aq) + 9H_2O(l) \leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+(aq) + 4H_4SiO_4^{0}(aq)$$

K-feldspar kaolinite silicic acid

Such reactions not only release soluble silica into the supergene zone, but also consume acid produced by the breakdown of sulfides. Many primary silicates weather in the secondary zone and an excellent review of silicate weathering has been given by Ollier (1984).

Further down the profile, below the gossan and leached zone, what is termed the oxide zone (sensu stricto) is encountered. In this zone many of the leached chemical components from the upper zones react and often form a bewildering array of new mineral phases and complex assemblages. Numerous well-known sulfide deposits owe their reputation to the extensive and extremely diverse mineralogy of their oxide zone and by way of example mention could be made of Tsumeb, Namibia, Bisbee, Arizona and Broken Hill, Australia (Wilson, 1977; Williams, 1990; Birch, 1999). This zone is commonly the source of highly aesthetically pleasing and colourful minerals, many containing metals combined with complex oxyanions, which are highly prized by mineral collectors.

At the base of the oxide zone, near the water table and the boundary between oxidising and reducing environments, occurs a zone of supergene enrichment. Bonanza grades (often many times greater than in the primary zone) of certain metals (particularly copper, silver and gold) are encountered. This enrichment zone has always been of great economic importance. Its existence and exploitation has been reported in many recent
gold and copper mining operations in Australia (Heithersay et al., 1990; Berkman and Mackenzie, 1998; Foggerty, 1998; Richardson and Moy, 1998).

Williams (1990) notes that even though there is a vast array of minerals that are found uniquely within supergene zones, the variety of anions that are available for the precipitation of secondary minerals is fairly restrictive. Therefore, there are a number of mineral species which are commonly reported in most base metal deposits (Table 1.1). The source of these anions is usually the direct breakdown of primary minerals (for example silicic acid and phosphate), the breakdown and subsequent oxidation of anions (sulfate and arsenate) and gases dissolved in water (oxygen and carbon dioxide).

Since in most cases the supergene zone only extends for a few hundred metres below the surface, temperature and pressure conditions vary little throughout the zone as a whole. However, the role of groundwater in the supergene zone is paramount and Williams (1990) states that all of the reactions that take place in the supergene zone of sulfide orebodies involve homogeneous or heterogeneous systems in the presence of water. The role of groundwater in the supergene zone has been recognised for a long time (Lindgren, 1913; Emmons, 1917), however knowledge of the complex interaction of ions in natural aqueous systems and mineral formation is far from perfect. Excellent references on general aqueous geochemistry in these environments include Garrels and Christ (1965) and Stumm and Morgan (1981).

Apart from water being directly involved in reactions, its importance lies in its role in dissolving minerals and transporting breakdown products, oxygen and carbon dioxide throughout the supergene zone. Regional groundwater systems beyond the orebody also play an important role, in transporting chemical components that can interact with the weathering orebody and form new mineral phases.

Changing pH of groundwater (often due to weathering of sulfides and subsequent
Table 1.1  Some common secondary minerals of base, coinage metals and supergene minerals investigated in this study

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<th>Olivenite</th>
<th>Adamite</th>
<th>Silicates</th>
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<th>Cuprite</th>
<th>Tenorite</th>
<th>Molybdates</th>
<th>Wulfenite</th>
<th>Powellite</th>
<th>Tungstates</th>
<th>Stolzite</th>
<th>Chromate</th>
<th>Crocoite</th>
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chemical reactions) in the supergene zone has pronounced effects on the geochemistry of the supergene zone as a whole. Groundwater pH often dictates which anion species dominates. An example of this is the variability of soluble phosphate concentrations at ambient conditions. At low pH (< 3) $H_3PO_4^0(aq)$ species dominate, at intermediate pH (3-7) $H_2PO_4^-(aq)$ dominates and at high pH (>7) $HPO_4^{2-}(aq)$ dominates (Baes and Mesmer, 1979; Stumm and Morgan, 1981). In the case of aqueous silicate species pH not only controls the dominant dissolved silica species but also limits its solubility. At 298K below pH 9 the maximum silica solubility is $10^{-2.71}$ mol L$^{-1}$ (Iler, 1979; Dove, 1995), as $H_4SiO_4^0(aq)$.

Variations in groundwater composition lead to different patterns of dissolved metal complexes (Williams, 1990). Changes in the concentrations of these complexes govern not only the availability of various ions for certain phases, but also play a role in determining the solubility of secondary minerals in the supergene zone. For example, apart from $Cu^{2+}(aq)$ and $SO_4^{2-}(aq)$ ions, an aqueous solution of copper sulfate also contains the following complex ion species in various concentrations, $Cu(OH)^+$, $CuSO_4^0(aq)$, $HSO_4^-(aq)$ and $Cu(OH)_2^0(aq)$. When systems become more complex the availability of metal ions to form certain phases becomes highly dependent on the interaction of other dissolved species. The formation of numerous metal complexes under ambient conditions is well-understood (Baes and Mesmer, 1979; Williams, 1990) and extensive tables exist listing the stability constants of these species (Smith and Martell, 1976; Martell and Smith, 1982). From these stability constants and knowledge of pH and total metal and ligand concentrations, computer programs such as COMICS (Perrin and Sayce, 1967) can be used to calculate total complex ion species distributions. Knowledge of which complex ion species are present allows an overall evaluation of which ions will be available in chemical reactions in the supergene zone.
Apart from the formation of discrete mineral phases the sorption of both cations and anions onto various mineral surfaces (particularly on iron(III), manganese(III,IV) oxyhydroxides and clay minerals) from aqueous solution also exerts a control on metal ion activities on groundwaters. Numerous workers have studied the phenomenon (some important references include Garrels and Christ, 1965; Vesely and Pekarek, 1972; Stumm and Morgan 1981; Tewari, 1981). The extent of adsorption is dependent on the concentration and the mineral surface topography (Krauskopf and Bird, 1995). Changes in pH of aqueous solutions also significantly affect the uptake of ions by various materials. For transition metal cations (such as copper, lead and zinc) a greater uptake of ions occurs with increasing pH. However, most sorption takes place in a narrow pH range (Farrah and Pickering, 1979). The sorption of oxyanions by iron oxyhydroxides is also well known, particularly for phosphate (Stumm and Morgan, 1981; Farrah and Pickering, 1976; Vesely and Pekarek, 1972). However, unlike cations, sorption of these oxyanions is favoured by decreasing pH. Fluctuations in groundwater pH in the supergene zone cause significant changes in anion and cation concentrations as they are adsorbed and released from various mineral surfaces.

The variability of the chemical conditions within supergene zones and changing groundwater conditions are reflected by complex paragenetic sequences and interlayering of minerals. Secondary mineral transformations within the supergene zone are common and are often observed as pseudomorphs and corroded crystals. An extremely common example of this is the pseudomorphing of azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, by malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$.

$$3\text{Cu}_2\text{CO}_3(\text{OH})_2(s) + \text{CO}_2(g) \rightarrow 2\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2(s) + \text{H}_2\text{O}(l)$$

malachite     azurite
Azurite is stable at 298 K under elevated p(CO$_2$) above 4.34 kPa, with the equilibrium partial pressure calculated from the above equation (Williams, 1990). Therefore, under normal atmospheric conditions or decreasing p(CO$_2$) azurite becomes unstable and transforms to malachite. This transformation is relatively slow and hence azurite and malachite are commonly observed to co-exist on the same specimen.

Diversity of mineral assemblages within a single supergene zone is often a reflection of subtle changes in groundwater geochemistry. An example of this is the occurrence and combination of basic copper phosphates libethenite, Cu$_3$PO$_4$(OH), pseudomalachite, Cu$_5$(PO$_4$)$_2$(OH)$_4$, and cornetite, Cu$_3$PO$_4$(OH)$_3$, within the same deposit. From accurately measured thermodynamic data, Magalhães et al. (1986, 1988) calculated stability fields for the basic copper phosphates (Figure 1.2), defined by copper activities and pH. It can be seen that the effect of changes in pH within a deposit will result in changes in mineral species formed. In Nature, the occurrence of these species is often

![Stability diagram for simple copper phosphates for log a(Cu$^{2+}$) versus pH after Williams (1990).](image-url)
related to depth, pH and redox potentials within the supergene zone of numerous
Australian copper orebodies (Crane et al., 1998; Sharpe, 1998).

Apart from mineral transformations, changes in groundwater conditions and ion
activities are often reflected in chemical zonation in minerals. Many structurally related
minerals that occur in the supergene zone form solid-solution series with a range of
compositions occurring in the same crystal (Palache et al., 1951; Williams, 1990). A
good example of this is the mimetite Pb₅(AsO₄)₃Cl-vanadinite Pb₅(VO₄)₃Cl –
pyromorphite Pb₅(PO₄)₃Cl series. It has been observed that mimetite has significant
amounts of phosphate and/or vanadate substituted for arsenate and vice versa (Palache et
al., 1951). These variations in the solid solution series are often observed as zoning
within crystals (Palache, 1951; Birch, 1999). Substitution in secondary minerals may
occur both for cations and anions (Williams, 1990).

Much has been written on the oxide zone and supergene geochemistry. Many
aspects of secondary mineral formation, chemical processes involved in the evolution of
oxide zones and concentrations of base metals in the supergene zone have been presented
in the literature (an excellent compilation of much of this work is provided by Williams,
1990). However, many aspects of supergene geochemistry remain sketchy and at best
poorly understood, including detailed aspects of many geochemical processes, kinetics of
crystallisation and solid-solution phenomena.

An understanding of the chemical processes of supergene geochemistry has a
number of practical applications. Firstly, the breakdown of primary minerals releases
various elements into the groundwater and this leads to the dispersion of these elements
from orebodies. Since geochemical exploration is based upon the detection of such
dispersion patterns in the supergene environment, these observations can be used for the
discovery of new orebodies. Secondary minerals have a buffering effect on the dispersion
of elements by controlling their concentrations in groundwater and may be viewed as intermediates between the immobile primary source and the free migration of ions. Therefore, an understanding of formation of various secondary minerals in the oxide zones of weathering sulfide orebodies provides an understanding of the overall dispersion of elements in the supergene zone.

Secondly, the mining of the supergene zone of many metallic ore deposits is economically important in numerous mining operations, since the supergene zone often contains significantly higher grades than the corresponding primary zone. However, these ores require significantly different metallurgical treatments due to the nature of the ore. Recent developments of large-scale hydrometallurgical processing techniques for supergene ores (Foggerty, 1998; Richardson and Moy, 1998) have highlighted the need for understanding the chemistry and mineralogy involved of such deposits. These deposits commonly contain a diversity of secondary mineral phases and assemblages (often more complex than the primary zone). Variation in these assemblages has significantly affected the extraction and processing properties of these ores and therefore directly influence the economics of the mining operation. Therefore, understanding the properties of secondary minerals, their formation and the chemical processes involved in the zone as a whole, can be useful for optimising the profitable exploitation of such ores.

Chemical considerations regarding the dispersion of elements in the natural environment can be usefully applied to heavy metals pollutant studies. Heavy metal pollutants derived from various sources in the surface and near surface environments undergo the same chemical processes that affect metals from orebodies. An obvious case involves old mining sites on which natural weathering processes are accelerated through exposure of primary minerals (many containing heavy metals) at the surface, the processing of these ores and their waste disposal. Control of pollutant metal ion
dispersion is often dependent on stable and metastable phases, many of which have direct counterparts with minerals that form naturally in supergene zones. Understanding chemical reactions occurring within supergene zones may assist in future environmental impact assessments, the rehabilitation of contaminated sites and consideration of further strategies to avoid or control heavy metal pollution.

This thesis focuses on some aspects of the chemical mineralogy of base metals of weathered sulfide orebodies. In particular, it covers oxyanion salts of copper, lead and calcium. Principal oxyanions investigated include SiO$_4^{4-}$, CrO$_4^{2-}$, MoO$_4^{2-}$, WO$_4^{2-}$ and others as they may be involved in these systems.

The thesis explores in detail:

(i) the chemistry and stability of chrysocolla formation and its relationships to other secondary copper minerals and its hydrometallurgical properties.

(ii) the structure and properties of polymorphs of PbCrO$_4$, together with their solid-solution series with PbSO$_4$.

(iii) structural relationships and solid-solution phenomenon in selected minerals of the scheelite group, especially powellite, wulfenite and stolzite.

A combination of single-crystal (for powellite) and powder X-ray methods, Raman microprobe measurements, equilibrium thermodynamics and sophisticated analytical techniques has been employed on both synthetic and natural materials to cast some light on the nature and properties of these groups of secondary minerals.

1.1 REFERENCES


CHAPTER TWO

THE CHEMISTRY, HYDROMETALLURGICAL PROPERTIES
AND STABILITY OF CHRYSOCOLLA FORMATION AND ITS
RELATIONSHIP TO OTHER SECONDARY COPPER MINERALS

2.0 INTRODUCTION

Chrysocolla is an abundant secondary copper mineral that occurs in many oxidised
copper orebodies (Roberts et al., 1990; Williams, 1990) and is commonly associated with
malachite and azurite. In Australia, particularly in the Cloncurry region, chrysocolla is
commonly associated with pseudomalachite and other copper phosphates (Day and
Beyer, 1995). The abundance of chrysocolla, particularly in Australia and western United
States of America, and its high copper content (30-40 weight %) makes it a potentially
important economic source of copper.

Chrysocolla is essentially a hydrated copper silicate but is known to have a highly
variable chemical composition from one location to another and even from one sample to
another from the same location (Sun, 1963; Newberg 1967; Chukrov et al., 1968; Van
Oosterwyck-Gastuche, 1970). Variable water content is frequently observed. Limited
substitution of Al$^{3+}$ for Cu$^{2+}$ (charge compensation is maintained by variation of the
number of protons present) is common, as is the presence of small amounts of Ca$^{2+}$ and
Mg$^{2+}$ the amount of which varies from sample to sample (Van Oosterwyck-Gastuche,
1970). The presence of other elements has been reported by various authors (Newberg,
1967; Chukrov et al., 1968) though these are generally are not consistent from sample to
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a: No location given 27-188\(^a\); Van Oosterwyck-Gastuche (1970).
b: No location given 03-0219\(^a\).
c: Star of Congo, Belgian Congo 11-322\(^a\); Identical to pattern given for plancheite and katangite Billet (1942).
d: Inspiration Mine Arizona; Sun (1963).
e: Emerald Isle, Arizona; Newberg (1967).
f: Chuquicamata, Chile; Newberg (1967).
g: Synthesised chrysocolla at 80\(^\circ\)C; Carriat et al. (1994).
h: Globe, Arizona; Pohlman and Olson (1976).
i: Miami, Arizona; Raghavan and Fuerstenau (1977).

\(^a\) Number refers to International Centre for Diffraction Data Powder Diffraction File for chrysocolla.
Chrysocolla samples generally give poor X-ray diffraction peaks and d-spacing values for previous X-ray studies are presented in Table 2.1. Many of the peak positions listed are either a broad peak range or the central position of a broad band. This implies that the crystal structure for chrysocolla is poorly defined. Previous authors [good summaries are provided by Newberg (1967) and Pohlman and Olson (1976)] have proposed a variety of structures. These include an amorphous gel, a solid solution of CuO.SiO$_3$.H$_2$O with varying compositions and a cryptocrystalline, opal-like structure. However, on the basis of electron diffraction experiments, Chukrov et al. (1968), showed that chrysocolla was not truly amorphous, but instead microcrystalline with a fibrous structure. They proposed an orthorhombic unit cell with an “ideal” formula of (Cu$_{2-x}$Al$_x$)H$_2$$_x$Si$_2$O$_5$(OH)$_4$. Van Oosterwyck-Gastuche and Gregoire (1971) also found chrysocolla to consist of fibrous striated microcrystals 500-3000 Å long and 65-70 Å in width. From electron and X-ray diffraction experiments they proposed an orthorhombic unit cell with parameters $a = 5.5$, $b = 17.7$, $c = 6.2$-8.8 Å (Figure 2.1a). By taking into account of sharp X-ray peak at 17.7 Å and the consistency of chemical analyses and density measurements, Van Oosterwyck-Gastuche and Gregoire (1971) proposed the structure to be that of a 1:1 intermediate between a layer lattice and a chain (Figure 2.1b); a structure which has an ideal formula of (Cu$_{8-x}$)(Si$_4$O$_{10}$)$_2$(OH)$_{12}$ ($x = H_2$, Al, Ca, Mg), with variable degrees of hydration. Van Oosterwyck-Gastuche and Gregoire (1971) also reported that the octahedral layer was only rarely entirely filled by copper. More usually aluminum, hydrated protons and traces of calcium and magnesium were present.

Using Cu XANES and EXAFS analyses of copper foil, cuprite (Cu$_2$O), tenorite (Cu$_2$O), dioptase (CuSiO$_3$.H$_2$O) and chrysocolla, McKeown (1994) showed that there were no detectable amounts of these minerals in chrysocolla, despite this being cited in the older literature. McKeown studied the Cu-O and Cu-Cu environments and from
Figure 2.1  A: atomic arrangement and B: structural elements of chrysocolla proposed by Van Oosterwyck- Gastuche and Gregoire, 1971)

Figure 2.2  The hypothetical Cu environment in chrysocolla from EXAFS. Linking CuO₄ units are highlighted with thick black bonds and rims around the oxygen atoms. The arrows indicate the strip of linking CuO₄ groups may extend beyond the diagram (McKeown, 1994).
EXAFS analyses proposed that chrysocolla contained CuO$_4$ units similar to those found in tenorite and diopside, but with a different arrangement where the CuO$_4$ units in chrysocolla are arranged in strips (Figure 2.2). McKeown did not provide any further insight into the silicate part of the structure.

Newberg (1967) defined a simple “dehydrated” chrysocolla with a formula of CuSiO$_3$.H$_2$O (the same reduced chemical formula as diopside). This formula was used in experimental studies on the formation of chrysocolla based on the following equation.

$$\text{Cu}^{2+}(aq) + \text{H}_4\text{SiO}_4 (aq) \rightarrow \text{CuSiO}_3\cdot\text{H}_2\text{O(s)} + 2\text{H}^+(aq)$$

He determined $\Delta G^\circ_f$ for a freshly precipitated “dehydrated” chrysocolla from solubility experiments and calculated a value of -288.4 kcal mol$^{-1}$ (1206.7 kJ mol$^{-1}$) at 298.2 K. Kiseleva et al. (1991) calculated a $\Delta G^\circ_f$ value for a natural chrysocolla from thermodynamic measurements derived from $\Delta H^\circ$ and $\Delta S^\circ$ values. The $\Delta G^\circ_f$ given was -12088.9 ± 54.7 kJ mol$^{-1}$ based on the complex formula

$$\text{Cu}_{0.84}\text{Al}_{0.59}\text{Ca}_{0.11}\text{Mg}_{0.08}\text{Na}_{0.02} [\text{Si}_{8.40}\text{O}_{20}(\text{OH})_{9.35}\text{H}_{1.66}\text{H}_2\text{O}]_{9.15}\text{H}_2\text{O}$$

Kiseleva et al. (1991) did not outline the formation reaction nor state whether $\Delta G^\circ_f$ was derived from the complex formula. Kiseleva et al. (1991) concluded that the $\Delta G^\circ_f$ value was similar to the value calculated by Newberg (1967) if their formula was simplified. However details of how they simplified the formula and hence the $\Delta G^\circ_f$ value of the simplified stoichiometry were not provided in their study.

The detailed structure of chrysocolla still remains unsolved, and no single-crystal X-ray structure is available. The pure Cu end member formula proposed by Van Oosterwyck-Gastuche and Gregoire (1971) as (Cu$_8$)(Si$_4$O$_{10}$)$_2$(OH)$_{12}$.nH$_2$O is based on structural information and may be reduced to CuH$_2$SiO$_4$.nH$_2$O, and which may be simply
rewritten as CuSiO$_3$.nH$_2$O. This idealised stoichiometry is the one used in the current study. More “hydrated” representations of chrysocolla, containing additional water molecules in the structure, will not affect the overall thermodynamic calculations. These additional water molecules are balanced in the calculations by an equal number of water molecules released during dissolution.

Most studies on the leaching of chrysocolla and copper-silicate bearing ores state their vulnerability to acid leach. Sullivan (1933) and others based the acid leaching process on the following reaction.

$$\text{CuO}.\text{SiO}_2.2\text{H}_2\text{O(s)} + 2\text{H}^+(\text{aq}) \leftrightarrow \text{Cu}^{2+}(\text{aq}) + \text{SiO}_2.\text{n(H}_2\text{O)(aq)} + (3-\text{n})\text{H}_2\text{O(l)}$$

Rearrangement of the above equation is, of course, the reverse of that which Newberg (1967) proposed for the formation of chrysocolla. It should be noted that in the reaction

$$\text{CuSiO}_3.2\text{H}_2\text{O(s)} + 2\text{H}^+(\text{aq}) \leftrightarrow \text{Cu}^{2+}(\text{aq}) + \text{H}_4\text{SiO}_4^8(\text{aq}) + \text{H}_2\text{O(l)}$$

$\text{H}_4\text{SiO}_4^8(\text{aq})$ is the dominant dissolved silica species in solutions at pH <9 and its concentration is independent of pH below 9 (Ilbr, 1979; Stumm and Morgan, 1981; Applin, 1987).

Most of the available literature also suggests that sulfuric acid leaching is the most effective and cheapest process for recovering copper from ores containing chrysocolla. Further, a number of studies have attempted to model the kinetics of sulfuric acid leaching of chrysocolla using fluid-solid reaction models (shrinking core models) and homogeneous reaction models. Details of these studies are now presented.
Prosper (1970) noted that when chrysocolla (0.1mm grain size) was reacted in 1M H$_2$SO$_4$, most of the copper was removed in 10 minutes. The leaching proceeded progressively from the outside of the mineral, grains resulting from such leaching exhibited an outer zone with <1% Cu and an inner region that was unleached. Between the inner and outer zone there was an altered zone with a Cu gradient that decreased towards the outer edge, and the conclusion was that the reaction was diffusion controlled. However with milder reactants such as 1M acetic acid with 1M sodium acetate (pH 4.5), the rate was much slower (several hours was required to remove the first 20% of Cu) and there was no sign of zonation. It was suggested that the rate of leaching in these experiments was controlled by the chemical reaction in the grains as opposed to diffusion. However, it was noted that other samples of chrysocolla showed similar trends to that with the strong acid. This suggests that the controlling mechanism for leaching varies with different chrysocolla samples.

Pohlman and Olson (1976) evaluated a number of characteristics that may be important in the acid leaching of chrysocolla. Surface area and pore size studies indicated a large surface area (350 m$^2$/gm) and an average pore size of 13 to 16 Å. Upon contact with acid, chrysocolla lost its porous structure and the surface area decreased to 24 m$^2$/gm. It also was observed that a leached particle lost its integrity when exposed to air. The same authors (Pohlman and Olson, 1974) proposed a non-protective diffusion mechanism and kinetic model for the leaching of chrysocolla in H$_2$SO$_4$(aq) based on the shrinking core model proposed by Wadsworth (1970) as follows

$$1-2/3 R - (1-R)^{2/3} + B[1-(1-R)^{1/3}] = YC_0t$$

where $B = 2D/r_0k$, $Y = 2Da/r_0$, $R =$ fraction reacted, $a =$ stoichiometry factor, $k =$ rate constant, $D =$ diffusion constant, $r_0 =$ initial particle radius, $C_0 =$ bulk concentration, $t =$ time. From observations of leached particles, Pohlman and Olson (1974) suggested that
diffusion of either H$^+$ into the lattice and/or Cu$^{2+}$ out were important variables in the reaction rate. Increasing diffusion path length through the product lattice, a shrinking interface giving less surface area to react, and the rate of chemical reaction at the unreacted core, were all seen as important rate-determining steps in the dissolution processes.

Hsu and Murr (1975) also proposed a kinetic model that was derived from the shrinking core model of Wadsworth (1970). It assumed that the ore particle structure is characterised by pores and channels (Figure 2.3) that extend from the particle surface through a reacted zone into an unreacted core.

![Figure 2.3](image.png)

**Figure 2.3** Idealised ore particle section showing pore channel structure and unreacted shrinking core (Hsu and Murr, 1975).

The model assumes that the diffusion of ions to and from the interface along an average reaction surface is so rapid that leaching is characterised by surface reaction. The kinetic equation they derived was as follows,

$$1 - (1-R)^{1/3} = (1/aK\rho_0) \ln (aK\rho_0 t + 1)$$

where $R$ = fraction reacted, $a$ = stoichiometry factor, $K = k/D$ ($k$ = rate constant and
D = diffusion constant, \( r_0 \) = initial particle radius, \( C_0 \) = bulk concentration, \( t \) = time. They observed that the reaction rate varied inversely with the mean particle radius. They also suggested that the role of diffusion in any form was of negligible importance in comparison to surface reaction phenomena.

In contrast, Khalezov et al. (1984) proposed that the dissolution of chrysocolla in \( \text{H}_2\text{SO}_4 \) was diffusion controlled. They observed that a silicic acid film formed during dissolution and postulated that this film had an inhibiting effect on dissolution rates by hindering diffusion to the mineral surface. Beisembaev et al. (1984) studied reaction rates of chrysocolla in \( \text{H}_2\text{SO}_4 \) at 298 and 323 K and suggested that optimal conditions for dissolution of chrysocolla were 5g \( \text{H}_2\text{SO}_4 \) L\(^{-1}\) at 298K.

There has also been a number of leaching studies on chrysocolla using different chemical treatments, particularly ammoniacal leaching (Habashi and Dugdale, 1973; Raghavan and Gajam, 1986). In general, it has been shown that less copper is extracted from chrysocolla with these solutions than is achieved using mineral acids. Ammoniacal leaching is usually applied to carbonate-rich copper ores, where acid leaching is not economic due to the rapid and selective consumption of the acid by carbonate material.

The abundance of chrysocolla in secondary copper ores, particularly in Australia, and its potential as an important ore mineral for copper means that furthering the understanding of factors influencing its hydrometallurgy may be of significant economic importance in terms of extraction and processing. The current work was undertaken in order to compare the leaching rates of different chrysocolla samples from various locations. Previous acid leaching rate studies (Prosser, 1970; Hsu and Murr, 1975; Pohlman and Olsen, 1974; Khalezov et al., 1984; Beisembaev et al., 1984) have all made mention of the highly variable nature of chrysocolla. However, their experiments involved chrysocolla samples from only one location. Furthermore in these previous
studies, leaching rates were discussed only in general terms and it was assumed that the leaching rate for chrysocolla is uniform from one location to another. Also, the literature reveals that suggested mechanisms for the dissolution of chrysocolla are contradictory. As mentioned previously Hsu and Murr (1975) assumed that the dissolution is reaction-controlled whereas, in contrast, Pohlman and Olsen (1974) and Khalezov et al. (1984) suggested that the dissolution is diffusion controlled. Furthermore, the simplistic model for the acid dissolution of chrysocolla proposed by Hsu and Murr (1975) may in fact only be a very sample-specific example and may not have the wide practical application suggested by the authors. By comparing the rates of dissolution of samples from different localities it was hoped to gain a greater insight into the controlling processes of the dissolution of chrysocolla. The leaching experiments conducted in this study were carried out under ambient conditions, using low concentrations of acid that would likely be employed for economic extraction of copper on a larger scale. Any differences in leaching rates of various chrysocolla samples detected here, could have significant implications for the economic extraction of copper from chrysocolla-dominant ores.

Apart from its obvious economic importance, the widespread distribution of chrysocolla, particularly in intensively weathered secondary zones and its association with other secondary copper minerals such as copper carbonates and phosphates has great importance on the interpretation of conditions controlling the paragenesis of oxide zones and their associated mineralogies. Calculations for the free energy of formation of chrysocolla (Newberg, 1967) have previously been based on solubility experiments using precipitation curves of hydrated copper silicates. There has been little published work on the free energy of formation of chrysocolla based on naturally occurring “aged” material. No comparative study of the variation of stability of chrysocolla from different
locations has previously been reported. In the current study this too has been addressed in an effort to further the understanding of the Cu(II)-silicate system.

2.1 EXPERIMENTAL

2.1.1 CHRYSOCOLLA SAMPLES

Chrysocolla samples studied were from the Ray mine, Arizona, the Rainbow mine and the Great Australia mine, both in the Cloncurry District, Queensland, an unspecified location in Chile and an unspecified location in Arizona. Samples ranged from light to intense blue colour. Macroscopic textures ranged from massive and earthy to transparent and glassy.

2.1.2 X-RAY METHODS

X-ray diffraction (XRD) analyses were performed using a Phillips PW1825-20 X-ray powder diffractometer (40 kV and 30 mA with a Cu target) and CuKα radiation. Results were analysed using the Traces software processing package (Diffraction Technology Pty. Ltd.). All samples were crushed and hand picked to remove visible mineral impurities before X-ray analysis.

2.1.3 LOW [H+] LEACHING EXPERIMENTS OF EXCESS CHRYSOCOLLA

A series of experiments were conducted to examine the rate of consumption of H⁺ when using low concentrations of sulfuric acid to leach different chrysocolla samples from various locations. All chrysocolla samples were crushed and hand picked under a microscope to eliminate other copper mineral impurities and to minimize quartz content. The samples were then dry ground and sieved. Sample fractions for the experiments were
collected between 1.0 and 0.085 mm sieve meshes. Ground samples were then washed with distilled water to remove dust, then dried in air at room temperature. Purity and crystallinity of samples were investigated using X-ray powder diffraction analysis (see previous section). The leaching experiments conducted were based on the following equation.

\[ \text{CuSiO}_3\cdot\text{H}_2\text{O}(s) + 2\text{H}^+(aq) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{H}_2\text{SiO}_4^-(aq) \]

The experiments involved reacting excess chrysocolla with a fixed amount of dilute sulfuric acid. Changes in \([\text{H}^+]\) with time were easily monitored by periodic pH measurements of the solution. Quartz and opal impurities are inert in dilute acid and have no affect on the acid concentration of the experiment. Dilute \(\text{H}_2\text{SO}_4\) solutions (approximately 0.005 M, about pH 2.1) were used with excess chrysocolla, where the amount of chrysocolla needed was small (1 gram was sufficient for each experiment). Since much lower acid concentrations were being used in these experiments than in previously published experiments, the rate of reaction was expected to be much slower. This allowed pH changes to be easily monitored over a longer period of time.

A weighed sample (1.000 g) of chrysocolla was suspended in a porous nylon cuff tied off by nylon line and suspended in 300 cm\(^3\) of \(\text{H}_2\text{SO}_4\) solution and constantly stirred (its pH being measured before the cuff was placed in the solution). A blank, containing only the nylon stocking cuff, was placed in the dilute acid in order to confirm its non-reactivity in the experiments. The cuff prevented the chrysocolla grains from being crushed by either the stirrer or by abrasion with other grains. This mechanism allowed the grain size to be kept constant, yet still allowed the free circulation of the acid solution around the mineral grains. Three identical experimental runs were repeated for each sample of chrysocolla. All experiments were maintained at a constant temperature of 298 K using a circulating water bath.
Monitoring of the solutions was undertaken at various intervals after the addition of the cuff containing chrysocolla. More measurements were taken at the beginning of the experimental run when it was observed that the pH changed most rapidly. All of the experiments were allowed to reach equilibrium, this being indicated by constant pH registered over a number of days. Final copper analysis was carried out using a Perkin Elmer 3030 atomic absorption spectrophotometer. The dissolved silica analysis was determined using a standard molybdosilicate colourimetric method. (Vogel, 1961).

2.1.4 GRAIN SIZE LEACHING EXPERIMENTS

Hsu and Murr (1975) reported a series of experiments involving the dissolution of “low-grade” chrysocolla particles of various sizes, containing 4.4% Cu, in sulfuric acid. As mentioned earlier, they proposed a simple model of dissolution based on a shrinking core model that assumes the rate to be under chemical reaction control. In the current study the method of Hsu and Murr (1975) was applied to see if the proposed dissolution model could be duplicated for much “higher grade” chrysocolla samples of different textures from different locations.

Some experimental details were modified from the method outlined by Hsu and Murr (1975) as a result of the amount of near “pure” chrysocolla from two locations being available. The first sample used was a massive, dull, earthy chrysocolla from the Great Australia mine, Cloncurry, Queensland, Australia. The second was a bright, glassy, translucent to transparent chrysocolla from the Ray mine, Arizona. Both samples were analysed for impurities using X-ray powder diffraction, giving similar X-ray patterns with broad peaks corresponding to chrysocolla. Quartz was the major impurity in both samples, with no other copper phases being detected. The bulk chrysocolla was crushed and separated into various size fractions using standard sieve sizes in a sieve shaker.
Some 100.0 cm$^3$ of 0.05M H$_2$SO$_4$ (adjusted to pH 1.1) was then reacted with 1.000 g of chrysocolla of each size fraction. In each case the reaction solution was constantly stirred (with care taken not to crush the chrysocolla) and maintained at 298 K in a waterbath. A 10.00 cm$^3$ sample of each of the reaction solutions was taken at intervals 0.5, 1, 2, 3, 4 hours and the aliquot was replaced with 10.00 cm$^3$ of stock acid solution to maintain overall acid concentration. A separate 1.000 gram sample of both chrysocolla samples (<63 micron fraction) was completely leached in 100.0 cm$^3$ of 1 M H$_2$SO$_4$ for 48 hours and solution was analysed to obtain the total leachable copper concentration. All analyses were carried out using a Perkin-Elmer 3030 AAS.

2.1.4.1 Scanning electron microscope investigation of leached particles

At the end of each of the leach experiments the remaining grains of the various size fractions were examined using a Jeol T-330 scanning electron microscope. Qualitative elemental mapping was carried out using an energy dispersive spectrometer (EDS) from Moran Instruments attached to the microscope and controlled by Moran Scientific software. Analyses were run at 20 kV and data were ZAF corrected.

2.1.6 EQUILIBRIUM CONSTANT AND ΔG°$^\circ$ OF CHRYSOCOLLA

Two different chrysocolla samples were used, one a massive dull blue structureless chrysocolla from the Great Australia mine, Cloncurry district, Queensland, Australia and the other a glassy bright blue chrysocolla from the Ray mine Arizona, USA. Both samples were checked for impurities using powder X-ray analysis. Excess chrysocolla (about one gram) was reacted with 250.0 cm$^3$ of 0.005 M aqueous H$_2$SO$_4$. The chrysocolla samples were held in a porous nylon sleeve, suspended in a sealed flask. N$_2$ was bubbled through the solution prior to commencement of experiment to expel any
dissolved CO₂. During the experiment the solution was constantly stirred and maintained at 298 K in a waterbath. The solutions were allowed to stand so that they could reach and maintain equilibrium (about 6 weeks estimated from previous trial runs). After eight weeks the pH of the solutions was measured using a Radiometer pHM 32 instrument with a combined electrode and filtered through a GF/F fibreglass filter. Compositions of the filtrate (Cu) were measured using a Perkin Elmer 3030 AAS.

2.2 RESULTS AND DISCUSSION

2.2.1 X-RAY EXAMINATION OF CHRYSOCOLLA

A single atom diffracts a beam of X-rays in equally all directions, but a large number of atoms which are arranged in a three-dimensional lattice diffracts an X-ray beam in only a few directions according to the Bragg equation, \( n\lambda = 2d \sin \theta \), where \( n = \) a whole number, \( \lambda = \) wavelength, \( d = \) layer spacing, \( \theta = \) diffraction angle.

Amorphous solids are characterised by almost completely random atom arrangements whereas the only tendency to “order” derives from fairly tight packing of the constituting atoms and an empirically demonstrated statistical preference for a particular interatomic distance. The resulting X-ray scattering curve is broad showing one or two maxima. In contrast to truly amorphous material, some solids (for example chrysocolla) are known to be partially crystalline. Such substances have regions where there is some degree of ordering mixed with large areas of disorder. These ordered regions are called “crystallites” and produce broad diffraction lines (Cullity, 1978).

2.2.1.1 Unleached chrysocolla.

X-ray profiles for the chrysocolla samples were all similar with peaks that were broad and low in relative intensity raised above a broad amorphous band between 15-50°
**Figure 2.4a** X-ray powder diffraction pattern for Arizona chrysocolla (Q represents quartz peaks).

**Figure 2.4b** X-ray powder diffraction pattern for Chile chrysocolla (Q represents quartz peaks).
Figure 2.4c  X-ray powder diffraction pattern for the Ray mine, Arizona chrysocolla (Q represents quartz peaks).

Figure 2.4d  X-ray powder diffraction pattern for Great Australia mine chrysocolla (Q represents quartz peaks).
Figure 2.4e  X-ray powder diffraction pattern for the Rainbow Mine, Queensland chrysocolla.

$2\theta$ (Figures 2.4a-e). Sharp peaks obvious in these samples are generally due to quartz impurities. The broad peak positions correspond well with those observed in previous studies (Table 2.1). Interestingly the 17.7 Å line described by Van Oosterwyck-Gastuche (1970) was absent in all cases, however this may be not be an anomalous observation as this line was not also observed in the work of others (see Table 2.1).

Comparison of the X-ray patterns of the different chrysocolla samples shows some differences in the relative sizes of the broad peaks compared to the broad intensity humps. The broadness of these peaks varies for different samples and there is also a slight shift in peak position. In both the Rainbow mine and Arizona samples a slight shoulder in the pattern was observed around 9.55 Å, and this is not present in other samples. Of the different chrysocolla samples examined, the material from Arizona (Figure 2.4a)
produced the most clearly defined X-ray powder pattern. The main 1.49 Å peak was sharper than that observed in other samples. Lesser peaks were not as broad and the relative intensities of the peaks were higher (compared to the broad intensity hump) than those observed in other samples. The X-ray pattern for the Rainbow mine chrysocolla shows the broad intensity hump to be of lower relative intensity and all peaks observed tend to be both broader and less distinct than other samples. This indicates that the degree of crystallinity in the Rainbow mine chrysocolla is less than that of the other chrysocolla samples studied. A slight shift in the peak centred around 2.85 Å may be due to changes in the lattice due to substitution of other ions replacing Cu\(^{2+}\) (such as Ca\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), etc). Great Australia mine, Ray mine and Chile chrysocolla X-ray patterns are similar and generally fall between the two cases highlighted above.

2.2.1.2 Leached chrysocolla.

The main feature of the X-ray traces from chrysocolla samples that were completely leached (Figure 2.5a-d) was a broad amorphous 'hump' (excluding peaks caused by impurities). This 'hump' was of much lower in intensity to that of the corresponding 'hump' in the unleached material and occurred over a much narrower range (25-35° 2θ). This shows that the chrysocolla structure was completely broken down during leaching.

2.2.1.3 Impurities in chrysocolla samples

Even after handpicking of the samples, impurities were still present in most samples. The major impurity present was quartz, as observed by other workers (Martinez, 1963; Pohlman and Olson, 1976; Raghavan and Fuerstenau, 1977). It is particularly difficult to completely remove quartz from samples because of its intimate association
Figure 2.5a  X-ray powder diffraction pattern for leached Chile chrysocolla.
Q represents quartz peaks.

Figure 2.5b  X-ray powder diffraction pattern for leached Arizona chrysocolla.
Q represents quartz peaks.
Figure 2.5c  X-ray powder diffraction pattern for leached Ray Mine chrysocolla. 
Q represents quartz peaks.

Figure 2.5d  X-ray powder diffraction pattern for leached Great Australia mine chrysocolla. 
Q represents quartz peaks.
with chrysocolla, where it is often present as thin layers (less than 0.1 mm thick) and small vugh coatings present throughout the bulk material. In the chrysocolla sample from the Ray and Great Australia mines a peak that did not correspond to either chrysocolla or quartz occurred at about 21.8° 2\θ. The origin of this peak was made clearer by study of the leached samples (Figures 2.5c and d). Here the peak was associated with a steep asymmetrical slope superimposed on the broad amorphous hump between 22-30.5° 2\θ. Another distinct peak was present at 31° 2\θ. These peaks and slope correspond to the silica polymorphs cristobalite and tridymite. Although these phases are generally high temperature polymorphs they can form metastably at low temperatures. At lower temperatures of formation and in the presence of alkalis and other cations, intermixing of cristobalite and tridymite may take place to form opal-CT. Opal-CT has a structure that has been loosely described as a disordered intergrowth of tridymite- and cristobalite-type stacking sequences (Frondel, 1962). Both polymorphs generally show a broad, low peak centred around 21° 2\θ. As the disordering increases the stronger low-tridymite diffraction lines become prominent in X-ray traces. It is suggested that this disordering is caused by the entrance of cations such as Al, Ca and Mg into the solid solution (Frondel, 1962). A difference in the opal structural ordering may exist between the Great Australia mine chrysocolla, which has dominant cristobalite lines at 21.8 and 35.9° 2\θ and the Ray mine chrysocolla, which does not have these lines.

2.2.2 LOW [H\+] LEACHING OF CHRSOCOLLA

Plotted results of pH versus time (in hours) are separated into five sets of experiments; one for each different chrysocolla. Each set consisted of three identical experimental runs. Plotted values in Figure 2.6 are the calculated average values of the three runs in each sample set (plots for each run in a set are presented in Appendix 2.1).
**Figure 2.6**  Average plots of pH *versus* time for leaching experiments.

**Figure 2.7a**  Average plots of [H⁺] *versus* time for leaching experiments.
The [H\(^+\)] \textit{versus} time was also averaged in the same way (Figure 2.7a). Figures 2.7b-d are the average plots of [H\(^+\)] \textit{versus} time for 0-12 hours, 0-72 hours, and 72-430 hours respectively. Table 2.2 gives a summary of relative [H\(^+\)] with respect to time. There was a distinct difference in the rate of acid consumption between experimental sets. Even within experimental sets using the same chrysocolla sample there was some variation in dissolution rates, particularly in the initial- to mid-time range of the experiments. The Arizona chrysocolla sample showed the greatest variation between experiments (Figures 2.6, 2.7a-d and Table 2.2). The cause of the variation is uncertain but may be the result of indeterminate localised effects in the structure of chrysocolla within the sample. Nevertheless, the runs were reasonably reproducible and the final equilibrium [H\(^+\)] for runs in each different set of experiments was very similar (Table 2.2).

The overall trend in all experiments was one of a rapid initial increase in pH and which progressively slowed as equilibrium was reached. Figure 2.7a shows that 90% of the H\(^+\) is consumed in less than 15% of the overall time taken to reach equilibrium. Equilibrium pH values ranged from 4.08 to 4.43

The use of less concentrated acid than that employed in previous studies significantly slowed the dissolution (Prosser, 1970; Hsu and Murr, 1975). Previous workers reported that in high concentrations of acid “complete” dissolution often occurred in a matter of hours. Table 2.2 shows that in the current study, for the majority of the experiments half the acid was consumed in less than 16 hours. However, the chrysocolla set from Arizona required twice as long to dissolve as other samples. In contrast, the samples from the Rainbow mine required less than 9 hours. In all experiments there is a significant decrease in the rate of acid consumption after 24 hours.

Closer examination of the early stages of the experiments (Figure 2.7b) showed that
Table 2.2  Summary of leaching experiments.

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</tbody>
</table>
for most experiments the consumption of protons was greatest over the first 30 minutes of each set. Most experiments had a similar consumption rate at this stage. However in all the experiments conducted on Rainbow mine chrysocolla consumption rate was significantly faster than other experiments. In this initial stage, surface reactions would be expected to dominate and the rate would therefore be a reflection of the size of particles and the degree of crystallinity of the samples. After the initial 30 minutes the consumption of $H^+$ slowed at different rates for each of the chrysocolla samples. On average Rainbow mine chrysocolla continued to have a comparably faster reaction rate than any of the other samples. The Chile, Great Australia and Ray mine chrysocolla samples all had comparable $H^+$ consumption rates. However, the rate for Arizona chrysocolla experiments slowed noticeably. When the concentration dropped to 0.0068 mol dm$^{-3}$ [$H^+$], definite separate groups of chrysocolla are observed, based upon the rate of consumption.

Equilibrium was taken to be at the point where the pH did not change for more than a week, and for most of the chrysocolla experiments this point was reached after about 30 days. As noted above, Arizona chrysocolla was a noticeable exception. On average, it took significantly longer for these experiments to reach equilibrium (about 42 days).

From the experimental data, $\ln [H^+]$ versus time and $[H^+]^{-1}$ versus time were reviewed (see Figures 2.8a and b) in order to determine whether the rate was a simple first- or second-order reaction. All reactions showed a similar pattern. The $\ln [H^+]$ versus time plot was, as expected, a curve and the $[H^+]^{-1}$ versus time plot was also non-linear. This indicated that the overall dissolution reaction is neither a simple first- or second-order reaction. Indeed, the reaction is approximately zero order with respect to $[H^+]$, in line with the diffusion-controlled mechanisms mentioned previously, for more than one half-life (Figure 2.7b).
Figure 2.7b  $[\text{H}^+]$ Concentration of leaching experiments 0 - 12 hours.

Figure 2.7c  $[\text{H}^+]$ Concentration of leaching experiments 0 - 72 hours.
Figure 2.7d  \([\text{H}^+]\) concentration of leaching experiments 260-430 hours.

2.2.2.2 SEM examination of leached grains

Examination of residual chrysocolla grains from the experiments showed that leaching had been selective. Some grains had leached completely, leaving only a colourless amorphous silica ‘husk’, whereas other grains appeared to show only minor surface leaching. This selective leaching may in part explain the variation that occurred between experimental runs in each sample set of chrysocolla (particularly the Arizona sample). It may also be indicative of the variable nature of chrysocolla occurring even at an extremely fine scale with an individual sample, particularly in samples that show distinct layering. The variation is thought likely to relate to variable crystallinity, or possibly to variations in cation substitution.
**Figure 2.8a** An example of \( \ln [H^+] \) *versus* time plot for chrysocolla leaching (Chile chrysocolla run A).

**Figure 2.8b** An example of \([H^+]^{-1}\) *versus* time plot for chrysocolla leaching (Chile chrysocolla run A).
2.2.2.2 Equilibrium copper concentration and dissolved silica analysis

Equilibrium copper analyses (Table 2.3) showed, as expected, a direct correlation between equilibrium pH values and copper concentration in solution. However, the variation in pH at equilibrium is not entirely accounted for by overall differences in the amount of copper, and this imbalance could be due to the presence of other substituted cations for Cu in the chrysocolla lattice. These cations would be released during dissolution, assuming the overall process was congruent with respect to cation movement. The Rainbow mine chrysocolla, which had the lowest copper concentration in solution at equilibrium, had an average final pH of 4.13. Ray mine chrysocolla had the highest equilibrium pH and a much higher copper content in solution, close to the theoretical maximum copper concentration for the amount of acid consumed. This

<table>
<thead>
<tr>
<th>Table 2.3</th>
<th>Summary of dissolved copper concentrations at equilibrium of leaching experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved copper concentration (mg dm$^{-3}$)</td>
<td></td>
</tr>
<tr>
<td>Chile 1</td>
<td>230</td>
</tr>
<tr>
<td>Chile 2</td>
<td>240</td>
</tr>
<tr>
<td>Chile 3</td>
<td>235</td>
</tr>
<tr>
<td>Arizona 1</td>
<td>220</td>
</tr>
<tr>
<td>Arizona 2</td>
<td>225</td>
</tr>
<tr>
<td>Arizona 3</td>
<td>230</td>
</tr>
<tr>
<td>Rainbow mine 1</td>
<td>210</td>
</tr>
<tr>
<td>Rainbow mine 2</td>
<td>205</td>
</tr>
<tr>
<td>Rainbow mine 3</td>
<td>210</td>
</tr>
<tr>
<td>Ray mine 1</td>
<td>245</td>
</tr>
<tr>
<td>Ray mine 2</td>
<td>245</td>
</tr>
<tr>
<td>Ray mine 3</td>
<td>240</td>
</tr>
<tr>
<td>Great Australia mine 1</td>
<td>225</td>
</tr>
<tr>
<td>Great Australia mine 2</td>
<td>220</td>
</tr>
<tr>
<td>Great Australia mine 3</td>
<td>220</td>
</tr>
</tbody>
</table>
indicates that the composition of Ray Mine chrysocolla is close to that of the assumed ideal composition of CuSiO$_3$.H$_2$O.

At equilibrium, a very fine white gel-like material was present in the flasks. From the powder XRD pattern, the material was found to be amorphous and when analysed was shown to be composed of silica, SiO$_2$. The solubility of silica in water is pH dependent and corresponds to 1.950 x 10$^{-3}$ mol dm$^{-3}$ at 298 K for pH values <9 where H$_4$SiO$_4$ dominates (Iler, 1979; Applin, 1987). Dissolved silica determinations gave values of 118(5) mg dm$^{-3}$ or 1.96 x 10$^{-3}$(9) mol dm$^{-3}$. These were in excellent agreement with the theoretical values. Thus, at equilibrium all solutions are limited by the maximum silica concentration.

Previous studies of the dissolution of chrysocolla have made mention of the variable nature of chrysocolla. However these studies have not examined the effect that this variability exerts on leaching rates on chrysocolla from different deposits. The current experiments highlight the variable nature of chrysocolla and its effects on dissolution. This variability, particularly in experiments using the same material, seems to suggest that initial dissolution rates may be dominated by physical factors. These include porosity and degree of crystallinity. Pohlman and Olsen (1974) also observed that chrysocolla leaching was not uniform and suggested that restricted diffusion through extremely small pore spaces of the lattice could control reaction rates. This diffusion would be highly variable depending on the degree of structural ordering throughout a grain.

From X-ray data, the Arizona chrysocolla was seen to be more crystalline and ordered in comparison to other specimens of chrysocolla, and in the leaching experiments it consistently showed a much slower though variable dissolution rate. The Rainbow mine chrysocolla, which shows a much lower degree of crystallinity, dissolves more
quickly. The rate of dissolution, as well as the time taken to achieve equilibrium appear to be influenced by the degree of crystallinity of the chrysocolla. Increasing degrees of crystallinity may affect the overall porosity of chrysocolla, with crystallites restricting the space in the pores and reducing the diffusion rate. In an extremely fine, well-crystalline chrysocolla diffusion will therefore be slower. Unfortunately it was not possible to examine the variability of the structure on a micro scale within individual mineral samples (only the overall crystallinity of samples was discerned) and it is possible that some samples may have widely different degrees of crystallinity within a single sample. The chemical substitution of chrysocolla does not seem to exert any great an effect either on the dissolution rates, or the time taken to reach equilibrium. However, the chemical variability of chrysocolla does exert a major influence on the equilibrium pH.

The dissolution appears to be congruent in terms of cations although the overall reaction is incongruent. Schnoor (1990) discussed incongruent dissolution in general terms and in the case of chrysocolla incongruent dissolution will result in migration of Cu\textsuperscript{2+} from the core of the mineral grain through a layer that is depleted in copper. This depleted zone has been observed in most of the leached grains in the current study. The reaction rate of the silicate lattice is limited by hydrolysis to H\textsubscript{4}SiO\textsubscript{4} and the solubility of amorphous silica. As the reaction proceeds, diffusion of Cu\textsuperscript{2+} through the depleted zone will become slower until it equals the rate of the surface-controlled dissolution of the silicate. At this point a “pseudo” steady-state is attained, in which the depleted layer thickness stabilises.

2.2.3 GRAIN SIZE VARIATION

2.2.3.1 Leached copper

There was a distinct difference in the rate at which copper leached from the two
different chrysocolla samples (Figures 2.9a and b) with differing grain sizes. Both samples leached at significantly slower rates compared with results reported by Hsu and Murr (1975).

Overall, smaller particles leached quicker in the initial stages of the experiment. At this stage, the clear divisions between size fractions reported by Hsu and Murr (1975), were not obvious. After initial dissolution the rate for the massive chrysocolla from the Great Australia mine for each size fraction was generally the same (except for the smallest size fraction). Chrysocolla from the Ray mine showed a similar trend, with a greater initial release of copper for smaller grain sizes and the subsequent reaction rate being similar for all size fractions. This is an entirely expected result, as the smaller the grain size the larger is the ratio of total surface area to acid.

2.2.3.2 Leached grain examination

For both chrysocolla samples, examination of leached grains after 4 hours showed that the grains had not leached evenly. Some were completely leached (composed entirely of amorphous silica) whilst others only showed limited variation in the thickness of a leached silica rim. Leached grains generally displayed three distinct zones: (1) an outer bleached (copper depleted) zone; (2) an inner relatively unaffected chrysocolla core and (3) a thin transition zone of partially depleted copper. However, this zonation was not always discernible in every grain. Figures 2.10a-d are EDS elemental maps of the relative Si and Cu distribution in partially leached chrysocolla grains (the lighter shading indicates higher concentrations of a specific element). Si distribution maps (Figures 2.10a and c) clearly show a lighter zone (higher Si content) around the rim of the grain corresponding to the leached zone composed of pure silica. The darker core (lower relative Si content) consists of unleached material (the darkest shade) and also of partially
Figure 2.9a  % of leached copper versus time for various particles sizes for Ray mine chrysocolla.

Figure 2.9b  % of leached copper versus time for various particles sizes for Great Australia mine chrysocolla.
FIGURE 2.10a  SEM X-Ray map of Si distribution of a partially leached Ray mine chrysocolla grain. Lighter shades indicate greater proportions of Si. The white area indicates the completely leached rim (grain is 2 mm across).

FIGURE 2.10b  SEM X-Ray map of Cu distribution of partially leached Ray mine chrysocolla grain of Figure 2.10a. Lighter shades indicate greater proportions of Cu. Cu has been completely leached from the outer rim (grain is 1 mm across).
FIGURE 2.10c  SEM X-Ray map of Si distribution of a partially leached Great Australia mine chrysocolla grain. The white outer area is the completely leached rim (grain is 2 mm across).

FIGURE 2.10d  SEM X-Ray map of Cu distribution of the partially leached Great Australia mine chrysocolla grain of Figure 2.10c. Cu has been completely leached from the outer rim.
leached chrysocolla (slightly lighter shade). The Si EDS maps highlight the relationship of the boundary between the core to depleted zone. Where the grain has only been slightly leached the boundary tends to be parallel to the grain edges. Where the leaching was more advanced (generally greater than 50%), the boundary becomes more uniform and circular in shape. In some elongated grains that do not have uniform thickness, the partial leaching pattern appears like a dumbbell with two separate cores. Cu distribution maps (Figures 2.10b and d) show that copper is completely absent in the outer rim of partially leached grains.

In air, the leached zone appears white and frosted. However, in solution it was clear and transparent with a visible blue core. In larger grains of both samples, the outer surface features of the leached zone (copper depleted) was dominated by angular surface cracks and fractures (Figures 2.11a, b and c) which extend through the depleted zone and abruptly end at the partially leached zone (Figure 2.10a and c). In the chrysocolla from Ray, some of the fractures were often sub-parallel with cross fractures and appeared to follow internal layers that were not apparent on unleached material (Figures 2.11b). In other grains the fracturing appears conchoidal. In more massive, grainy chrysocolla the fracture pattern appeared more polygonal (similar to shrinkage cracks) and followed no obvious trend. Surface cracks are seen in all grains down to 100 microns in size. Extensive surface etching and pitting (Figures 2.11c) is present on most grains. The formation of surface pitting may be indicative of the porous nature of chrysocolla, with initial dissolution focused on these pores.

Different chrysocolla samples leach copper at significantly different rates. The initial release of copper appears to be influenced by grain size with the smaller grain size (greater total surface area) exhibiting the greatest extent of copper leaching. However, with time, the overall rate of dissolution becomes independent of grain size, and other
FIGURE 2.11a  Polygonal fracture pattern of partially leached Ray mine chrysocolla grain.

FIGURE 2.11b  Surface features of partially leached Ray chrysocolla grain (note the sub-parallel fracture pattern).
FIGURE 2.11c  Surface features of partially leached Great Australia mine chrysocolla grain (note the rilling and pitting of surfaces).

FIGURE 2.11d  Close up of the surface of partially leached Ray mine chrysocolla grain with the sub parallel surface fracturing (note the absence the surface pitting).
factors must therefore influence the overall rate. The rate of acid diffusion through the chrysocolla may become the significant factor. Both the Great Australia and the Ray mine chrysocolla leach rates were significantly slower than the results obtained by Hsu and Murr (1975). When current results were substituted into the kinetic model of Hsu and Murr (1975) (see Appendix 2.2) and plotted, both chrysocolla samples in this study exhibited broadly similar trends (Figure 2.12A and B). However, when compared to the results obtained by Hsu and Murr, the trends were dissimilar (Figure 2.12C). This suggests that the material Hsu and Murr used in their study was significantly different and that the overall rate was controlled by other influences.

The material used by Hsu and Murr (1975) was termed “low-grade” chrysocolla containing only about 5% copper. Pure chrysocolla contains about 30-40% copper. The chrysocolla used in the current experiments was of high purity (quartz and opal being the only impurities) and consequently the rate of leaching was considerably slower. Hsu and Murr (1975) gave no detailed description of the material, nor any supportive X-ray data or reports of impurities within the material. It is well-known that chrysocolla is often intimately associated with other copper minerals, particularly malachite, and that the presence of these other phases would influence the overall rate of copper release. The dissolution of malachite is extremely rapid and its dissolution products are copper ions and carbon dioxide gas. Compared to malachite the rate for pure chrysocolla is slower and produces both copper ions and silicic acid, where the latter has low solubility at low pH and would therefore precipitate amorphous silica. If malachite was present in the sample, the dissolution rate and release of copper ion would be surface-reaction dominated with diffusion through the grain being of negligible significance as the surfaces dissolve rapidly. For chrysocolla, with a slower surface reaction rate, diffusion factors would have a greater influence on dissolution. In their
Figure 2.12  Plot of experimental leaching data for A: Ray mine chrysocolla; B: Great Australia mine chrysocolla and C: Hsu and Murr’s (1975) “low-grade” chrysocolla according to the shrinking-core model formula proposed by Hsu and Murr (1975).
chrysocolla experiments which contained malachite as an impurity, Raghavan and Fuerstenau (1977) noted that the malachite tended to concentrate in the finer grain size fractions. If this was the case in the Hsu and Murr experiments, then the trend of an accelerated leach rate in the finer grain size fractions inferred would be because of the potentially higher malachite content.

It has been suggested by Romankiv (1962), that in the non-agitated solution the leaching reaction proceeds very slowly and that diffusion processes dominate. Hsu and Murr (1975) suggested that the rate of fluid flow would be near zero in such a static system. The chemical reaction between the leachable particle and the solution at the boundary surface would quickly attain equilibrium, independently of particle size, and diffusion would be the rate-controlling factor. With increased stirring the surface reaction rate would be the rate-determining step. However, the agitation of particles, either deliberately or through increased stirring, may also cause further abrasion and fracturing of mineral grains, thus exposing more surface area and reducing the overall influence of diffusion.

Empirically, the current experiments show that the inhomogeneity of chrysocolla affects the rate of acid leaching to such an extent that it is virtually impossible to use the mineral chrysocolla, as a model for the kinetics of hydrometallurgical processing of copper ores.

2.2.4 STABILITY OF CHRSYOCOLLA

The chemical analyses of equilibrium mixtures of chrysocolla are presented in Tables 2.4 and 2.5. Experiments on the Ray mine chrysocolla gave significantly more copper in solution at equilibrium than the material from the Great Australia mine. An ion charge balance was conducted in order to compare the amount of acid consumed with the
Table 2.4  Equilibrium data $^a$ for the dissolution of Ray mine chrysocolla in H$_2$SO$_4$(aq) at 298.2 K.

<table>
<thead>
<tr>
<th>$[\text{Cu}^{2+}]_t$</th>
<th>$[\text{Cu}^{2+}]_e$</th>
<th>$[\text{H}_2\text{SiO}_4]$</th>
<th>pH</th>
<th>I$^b$</th>
<th>$\gamma_{\text{Cu}^{2+}}$</th>
<th>log K</th>
<th>$\Delta G_{\text{reaction}}^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.81 x 10$^{-3}$</td>
<td>2.89 x 10$^{-3}$</td>
<td>1.95 x 10$^{-3}$</td>
<td>4.41</td>
<td>0.0119</td>
<td>0.641</td>
<td>3.38</td>
<td>-19.3</td>
</tr>
<tr>
<td>4.16 x 10$^{-3}$</td>
<td>2.90 x 10$^{-3}$</td>
<td>1.95 x 10$^{-3}$</td>
<td>4.42</td>
<td>0.0119</td>
<td>0.641</td>
<td>3.39</td>
<td>-19.4</td>
</tr>
<tr>
<td>4.82 x 10$^{-3}$</td>
<td>2.90 x 10$^{-3}$</td>
<td>1.95 x 10$^{-3}$</td>
<td>4.44</td>
<td>0.0119</td>
<td>0.641</td>
<td>3.44</td>
<td>-19.6</td>
</tr>
<tr>
<td>4.79 x 10$^{-3}$</td>
<td>2.88 x 10$^{-3}$</td>
<td>1.95 x 10$^{-3}$</td>
<td>4.44</td>
<td>0.0119</td>
<td>0.641</td>
<td>3.45</td>
<td>-19.7</td>
</tr>
<tr>
<td>average</td>
<td>3.42(3)</td>
<td>-19.5(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Concentrations are given in molar units and $\Delta G^\circ$ values as kJ mol$^{-1}$; subscripts t and e refer to total and free ion concentrations, respectively; $^b$Ionic strength.

Table 2.5  Measured total cation $^a$ concentrations at equilibrium for Great Australia mine chrysocolla at 298.2 K.

<table>
<thead>
<tr>
<th>pH</th>
<th>$[\text{Cu}^{2+}]$</th>
<th>$[\text{Ca}^{2+}]$</th>
<th>$[\text{Mg}^{2+}]$</th>
<th>$[\text{K}^+]$</th>
<th>$[\text{Na}^+]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.30</td>
<td>4.30 x 10$^{-3}$</td>
<td>1.16 x 10$^{-4}$</td>
<td>2.06 x 10$^{-4}$</td>
<td>2.09 x 10$^{-4}$</td>
<td>1.91 x 10$^{4}$</td>
</tr>
<tr>
<td>4.29</td>
<td>4.20 x 10$^{-3}$</td>
<td>9.00 x 10$^{-5}$</td>
<td>2.69 x 10$^{-4}$</td>
<td>4.33 x 10$^{-4}$</td>
<td>6.00 x 10$^{-5}$</td>
</tr>
<tr>
<td>4.29</td>
<td>4.19 x 10$^{-3}$</td>
<td>9.30 x 10$^{-5}$</td>
<td>2.61 x 10$^{-4}$</td>
<td>2.94 x 10$^{-4}$</td>
<td>1.74 x 10$^{-4}$</td>
</tr>
<tr>
<td>4.27</td>
<td>4.20 x 10$^{-3}$</td>
<td>1.17 x 10$^{-4}$</td>
<td>2.64 x 10$^{-4}$</td>
<td>6.21 x 10$^{-4}$</td>
<td>4.30 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

$^a$Concentrations are given in molar units.
amount of copper released from the Ray mine chrysocolla was consistent. However an equivalent charge balance on the Great Australia mine chrysocolla was not acceptable until other ions were taken into account. The concentration of dissolved silica cannot exceed the maximum silica solubility (about 0.00195 M at 298 K below pH 9) and that above this concentration amorphous silica is precipitated. It was shown previously that this situation was that obtained in the leach experiments.

From these results, total ionic species concentrations at equilibrium were calculated using the COMICS speciation program (Perrin and Sayce, 1967) which gave free concentrations of Cu$^{2+}$(aq) and H$_2$SiO$_4^0$(aq), together with those of all other species taken into account. Concentration values calculated by COMICS for various species are set out in Appendix 3. Stability constant data for H$_4$SiO$_4^0$(aq), H$_2$SiO$_4^{2-}$(aq), H$_3$SiO$_4^-(aq)$, SO$_4^{2-}$(aq), HSO$_4^-(aq)$, CuSO$_4^0$(aq), CuOH$^+$(aq), Cu(OH)$_2^0$(aq), Cu(OH)$_3^0$(aq), Cu(OH)$_4^0$(aq), Cu$_2$OH$_2^{2+}$(aq), Cu$_2$(OH)$_2^{2+}$(aq) and Cu$_3$(OH)$_4^{2+}$(aq) were taken from the compilation of Smith and Martell (1976) and are presented in Appendix 1. From COMICS, it was noted that at equilibrium the dominant species present are Cu$^{2+}$(aq), CuSO$_4^0$(aq), SO$_4^{2-}$(aq) and H$_4$SiO$_4^0$(aq). The presence of other ions in solution influences the overall activity of any particular ion. Concentration and activity are related by the activity coefficient, $a_i = m_i \gamma_i$ where $a_i =$ activity, $m_i =$ molal concentration and $\gamma_i =$ activity coefficient. Activity coefficients for Cu$^{2+}$(aq) were calculated for the ionic strength, I.

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

where $c_i =$ concentration and $z_i =$ charge, coupled with the extended Debye-Hückel equation

$$\log \gamma = -Az^2 \left( \frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right)$$
where \( A \) is a constant depending on temperature and dielectric constant of the solvent.

This is 0.509 for water at 298K. \( \text{H}_2\text{SiO}_4^\circ \, (\text{aq}) \) was taken to have an activity coefficient of unity. Calculated ionic strengths and other relevant data are given in Tables 2.4 and 2.6.

### 2.2.4.1 Pure chrysocolla

The equilibrium constant for the dissolution reaction for pure chrysocolla

\[
\text{CuSiO}_3\text{H}_2\text{O}(s) + 2\text{H}^+(aq) \leftrightarrow \text{Cu}^{2+}(aq) + \text{H}_2\text{SiO}_4^\circ(aq) + \text{H}_2\text{O}(l)
\]

can be expressed in terms of activities as

\[
K = \frac{a_{\text{H}_2\text{SiO}_4^\circ} \cdot a_{\text{Cu}^{2+}}}{a_{\text{H}^+} \cdot a_{\text{CuSiO}_3\text{H}_2\text{O}}}
\]

\[
= \frac{m_{\text{H}_2\text{SiO}_4^\circ} \cdot m_{\text{Cu}^{2+}}}{m_{\text{H}^+} \cdot m_{\text{CuSiO}_3\text{H}_2\text{O}}} \cdot \frac{\gamma_{\text{H}_2\text{SiO}_4^\circ} \cdot \gamma_{\text{Cu}^{2+}}}{\gamma_{\text{H}^+} \cdot \gamma_{\text{CuSiO}_3\text{H}_2\text{O}}}
\]

or

\[
\log K = \log m_{\text{H}_2\text{SiO}_4^\circ} + \log m_{\text{Cu}^{2+}} + 2 \, \text{pH} + \log \gamma_{\text{Cu}^{2+}}
\]

when \( \gamma_{\text{H}_2\text{SiO}_4^\circ}(\text{aq}) = 1 \).

### 2.2.4.2 Impure chrysocolla

For substituted chrysocolla, where cations such as \( \text{Ca}^{2+}, \text{Na}^+, \text{Mg}^{2+}, \text{K}^+, \text{etc} \) replace \( \text{Cu}^{2+} \), the assumption \( a_{\text{CuSiO}_3\text{H}_2\text{O}} = 1 \) is no longer valid, and the following is obtained

\[
K \cdot a_{\text{chrysocolla}} = \frac{a_{\text{H}_2\text{SiO}_4^\circ} \cdot a_{\text{Cu}^{2+}}}{a_{\text{H}^+}}
\]

Where \( a_{\text{chrysocolla}} = \) the activity of chrysocolla in the solid solution. If \( \frac{a_{\text{H}_2\text{SiO}_4^\circ} \cdot a_{\text{Cu}^{2+}}}{a_{\text{H}^+}} \) is calculated in the same way as above, and the function is let to be \( f \),

\[
\gamma_{\text{chrysocolla}} = \frac{f}{a_{\text{chrysocolla}} K}
\]
where $N_{\text{chrysocolla}}$ is the mol fraction of chrysocolla. This can be expressed as the fraction of $\text{Cu}^{2+}$ of the total cations (A) in chrysocolla formula $\text{AH}_2\text{SiO}_4$ where $A = (\text{Cu}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}, 2\text{Na}^+, 2\text{K}^+)$ etc. The fraction was calculated as follows:

$$N_{\text{chrysocolla}} = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^{2+}][\text{Ca}^{2+}][\text{Mg}^{2+}]0.5[\text{Na}^+]0.5[\text{K}^+] \text{ etc}}$$

The concentrations of monovalent cations such as $\text{Na}^+$ and $\text{K}^+$ are taken as half since two ions are required for charge balance.

From analysis of the aqueous equilibrium solution, chrysocolla from the Great Australia mine is not pure copper silicate but has a number of other cations substituted for the copper in the structure. However, from the overall charge balance at equilibrium, it can still be assumed that the overall dissolution of this chrysocolla is congruent in terms of cations. The COMICS program was used to calculate the ion speciation with the additional cations (Appendix 3). The additional stability constant data for $\text{CaOH}^+(\text{aq})$, $\text{MgOH}^+(\text{aq})$, $\text{KOH}^+(\text{aq})$, $\text{NaOH}^+(\text{aq})$, $\text{CaHSO}_4^+(\text{aq})$, $\text{CaSO}_4^+(\text{aq})$, $\text{MgHSO}_4^+(\text{aq})$, $\text{MgSO}_4^+(\text{aq})$, $\text{KSO}_4^+(\text{aq})$, $\text{NaHSO}_4^+(\text{aq})$, $\text{NaSO}_4^+(\text{aq})$, $\text{Ca(H}_2\text{SiO}_4)^+(\text{aq})$, $\text{Mg(H}_2\text{SiO}_4)^+(\text{aq})$, $\text{Ca(H}_2\text{SiO}_4)^0(\text{aq})$ and $\text{Mg(H}_2\text{SiO}_4)^0(\text{aq})$ were taken from the compilation of Smith and Martell (1976) listed in Appendix 1. Calculated equilibrium concentrations for $\text{Cu}^{2+}(\text{aq})$ are presented in Table 2.6. If these values are used to calculate $\gamma_{\text{chrysocolla}}$ (assuming that it does not equal 1 for impure chrysocolla) then the calculated $K$ is assumed to equal $f$ as outlined above. It is assumed that $K_{eq}$ is equal to the average calculated $K$ value of the Ray mine chrysocolla. $N_{\text{chrysocolla}}$ is calculated using the ratio of the concentration of charge for $\text{Cu}^{2+}$ over the total cation charge concentration (Table 2.6). From this information the average $\gamma_{\text{chrysocolla}}$ was calculated as 0.51(4) (Table 2.6).
Table 2.6  Equilibrium data\(^a\) for the dissolution of Great Australia mine chrysocolla in H\(_2\)SO\(_4\)(aq) at 298.2 K (assuming \(\gamma_{\text{chrysocolla}} \neq 1\)).

<table>
<thead>
<tr>
<th>[Cu(^{2+})](_e)</th>
<th>[H(_2)SiO(_4)](^-)</th>
<th>pH</th>
<th>(I^b)</th>
<th>(\gamma_{\text{Cu}^{2+}})</th>
<th>(f)</th>
<th>(N)</th>
<th>(\gamma_{\text{chrysocolla}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.57 x 10(^{-3})</td>
<td>1.95 x 10(^{-3})</td>
<td>4.30</td>
<td>0.0119</td>
<td>0.641</td>
<td>1278</td>
<td>0.89</td>
<td>0.55</td>
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<tr>
<td>2.50 x 10(^{-3})</td>
<td>1.95 x 10(^{-3})</td>
<td>4.29</td>
<td>0.0121</td>
<td>0.639</td>
<td>1184</td>
<td>0.88</td>
<td>0.51</td>
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<tr>
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<td>1.95 x 10(^{-3})</td>
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<tr>
<td>2.51 x 10(^{-3})</td>
<td>1.95 x 10(^{-3})</td>
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<td>0.640</td>
<td>1068</td>
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<td>0.47</td>
</tr>
<tr>
<td>average</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.51(4)</td>
</tr>
</tbody>
</table>

\(^a\)Concentrations are given in molar units and \(\Delta G^o\) values as kJ mol\(^{-1}\); \(e\) refers to free ion concentrations; \(^b\) Ionic strength.

Table 2.7  Equilibrium data \(^a\) for the dissolution of Great Australia mine chrysocolla in H\(_2\)SO\(_4\)(aq) at 298.2 K (assuming \(\gamma_{\text{chrysocolla}} = 1\)).

<table>
<thead>
<tr>
<th>log K</th>
<th>(\Delta G^o_{\text{reaction}})</th>
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</thead>
<tbody>
<tr>
<td>3.11</td>
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</tr>
<tr>
<td>3.08</td>
<td>-17.6</td>
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<tr>
<td>3.08</td>
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</tr>
<tr>
<td>3.04</td>
<td>-17.3</td>
</tr>
<tr>
<td>average</td>
<td>3.08(4)</td>
</tr>
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</table>

\(^a\)\(\Delta G^o\) values given as kJ mol\(^{-1}\)
2.2.4.3 Free energy of formation

The Standard Gibbs free energy of a reaction can be calculated using the following equation,

$$\Delta G^o_{\text{reaction}} = -2.303 \ RT \ \log \ K$$

where \( K \) is the equilibrium constant for the reaction, \( T \) is the temperature, \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)).

$$\Delta G^o_{\text{reaction}} = \Delta G^o_{\text{f(products)}} - \Delta G^o_{\text{f(reactants)}}$$

This equation and thermodynamic data in Appendix 1 were used to calculate the free energy of formation of chrysocolla at 298.2 K. The values are presented in Tables 2.4 and 2.7. The average calculated \( K \) value for the dissolution was 3.42(3). The average free energy of reaction for the Ray mine chrysocolla (pure chrysocolla) was calculated to be -19.5 \( \pm \) 0.2 kJ mol\(^{-1}\) at 298.2 K. The calculated \( \Delta G^o_{f} \) of Ray mine chrysocolla was -1223.2 \( \pm \) 2.4 kJ mol\(^{-1}\) at 298.2 K.

To compare the difference in the \( \Delta G^o_{f} \) values, Great Australia mine chrysocolla was assumed to have \( \gamma_{\text{chrysocolla}} = 1 \). The results are presented in Table 2.7. The average calculated \( \Delta G^o \), was -17.5 \( \pm \) 0.5 kJ mol\(^{-1}\) at 298.2 K. The average \( \Delta G^o_{f} \) is -1225.2 \( \pm \) 2.4 kJ mol\(^{-1}\) at 298.2 K. There is only slight difference in the value (2.0 kJ mol\(^{-1}\)) compared to pure chrysocolla which is within experimental error.

As expected \( \Delta G^o_{f} \), is significantly more negative than the value for freshly precipitated "dehydrated" chrysocolla calculated by Newberg (1967) which was -288.4 kcal mol\(^{-1}\) (-1206.7 kJ mol\(^{-1}\)) at 298.2 K. The calculated \( \Delta G^o_{f} \) for natural chrysocolla was also significantly more negative than the -2.8 kcal mol\(^{-1}\) (-11.72 kJ mol\(^{-1}\)) difference, which Newberg (1967) attributed to "aged" reactions to form dioptase. This difference in \( \Delta G^o_{f} \) of naturally occurring chrysocolla would be a reflection of the degree of crystallinity and size of crystals. The freshly precipitated amorphous copper silicate has a
less negative $\Delta G^o_f$ (hence being less stable) and as the chrysocolla becomes more crystalline over time, $\Delta G^o_f$ becomes more negative.

Diopside is a rare copper silicate mineral that is chemically related to chrysocolla. It has an identical reduced chemical stoichiometry (CuSiO$_3$.H$_2$O). Diopside has a very definite and different crystalline structure to that of chrysocolla and one which has been well established by previous studies (Ribbe et al., 1977; Belov et al., 1978). Unlike chrysocolla, which has a poorly defined mixed layer lattice and a chain structure, diopside is made up of six-membered rings of SiO$_4$ tetrahedra linked by hydrogen bonded H$_2$O and Cu(II) ions positioned in octahedral sites (Lima-de-Faria, 1994). Recent thermodynamic data was derived from calorimetric measurements of diopside (Kiseleva et al., 1993), $\Delta G^o_f$ values were based on the formula CuSiO$_3$.H$_2$O and calculated as $-1220.8 \pm 4.0$ kJ mol$^{-1}$. These values are very close to the derived value for “aged” chrysocolla and within experimental error of calculated $\Delta G^o_f$ values for “natural” chrysocolla. The similar values of $\Delta G^o_f$ for both chrysocolla and diopside would tend to suggest that both minerals should have a similar abundance in oxide zones and commonly form intimate associations. However, there is little evidence in the literature of direct pseudomorphing or replacements of the two minerals. Chrysocolla is far more abundant and widespread in cupriferos oxides zones than diopside, which is restricted to only a few locations around the world, notably Tsumeb in Namibia, Tiger in Arizona and Russia (Roberts et al., 1990). The rarity of diopside compared to chrysocolla must therefore be related to kinetic factors affecting the ease and frequency of formation of cyclic silicic polymers at low temperatures. The limits of concentration of dissolved silica in aqueous solutions at 298 K and the importance of supersaturation on geological systems have been reviewed by many workers (Iler 1979; Crerar et al., 1981; Stumm & Morgan 1981; Dove 1995). Silicon-29 NMR studies have reported a wide range of
dissolved silicic monomeric and polymeric anions in aqueous silica solution (Harris and Newman, 1977; Glasser and Lachowski, 1980a; Harris et al., 1980; Harris et al., 1981; Harris et al., 1984). These silica polymers include chains, rings, rings with side groups, etc (Glasser and Lachowski, 1980b). Even though these NMR studies may not be directly applied to geochemical systems because of the high dissolved silica concentrations and high pH values involved, they do indicate the potential to form a variety of dissolved silica species. The rate of formation and nature of silicic polymers is complex and dependent on a number of factors including pH, time, silica concentration and temperature (Harris and Newman, 1977; Iler, 1979; Harris et al., 1980; 1981; Glasser and Lachowski, 1980a; Crerar et al., 1981). All studies on dissolved silicic acid polymers have concluded that their formation is favoured by basic conditions. The existence of an aqueous cyclic six membered ring polymer has not been reported in the literature, though cyclic tetramers have been reported (Harris et al., 1984) and as such, given optimal conditions and time, it would be possible (though rare) to form cyclic hexamers in sufficient concentrations in groundwaters in order to interact with oxidising copper minerals and to form dioptase. Nevertheless, they must form under the same ambient conditions in the supergene zone for dioptase to exist at all!

2.2.5 CHRYSOCOLLA IN THE OXIDE ZONE

Recent exploitation of oxide copper resources in Australia has facilitated an examination of supergene mineral distributions in several orebodies that have been subjected to intense weathering. These include deposits at Goonumbla or Northparkes in NSW (Heithersay et al., 1990; Crane et al., 1998) and several smaller deposits in the Mt. Isa Block in northwest Queensland (Ball, 1908; Carter et al., 1961; Day and Beyer, 1995). The consequences of the intense weathering of these deposits include the
mobilization of silica and subsequent formation of considerable quantities of chrysocolla
and secondary silica in the oxidized zones. Furthermore, all of these deposits are
characterized by an abundance of the secondary copper phosphates libethenite
(Cu$_2$PO$_4$OH) and pseudomalachite (Cu$_5$(PO$_4$)$_3$(OH)$_4$) associated with smaller amounts of
cornetite (Cu$_3$PO$_4$(OH)$_3$) and turquoise (CuAl$_6$(PO$_4$)$_4$(OH)$_8$.4H$_2$O).

Although the secondary mineral distributions in these deposits vary, a number of
recurring paragenetic relationships are evident. The copper carbonates malachite and
azurite are seldom replaced by chrysocolla, nor are the secondary copper phosphates.
Chrysocolla and/or secondary silica frequently envelop copper carbonates and
phosphates, and are therefore the more stable phases in such environments. Repeated
observations of these phenomena across a number of sites has prompted an investigation
into the equilibrium chemistry of these minerals.

Relationships between the secondary copper carbonates and chrysocolla are
comparatively simple and have widespread application to observations of natural
assemblages. Thermodynamic data for the stability field calculations are given in
Appendix 1. Firstly, at CO$_2$ pressures sufficiently high to make azurite stable with respect
to malachite (ca 10$^{-1.35}$; Williams 1990), chrysocolla cannot replace azurite if the $\Delta$G°$_f$
value for Newberg (1967) "aged" chrysocolla (-1218.4 kJ mol$^{-1}$) is used in the
calculations (Figure 2.13). For the following equation,

$$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2(s) + 3\text{H}_4\text{SiO}_4^{\circ}(aq) \rightleftharpoons 3\text{CuSiO}_3.\text{H}_2\text{O}(s) + 4\text{H}_2\text{O}(l) + 2\text{CO}_2(g)$$

azurite                                          chrysocolla

at or above the given pressure there is no achievable activity of H$_4$SiO$_4^{\circ}$(aq) at which
azurite becomes unstable with respect to chrysocolla. However, if the $\Delta$G°$_f$ of crystalline
chrysocolla from the Ray Mine calculated from this study (-1223.2 kJ mol\(^{-1}\)) is adopted instead, there is a slight but significant shift in the stability fields of the mineral phases. This shift produces a small stability region where it is possible for direct replacement of chrysocolla by azurite to occur (Figure 2.13). However, such extreme activities \((H_4SiO_4)^0(aq)\) activity \(> 10^{-3.5}\) and \(CO_2\) partial pressure \(> 10^{-1.35}\) kPa) would rarely be encountered in the natural environment. Thus the remarkable examples of chrysocolla coating azurite at Northparkes (Crane et al., 1998) appear to have formed simply by the later crystallization of chrysocolla on pre-existing azurite. Similar assemblages are found in the Queensland deposits mentioned previously, where azurite occurs near the surface.

However, mention should be made of reports of chrysocolla pseudomorphs after azurite and malachite (see, for example, Thompson, 1980; Bywater, 1984). Such observations are readily explained by reference to Figure 2.13 which shows that while azurite may be replaced directly by chrysocolla under extremely high \(H_4SiO_4\)^0(aq) activities, malachite can be easily transformed to chrysocolla under more realistic environmental conditions, viz:

\[
Cu_2CO_3(OH)_2(s) + 2H_4SiO_4^0(aq) \leftrightarrow 2CuSiO_3.H_2O(s) + 3H_2O(l) + CO_2(g)
\]

malachite               chrysocolla

Furthermore, other conditions exist such that chrysocolla can only form coatings on pre-existing malachite. Thus, reported chrysocolla pseudomorphs after malachite are seen as arising simply from the existence of the appropriate chemical conditions, whereas reported occurrence of chrysocolla pseudomorphs after azurite are in fact more likely to be chrysocolla after malachite after azurite. Many specimens showing the formation of secondary silica and chrysocolla (especially in the upper sections of oxidized zones in the
Figure 2.13  Stability fields for chrysocolla versus malachite and azurite at 298.2 K. The dashed line represents the limit of silicic acid activity in equilibrium with amorphous silica. The black line represents the stability field for Ray mine chrysocolla $\Delta G^\circ_r$ and the pink line represents the stability field for “aged” chrysocolla based on $\Delta G^\circ_r$ calculated by Newberg (1967).
Mt. Isa Block) are known, the intense silicification of these bodies being directly related to the high degree of weathering of the enclosing rocks.

At the Great Australia mine, abundant secondary quartz, chalcedony and chrysocolla occur throughout the oxidized zone of the Main and B Tangye Lodes. In the former, secondary quartz completely enclosing otherwise unaltered malachite, cuprite and native copper crystals was common at depths below 20 m and a completely silicified goethitic gossan was a feature of upper levels of the B Tangye Lode. Secondary silica infiltration of this section of the deposit gave a characteristic brown, cherty material studded with kernels of native copper and cuprite, and occasional chalcocite and digenite, which had been rendered impervious to subsequent attack by aqueous solutions and persisted to within 10 m of the surface.

Chrysocolla-coated malachite has been recovered from the Trafalgar, Warwick Castle, Desolation and Mt. Glorious deposits, and mines grouped around the Blockade mine, near Mt. Isa. Chrysocolla pseudomorphs after malachite are present in these deposits as well, especially at the Trafalgar mine.

Relationships between the secondary copper phosphates and chrysocolla are similar to the above in some respects, but more complex. Figure 2.14A and B shows equilibrium conditions calculated for these species, for pH values between 3 and 7, where $\text{H}_4\text{SiO}_4^{0}(\text{aq})$ and $\text{H}_2\text{PO}_4^{-(\text{aq})}$ are the dominant dissolved silica and phosphate species, respectively for the following equations:

\[
\text{Cu}_2\text{PO}_4(\text{OH})(\text{s}) + 2\text{H}_4\text{SiO}_4^{0}(\text{aq}) \leftrightarrow 2\text{CuSiO}_3.\text{H}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{H}_2\text{PO}_4^{-(\text{aq})} + \text{H}^+(\text{aq})
\]

libethenite \hspace{1cm} \text{chrysocolla}

\[
\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4(\text{s}) + 5\text{H}_4\text{SiO}_4^{0}(\text{aq}) \leftrightarrow 5\text{CuSiO}_3.\text{H}_2\text{O}(\text{s}) + 4\text{H}_2\text{O}(\text{l}) + 2\text{H}_2\text{PO}_4^{-(\text{aq})} + 2\text{H}^+(\text{aq})
\]

pseudomalachite \hspace{1cm} \text{chrysocolla}
\[
\text{Cu}_3\text{PO}_4(\text{OH})_2(\text{s}) + 3\text{H}_4\text{SiO}_4^0(\text{aq}) \leftrightarrow 3\text{CuSiO}_3\cdot\text{H}_2\text{O}(\text{s}) + 3\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}^+(\text{aq})
\]

Cornetite \hspace{1cm} \text{Chrysocolla}

Thermodynamic data for the copper phosphates, based on constants calculated by Magalhães et al. (1986, 1988) are given in Appendix 1. Reference to this data leads to a remarkable conclusion. There is no achievable \(\text{H}_4\text{SiO}_4^0(\text{aq})\) activity when libethenite is the thermodynamically stable secondary copper phosphate, such that chrysocolla can replace libethenite. It must form together with it, when silica concentrations exceed saturation. Thus the phosphate-silicate assemblages from the upper levels of the Northparkes oxidized zones are explained where silica and chrysocolla coat, but do not replace, libethenite. Subsequent dissolution of libethenite with changing solution chemistry has led to the preservation of chrysocolla and secondary silica endomorphs.

Again, by reference to Figures 2.14A and 2.14B, it is possible to explain the occurrence of chrysocolla and secondary silica on pseudomalachite, despite the fact that saturated solutions of silicic acid do approach values which would lead to chemical attack. Phosphate values must fall to levels consistent with the stability of cornetite for chrysocolla to directly replace the copper phosphates. Abundant crystalline libethenite in the outcrop at the Hardway and Warwick Castle deposits further attest to the stability of libethenite over chrysocolla under all naturally achievable chemical conditions.

Many examples of the preservation of pseudomalachite in highly silicified secondary copper ores have been encountered. Chrysocolla and chalcedony coat and embed both pseudomalachite and libethenite in the Main Lode at the Great Australia Mine, and commonly in the Trafalgar deposit.

Other relationships observed in Nature can be attributed to kinetic factors.
Figure 2.14  Stability field diagrams for the secondary copper phosphates \textit{versus} chrysocolla at 298.2 K; A: log activity of H$_2$PO$_4^-$ = -4 and B: log activity of H$_2$PO$_4^-$ = -6. The dashed line represents the limit of silicic acid activity in equilibrium with amorphous silica. The black line represents the stability field for Ray mine chrysocolla $\Delta G^\circ_T$ and the pink line represents the stability field for "aged" chrysocolla based on $\Delta G^\circ_T$ calculated by Newberg (1967).
Rhythmically banded pseudomalachite—chrysocolla crusts from Northparkes are seen as arising from silica interaction with previously mentioned pseudomalachite-malachite assemblages (i.e., replacement of malachite by chrysocolla). The failure to observe pseudomalachite-cornelite transitions can be attributed to the preservation of chemical conditions such that pseudomalachite remains stable, coupled with the fact that compact crusts of pseudomalachite are rather slow to dissolve in aqueous solutions at room temperature. The preservation of pseudomalachite in the upper sections of oxidized ores of the Mt. Isa Block, particularly at Mt. Glorious and Great Australia is also due to this kinetic influence.

2.3 REFERENCES


Hsu, P. C. and Murr, L. E. (1975) A simple kinetic model for sulfuric acid leaching of


and Sons, New York.


CHAPTER THREE

THE LEAD(II) CHROMATE (VI) - LEAD(II) SULFATE(VI) SOLID SOLUTION SERIES UNDER AMBIENT CONDITIONS.

3.0 INTRODUCTION

Normal lead(II) chromate(VI), PbCrO$_4$, has attracted much scientific interest for over two centuries since the discovery of its naturally occurring polymorph, the mineral crocoite (Mellor, 1931; Williams, 1974). Crocoite forms attractive intense red to orange crystals (Figure 3.1a) and synthesised compounds form bright yellow to orange precipitates that have been extensively used as pigments.

Lead(II) chromate(VI) is known to form a number of polymorphs (Jaeger and Germs, 1921; Wagner et al., 1932; Collotti et al., 1959; Knight, 2000). Both the monoclinic (crocoite) and orthorhombic polymorphs can easily be precipitated from aqueous lead(II) and chromate(VI) solutions under ambient conditions. However, the orthorhombic phase is unstable under such conditions and quickly transforms to the monoclinic phase (Wagner et al., 1932; Quittner et al., 1932).

High temperature investigations (greater than 800 K) of both natural and artificial lead(II) chromate(VI) crystals have revealed other phases (Jaeger and Germs, 1921; Pistorius and Pistorius, 1962; Knight, 2000). Jaeger and Germs (1921) investigated phase changes based on observed thermal changes with increasing temperature of both natural and artificial monoclinic lead(II) chromate(IV) and they reported three phases. From room temperature to 980 K, a monoclinic or what they termed an $\alpha$-form was the stable phase. A $\beta$-form was stable between 980 K and 1056 K (the nature of which was unclear).
Figure 3.1a  Crocoite crystals (up to 8 cm) from the Adelaide mine, Dundas, Tasmania (Albert Chapman Collection, Australian Museum, Specimen No. 50680; photograph by David Barnes, courtesy of the NSW Department of Mineral Resources).

Figure 3.1b  Anglesite crystals (up to 5 cm) from the Montepoli, Sardinia (Albert Chapman Collection, Australian Museum, Specimen No. 50338; photograph by Carl Bento, courtesy of the Australian Museum
and a $\gamma$-form was stable between 1056 K (1065 K for crocoite) with a melting point at 1193 K. The transformation at 1056 K showed the greatest thermal change. Jaeger and Germs (1921) also noted that some crocoite specimens showed only one transition at 1056 K. Wagner et al., (1932) suggested that one of these high temperature forms corresponded to a tetragonal polymorph. Powder X-ray diffraction investigations conducted by Pistorius and Pistorius (1962) reported a phase, sampled at 1003 K, that did not correspond to either anglesite, PbSO$_4$ (an orthorhombic structure), nor wulfenite, PbMoO$_4$ (a tetragonal structure). The phase was reported to have been quenchable to room temperature but with degraded crystallinity. A second sample, quenched from 1080 K, also displayed an anomalous X-ray diffraction pattern. This phase did not correspond to a crocoite, anglesite or wulfenite related structure. It was unclear whether this was the $\beta$-phase reported by Jaeger and Germs (1921) or a high temperature decomposition product. Knight (2000), using a crocoite crystal from Dundas, Tasmania, reported a structural transformation from the monoclinic phase (Figure 3.2) to an orthorhombic phase at 1073 K (Figure 3.3). This transformation was found to be reversible in the absence of air. There was no evidence of Jaeger and Germs' intermediate $\beta$-phase between 980 K and 1073 K. Knight suggested that low level impurities in the natural material may suppress the formation of the $\beta$-form. He also proposed that the anomalous patterns published by Pistorius and Pistorius (1962) were not intermediate phases but decomposition products in air.

The crystal structure of monoclinic lead chromate has been well-established by various X-ray investigations (all using crocoite). Early X-ray studies were carried out by Gossner and Mussgnug (1930). Brill (1931) deduced that crocoite belonged to the space group $P2_1/n$ and Von Gliszczyński (1939) showed that crocoite was isomorphous with the monazite structure. These early studies established approximate cell parameters $a = 7.10$, $b = 7.40$, $c = 6.80$ Å and $\beta = 102.72^\circ$ and showed that there were four PbCrO$_4$. 
Figure 3.2  Atomic arrangement chromate tetrahedra in monoclinic lead chromate (crocoite) at 573 K (after Knight, 2000).

Figure 3.3  The crystal structure of high temperature (1073 K) orthorhombic lead chromate with the barite structure (after Knight, 2000). Thermal ellipsoids are shown at 50% probability.
molecules in the unit cell. Brody (1942) investigated the crystal structure of crocoite using Weissenberg data and determined the approximate positions of the lead and chromium atoms within the structure using a Patterson syntheses. An accurate crystal structure of crocoite (including oxygen positions) was proposed independently by Quareni and de Pieri (1964) and Naray-Szabo and Argay (1964) using 2D refinement techniques. However, the nature of the CrO$_4^{2-}$ tetrahedron was different in each structure. Quareni and de Pieri (1964) proposed that the tetrahedron was significantly distorted, whereas Naray-Szabo and Argay (1964) suggested that there was no distortion. Further refinement by Quareni and de Pieri (1965) using a 3D refinement technique proved that the tetrahedron was distorted.

![Diagram](image.png)

**Figure 3.4** The spacial relationship of lead atoms (solid black circles) to chromate tetrahedra (pyramids) in monoclinic crocoite from the 3D refinement by Quareni and de Pieri (1965). The numbers represent atomic distances between lead atoms and oxygen atoms (Å).
From the Quareni and de Pieri (1965) refinement (Figure 3.4) the chromium atoms are surrounded by a distorted tetrahedral arrangement of oxygen atoms with an average Cr-O distance of 1.65Å and the O-Cr-O bond angles ranging from 105.7° to 113.7°. Seven chromate groups surround the lead atom, with Pb-Cr distances from 3.32 to 4.15Å. Ten oxygen atoms bond to lead with Pb-O distances ranging from 2.53 to 3.44 Å. Thermal expansion tensors between 60 K and 1000 K have been reported for the monoclinic phase by Knight (1996, 2000). Major d-spacing and intensities for the monoclinic phase (crocoite) are presented in Table 3.1.

Collotti *et al.* (1959) investigated the structure of orthorhombic lead chromate formed under ambient conditions. Synthesis of the phase was achieved using Pb(NO₃)₂ and K₂CrO₄ solutions at room temperature. Cell parameters were calculated using Lipson’s method from X-ray powder diffraction patterns. Reported structural parameters were \(a = 8.67 \pm 0.03\), \(b = 5.59 \pm 0.01\) and \(c = 7.13 \pm 0.02\) Å. They proposed that the most probable space group for orthorhombic lead (II) chromate (VI) was \(Pnma\) (barite-type structure). This took into account the reported isomorphism that occurs with PbSO₄. The relative positions of the atoms were calculated on a trial and error basis. The average Cr-O distance was calculated as 1.65 Å and the Pb-Cr distance as 3.63 Å. The short Cr-O bondlengths suggest evidence for multiple bonding in CrO₄²⁻. More detailed structural information is lacking on the metastable orthorhombic phase at ambient temperatures. There have been neither single crystal investigations nor recent refinements of the orthorhombic crystal structure at ambient conditions. However, Knight (2000) reported a refined crystal structure using Reitveld methods for an orthorhombic phase (Figure 3.3) derived from the high temperature phase transition of crocoite. Calculated cell parameters were reported as \(a = 8.79861(4)\), \(b = 5.73422(2)\) and \(c = 7.27402(3)\) Å with a unit cell volume of 366.997 Å³. Selected bond lengths of the closest Pb-O bonds ranged from
Table 3.1  
Major $d$-spacing and intensity values for A: monoclinic PbCrO$_4$ (crocoite), B: orthorhombic PbCrO$_4$ and C: orthorhombic PbSO$_4$ (anglesite).

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<td>2.031 (34)</td>
</tr>
<tr>
<td></td>
<td>2.020 (40)</td>
<td>2.252 (25)</td>
<td>2.028 (48)</td>
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<tr>
<td></td>
<td>1.841 (70)</td>
<td>2.243 (10)</td>
<td>1.973 (21)</td>
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<tr>
<td></td>
<td>1.801 (40)</td>
<td>2.090 (25)</td>
<td>1.793 (15)</td>
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<tr>
<td></td>
<td>1.771 (35)</td>
<td>1.978 (20)</td>
<td>1.703 (16)</td>
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<tr>
<td></td>
<td>1.763 (35)</td>
<td>1.967 (14)</td>
<td>1.621 (19)</td>
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<tr>
<td></td>
<td>1.710 (55)</td>
<td>1.847 (25)</td>
<td>1.611 (10)</td>
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2.640(5) to 3.036(5) Å and Cr-O bonds ranged from 1.569(6) to 1.652(4) Å. O-Cr-O bond angles ranged from 107.9(3) to 113.9(4)°. Major d-spacing and intensities for orthorhombic lead chromate are presented in Table 3.1.

Quareni and de Pieri (1965) noted that the spatial arrangements and interatomic distances in the orthorhombic and monoclinic phases of PbCrO₄ were similar. Average distances of the Cr-O bonds of both phases correspond exactly to average values found in crocoite. Quareni and de Pieri (1965) suggested that this was due to multiple bonding in the CrO₄²⁻ ion. They pointed out similarities in coordination of the two structures around a centre of symmetry. The principle difference concerned the orientation of the CrO₄²⁻ tetrahedra. Knight (2000) suggested that these orientations only required a modest displacement and rotation to transform from the monazite-type to the barite-type structure. From observations of the transformation of crocoite at high temperatures Knight (2000) proposed that the increasing tensor expansion and separation of Cr with increasing temperature allowed rotation of the large rigid chromate units into symmetry positions which coincided with the barite structure.

O’Connor and Buchanan (1952) claimed a synthesis of large (5 mm), stable, orthorhombic lead chromate crystals at 348 K though no supporting X-ray analysis was undertaken. The existence of a tetragonal lead chromate had been suggested by Wagner et al., (1932). However there have been no further investigations or reports in the literature regarding this phase.

Crocoite, the naturally occurring monoclinic polymorph, is a rare secondary mineral occurring in oxidised zones of lead orebodies from a few locations around the world (Palache et al., 1951; Williams, 1974). The two most notable locations include Berezov, Russia (where it was first discovered) and the Dundas mining district, western Tasmania, Australia. In the Dundas area, several mines have produced a variety of crystal
habits for more than a century (Lancaster, 1977; Haupt, 1988). The most notable deposit, the Adelaide mine, produced crystalline masses over 45 cm in length with individual crystals up to 15 cm (Haupt, 1988). In the Dundas district, crocoite is associated with a variety of other secondary lead minerals (Pettard, 1896; Haupt, 1988) including normal lead sulfate PbSO₄, anglesite. Recently, a more unusual occurrence of crocoite has been recorded in a coal seam in the Cretaceous Greymouth coalfield in New Zealand (Zhongsheng et al, 2001).

The intense colour of crocoite crystals and the bright yellow powder it produces when crushed has attracted much interest since its discovery in the mid 18th century as a source of yellow pigment. A comprehensive summary of the early history of crocoite is presented by Williams (1974). Early chemical analysis of crocoite proved problematic with consistent chemical results being elusive (Williams, 1974). Vauquelin (1797) demonstrated that crocoite contained the yet undiscovered element chromium. After the discovery of chromium, chemical analysis of crocoite has been remarkably consistent (Table 3.2) from specimen to specimen and from location to location (Liversidge, 1895; Laurent, 1967; Williams, 1974; Southwood and Viljoen, 1986; Knight, 2000). Numerous workers including Liversidge (1895) and Palache (1896) have carried out accurate goniometer measurements of crocoite, and these further attest to the consistency of the material. Lead chromate has significant applications in industry, forming the basis for production of “chrome yellow” pigments, and Mellor (1931) has summarised much of the early work on the synthesis of lead chromate compounds. Synthesis techniques focused on increasing the purity, clarity, consistency and stability of the colour of compounds used as paint pigments. Numerous commercial names have been attributed to the same compound depending on the tone of colour that was achieved. The most commonly
Table 3.2  Selected analytical data\(^a\) (%) for crocoite from various locations.

<table>
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<tr>
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<td>PbO</td>
<td>69.06</td>
<td>67.91</td>
<td>68.50</td>
<td>68.82</td>
<td>66.82</td>
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<tr>
<td>CrO(_3)</td>
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<td>31.73</td>
<td>32.76</td>
<td>31.16</td>
<td>30.99</td>
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<td>Total</td>
<td>100.00</td>
<td>99.64</td>
<td>99.26</td>
<td>99.98</td>
<td>97.81</td>
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<th>6</th>
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<th>9</th>
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<tbody>
<tr>
<td>PbO</td>
<td>68.35</td>
<td>67.48</td>
<td>69.23</td>
</tr>
<tr>
<td>CrO(_3)</td>
<td>30.35</td>
<td>30.60</td>
<td>30.45</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>-</td>
<td>0.30</td>
<td>0.05</td>
</tr>
<tr>
<td>Total</td>
<td>98.70</td>
<td>98.38</td>
<td>99.63</td>
</tr>
</tbody>
</table>

\(^a\)Analyses 2-8 recalculated from Williams (1974) where necessary; 1: theoretical value for lead chromate; 2: Beresov, Russia (Pfaff, 1816); 3: Beresov, Russia (Berzelius, 1818); 4: Beresov, Russia (Baerwald, 1882); 5: Dundas Tasmania (Liversidge, 1895); 6: Nontron, France contains 1.10 % SiO\(_2\) (Laurent et al., 1967); 7: Tochil'naya Gora, Russia (Bushmakin and Kainov, 1978); 8: Argent Mine South Africa (Southwood and Viljoen, 1986); 9: Dundas, Tasmania (Knight, 2000).

encountered names are chrome yellow and lemon chrome (Mellor, 1931; Ryan and Williamson, 1959).

Numerous workers (Mellor, 1931; Clay and Watson, 1948; Ryan and Williamson, 1959) have noted that lead chromate precipitates exhibit different colours under different conditions of formation. These range from pure lemon yellow through dark yellow and orange to a deep orange red. Mellor (1931) listed a number of factors which have been suggested for this diversity of colour, including basicity of formation conditions, hydration, and average grain size. Numerous patents have been taken out on specific procedures to produce certain lead chromate shades. Ryan and Williamson (1959) suggested that variation in the colour is largely due to “aging” of the precipitate (crystal growth). Clay and Watson (1948) observed that the reaction of different soluble lead
compounds (lead(II) nitrate and lead(II) acetate) with both soluble chromate and
dichromate ions often resulted in precipitates with slightly different shades of yellow.
They suggested that differences in colour were related to different crystal habits of
lead(II) chromate.

The stability of the colour of lead chromate precipitates has been commented on
by most workers and has been the focus of research in the paint industry. Many workers
(Mellor, 1931; Clay and Watson, 1948; Ryan and Williamson, 1959) have noticed a
reddening of lead chromate pigments over time, particularly in the initial formation and
washing of precipitates. It has been assumed by most workers that this is the result of an
orthorhombic lead chromate phase transforming to the monoclinic phase (Quittner et al.,
1932; Wagner et al., 1932; Clay and Watson, 1948; Ryan and Williamson, 1959). Clay
and Watson (1948) suggested that orthorhombic lead chromate could be preserved for
several months if the precipitate was left in the presence of the lead-containing mother
liquor and that the transformation only occurred during washing and drying of the
precipitate. Other authors found that the transformation was almost immediate (Ryan and
Williamson, 1959; Wagner et al., 1932). Quittner et al. (1932) pointed out that the lead
salt solution used should be neutral and the synthesis should be carried out at room
temperature to form the orthorhombic modification which forms a bright yellow
precipitate.

Lead(II) chromate is often co-precipitated with other anions, particularly sulfate
and molybdate ions, to produce mixed phases of different colours. These solid solution
phases are also extensively used as pigments. For example, shades of yellow are
produced by mixing sulfate with chromate (Mellor, 1931; Ryan and Williamson, 1959;
Suquet and Launay, 1988). Mixing chromate and molybdate produces orange shades
(Bishop and Hanke, 1961). It has been found that by varying the ratio of other anions to
chromate ions a wide range of coloured compounds can be produced. Numerous patents exist regarding specific mixtures and industrial production of such compounds. Bishop and Hanke (1961) reported synthesizing a mixed lead chromate–molybdate compound, which was tetragonal with a maximum ratio of 6:4 with respect to chromate to molybdate. Increasing amounts of chromate above 60 mol% produced a monoclinic phase.

Normal lead(II) sulfate (PbSO₄) only forms an orthorhombic phase under ambient conditions, and occurs in Nature as the mineral anglesite (Figure 3.1b). Jaeger and Germs (1921) reported a high temperature monoclinic polymorph (transition temperature 1137 K). Anglesite has the barite structure with space group \textit{Pnma} and is isomorphous with orthorhombic lead(II) chromate. The structure of anglesite was first reported by James and Wood (1925) who determined the space group and the fact that there were four PbSO₄ units in the unit cell. A number of refined X-ray single-crystal studies have been published on anglesite and the structurally related minerals celestite (SrSO₄) and barite (BaSO₄) (Sahl, 1963; Hawthorne and Ferguson, 1975; Hill, 1977; Miyake et al., 1978). Most studies have mentioned the difficulty of refining accurately the positions of the oxygen atoms due to the presence of the heavy, strongly absorbing lead atoms. It was found that anglesite, celestite and barite displayed comparable geometries. Lead is 12-coordinated based on bond strength sums (Miyake et al., 1978). Jacobsen et al. (1998) refined the structure of anglesite and presented the parameters \( a = 6.9549(9) \), \( b = 8.4723(11) \) and \( c = 5.3973(8) \) Å with a cell volume of 318.03 Å³. Pb-O bond lengths range from 2.609(7) to 3.271(4) Å and the S–O from 1.460(7) to 1.487(5) Å. Bond angles in the \( \text{SO}_4^{2-} \) tetrahedron range from 107.6(1)° to 112.3(2)°. The tetrahedra are equally distorted in anglesite, celestite and barite and different metal cations do not affect the size or shape of the tetrahedra. Analysis of thermal displacement parameters suggests that the
SO₄²⁻ tetrahedra behave as rigid molecular groups. Major d-spacing and intensities for anglesite are presented in Table 3.1.

Anglesite is a very common secondary mineral derived from the weathering of galena, PbS, and various lead sulfosalts. It is often observed as the first formed mineral during the weathering of lead-bearing orebodies (Palache et al., 1951). Subsequent alteration or replacement of anglesite by other secondary minerals is a reflection of changing groundwater geochemistry associated with a relative lowering of sulfate concentrations away from the centre of oxidation (Williams, 1990).

Various workers have studied the artificial lead chromate-sulfate solid solution series (Jaeger and Germs, 1921; Bădescu, 1977; Chernysheva et al., 1985; Suquet and Launay, 1988). All reported that the chromate end member was monoclinic and the sulfate end member was orthorhombic. However, some workers reported that the system was a complete solid solution series and that increasing sulfate content stabilized the orthorhombic form (Bădescu, 1977). Other workers have suggested that the series is incomplete and that the substitution of sulfate into the monoclinic form is limited (Jaeger and Germs, 1921; Chernysheva et al., 1985).

Jaeger and Germs studied the lead chromate-sulfate binary system using thermal analysis based on phase diagrams. They reported a gap in the system between 30 and 40 mol% SO₄²⁻ and that mixed crystals had transition phases at 1021, 1147 and 1207 K. No attempt has been reported in the literature to further investigate the nature of these transitions and their structures remain unknown. Clay and Watson (1948) reported that the monoclinic solid solution series only exists up to 30 mol% SO₄²⁻ and that between 30 and 90 mol% both a monoclinic and orthorhombic form existed. Ryan and Williamson (1959) suggested that the orthorhombic form in the system is only stable in compounds with 90-100 mol% SO₄²⁻ and that a monoclinic form can accommodate up to 50 r mol%
SO\textsubscript{4}\textsuperscript{2-}. Chernysheva et al. (1985) observed that the monoclinic solid solution series under ambient conditions existed up to 35 mol\% SO\textsubscript{4}\textsuperscript{2-} and the orthorhombic series was continuous between 65 - 100 mol\% SO\textsubscript{4}\textsuperscript{2-}. Between 35-65 mol\% SO\textsubscript{4}\textsuperscript{2-}, a gap existed in the series where both orthorhombic and monoclinic phases were present.

Suquet and Launay (1988) investigated various commercial, synthetic lead chromosulfate pigments of varying sulfate content (between 0 and 50\%). They calculated unit cell parameters by measuring \textit{d}-spacing values from powder X-ray diffraction patterns and refining the parameters using a least-squares method. They reported a consistent decrease in all three cell parameters with increasing sulfate content to 38\% SO\textsubscript{4}\textsuperscript{2-}. A pigment with a sulfate content of 50\% consisted of a monoclinic and an orthorhombic phase. IR measurements on similar pigments in the 1500-200 cm\textsuperscript{-1} range showed that with increasing SO\textsubscript{4}\textsuperscript{2-} content, the emergence of the SO\textsubscript{4}\textsuperscript{2-} \textit{v}\textsubscript{3} and \textit{v}\textsubscript{4} bands became prominent as the CrO\textsubscript{4}\textsuperscript{2-} \textit{v}\textsubscript{3} band decreased in intensity. The increase in the SO\textsubscript{4}\textsuperscript{2-} \textit{v}\textsubscript{4} peak intensity was linear with increasing sulfur content. Suquet and Launay (1988) proposed that observed shifts in frequencies of the SO\textsubscript{4}\textsuperscript{2-} and CrO\textsubscript{4}\textsuperscript{2-} \textit{v}\textsubscript{3} bands with increasing amounts of sulfate in the solid solution series suggested an overall decrease in the Cr-O and S-O bond strengths and hence an increase in solubility.

Some workers (Quittner et al., 1932; Clay and Watson, 1948) have mentioned limited sulfate substitution in the orthorhombic lead chromate phase but that these compounds are also metastable and convert to the stable monoclinic form. There is no indication in the literature as to what extent sulfate substitution occurs in orthorhombic lead chromate. Even though mixed lead chromate - sulfate phases are easily synthesised there have been no reports in the literature of any significant sulfate substitution in crocoite nor chromium substitution in anglesite.
Despite extensive studies on the properties of the lead chromate-lead sulfate system, many conflicting reports remain in the literature concerning the stabilities of orthorhombic versus monoclinic lead chromate, how stabilities are modified by substitution of sulfate in the lattice and the extent of solid solution in the various phases that have been synthesized (Jaeger and Germs, 1921; Ryan and Williamson, 1959; Bădescu, 1977; Chernysheva et al., 1985; Suquet and Launay, 1988; Knight, 2000). There is also confusion concerning the synthesis of orthorhombic lead(II) chromate (Quittner et al., 1932; Wagner et al., 1932; Collotti et al. 1959; Ryan and Williamson, 1959).

Few studies (Wagner et al., 1932 and Collotti et al., 1959) have investigated the nature of orthorhombic lead(II) chromate(VI) under ambient conditions. No thermodynamic data on its stability nor solubility exist in the literature. Nearly all studies on sulfate substitution in lead(II) chromate have only dealt with substitution into the monoclinic phase. No systematic study has been undertaken to establish the extent of the solid solution series limits of the orthorhombic lead(II) chromate(VI)–lead(II) sulfate(VI) series under ambient conditions.

Attention was drawn to this system during a comprehensive study of the chemical mineralogy of lead minerals containing oxyanions, in view of its relationship to the dispersion of Cr(VI) in the natural environment. The lack of recent comprehensive studies of crocoite mineralogy and a recent discovery of yellow anglesite with crocoite in the Red Lead mine, Dundas, Tasmania suggested the need for a study of phase relationships of these two minerals under ambient temperatures. It was hoped this study would establish the limits of solid solution in both orthorhombic and monoclinic cases, determine the relative stabilities of the various species involved, and find the reasons underlying apparent non-reproducible synthesis of some phases.
3.1 METHODS

3.1.1 SYNTHESIS AND IDENTIFICATION OF ORTHORHOMBIC LEAD CHROMATE

A sample of pure orthorhombic lead chromate was synthesized using the method outlined by Collotti et al. (1959). This involved mixing 25 cm$^3$ of 0.1 M aqueous K$_2$CrO$_4$ with 25 cm$^3$ of 0.1 M aqueous Pb(NO$_3$)$_2$ at 298 K. The precipitate was filtered off on a porosity 4 Pyrex glass sinter, washed with water then acetone, sucked dry at the pump and then immediately subjected to X-ray powder diffraction analysis. X-ray powder diffraction measurements were carried out with a Philips PW1925-20 powder diffractometer using CuK$\alpha$ radiation ($\lambda = 1.5418\text{Å}$) and pure silicon as standard. Unit cell parameters were refined using the least-squares program LAPOD (Langford, 1973). Attempts were undertaken to synthesise large orthorhombic crystals using the method outlined by O’Connor and Buchanan (1952).

3.1.2 SYNTHESIS AND IDENTIFICATION OF ORTHORHOMBIC LEAD(II) CHROMATE- LEAD(II) SULFATE SOLID SOLUTION SERIES

A range of solutions with sulfate to chromate ratios varying from 0:100 to 100:0 were made up from aqueous 0.125 M K$_2$CrO$_4$ and 0.125 M K$_2$SO$_4$ solutions mixed in various proportions to a total volume of 50.0 cm$^3$. Then, 50.0 cm$^3$ of aqueous 0.125 M Pb(NO$_3$)$_2$ solution was added to the chromate/sulfate solution with constant stirring. All solutions were maintained at 298 K. After 5 minutes, half the precipitate was filtered off through a porosity 4 pyrex glass sinter, washed with water then acetone, sucked dry at the pump and then immediately subjected to X-ray powder diffraction analysis with a silicon standard. The remaining precipitate was maintained in its mother liquor and heated to 333 K for 24 hours to allow completion of the transformation of the orthorhombic lead.
chromate phase to the monoclinic phase. The precipitate was filtered, washed and dried as above. Similar experiments were performed at 298 K in order to assess the stabilities of the various phases over time and synthesised solids were periodically checked for stability using X-ray powder diffraction methods. Other precipitation experiments involved the use of 0.0625 M potassium dichromate instead of potassium chromate (vide infra).

3.1.3 SOLUBILITY PRODUCT OF ORTHORHOMBIC LEAD CHROMATE

A series of solutions (25.00 cm$^3$) of aqueous 0.0500 M Pb(NO$_3$)$_2$ solution were mixed with 25.00 cm$^3$ of aqueous 0.0505 M K$_2$CrO$_4$, both of which had been thermostatted at 298 K. The mixtures were maintained at temperature for five minutes (metastable equilibrium between orthorhombic lead(II) chromate is quickly established, as evidenced by constant pH readings), and the pH of the supernatant was measured using a Radiometer PHM93 pH meter with a PHC 2401 combination electrode. Aliquots of the supernatants were filtered through a 0.25μ fibreglass filter paper and 25.00 cm$^3$ aliquots were acidified with 5.00 cm$^3$ of aqueous 1M HNO$_3$ to avoid any subsequent precipitation of the more thermodynamically stable monoclinic phase. Lead in solution was determined using a Perkin-Elmer 3030 atomic absorption spectrophotometer with matched standards (PbCrO$_4$ in aqueous HNO$_3$).

3.1.4 CROCOITE SAMPLES

Numerous crocoite samples were collected in situ from a number of mines in the Dundas area. These included the Adelaide, Red Lead, Dundas Extended, Platt, and West Comet mines. The Museum of Victoria and Ralph Bottrill provided the samples of chromian anglesite used in this study. Samples of crocoite from the Happy Jack mine
were provided by the Western Australian Museum. Crocoite specimens from Callenberg, Germany came from the author's collection. Crocoite from Luzon Philippines was obtained from Professor Laurie Lawrence, Sydney.

3.1.5 ELECTRON MICROPROBE ANALYSIS

Polished sections of selected crocoite and anglesite samples were initially inspected by reflected light microscopy. Samples were then carbon coated and analyzed using a JEOL JXA-8600 electron microprobe, controlled by JEOL software, with a beam current of 20 kV. Three wavelength dispersive spectrometers and an energy dispersive spectrometer controlled by Moran Scientific software were employed for the analyses. Analyses were calibrated against pure arsenic, chromium and copper metal, apatite and galena standards.

3.1.6 RAMAN MICROPROBE SPECTROSCOPY

No special sample preparation was required for Raman microprobe spectroscopy, though some samples were sectioned, embedded in resin and polished. The samples were orientated on the stage of an Olympus BHSM microscope equipped with 10x, 20x, and 50x objectives, being part of a Renishaw 1000 Raman microscope system which included a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm), at a resolution of 2 cm\(^{-1}\) in the range between 100 and 4000 cm\(^{-1}\). Repeated acquisition using the highest magnification were accumulated to improve signal to noise ratio in the spectra. The spectra were calibrated using a 520.5 cm\(^{-1}\) line of a silicon wafer.
3.2 RESULTS AND DISCUSSION

3.2.1 SYNTHESIS OF PURE ORTHORHOMBIC AND MONOCLINIC LEAD CHROMATE

The powder X-ray diffraction pattern of freshly precipitated pure orthorhombic lead chromate (Figure 3.5B) gave refined cell parameters of $a = 8.687 \pm 0.001$, $b = 5.591 \pm 0.001$, $c = 7.113 \pm 0.001$ Å and a cell volume of $345.5 \pm 0.1$ Å$^3$. These values are in excellent agreement within experimental error of those reported by Collotti et al. (1959). The parameters for orthorhombic lead chromate precipitate are different from the high temperature orthorhombic transformation reported by Knight (2000). This may be due to the thermal expansion of the orthorhombic phase at high temperatures. However, though both have the same structure ($Pnma$) the relationship of the two is unclear, as the high temperature orthorhombic phase was unstable below 1068 K and completely transformed back the monoclinic phase at room temperature.

As expected, orthorhombic lead chromate is unstable under ambient conditions. The transformation of the orthorhombic form to the monoclinic form occurred rapidly. Parameters for the monoclinic phase are $a = 7.120 \pm 0.001$, $b = 7.431 \pm 0.001$, $c = 6.789 \pm 0.001$ Å and $\beta = 102.6 \pm 0.1^\circ$. The cell volume was $351.1 \pm 0.1$ Å$^3$. This is in excellent agreement with previously published data (Williams, 1974; Effenberger and Pertlik, 1986; Knight, 2000).

The transformation was always associated with a darkening in colour of the precipitate from a bright lemon yellow to a more yellow orange colour typical of monoclinic lead chromate and consistent with previous observations (Ryan and Williamson, 1959). The associated X-ray pattern of precipitates that were allowed to stand showed a mixed orthorhombic and monoclinic pattern. The refined cell parameters of monoclinic lead chromate were also identical within experimental error to previous
Figure 3.5  Powder X-ray diffraction traces for A: pure orthorhombic PbSO₄ (anglesite); B: pure orthorhombic PbCrO₄; C: the single orthorhombic phase formed when Cr:S equals 8:2; D: the two orthorhombic phases formed when Cr:S equals 6:4.
reported values.

This phase change was found to be faster if the solid was left in contact with the original mother liquor, with complete transformation occurring in a few hours. This is contrary to results reported by Clay and Watson (1948) who stated that the orthorhombic phase could be preserved for several months in contact with the mother liquor. If the reaction mixture was heated the transformation occurred within minutes. Also, the addition of acid to either the precipitate or mother liquor accelerated the transformation. However, if the precipitate was immediately filtered the resulting solid was somewhat more stable if kept dry, but transformation to the thermodynamically stable monoclinic modification still occurred over a few weeks under ambient conditions, and faster at higher temperatures. The slow transformation to the monoclinic phase was indicated by a gradual reddening of the precipitate. All synthetic monoclinic lead chromates have a distinctive yellow-orange colour. Precipitates that had been left in the mother liquor and heated for 24 hours were slightly darker (more red in colour) than precipitates which were filtered immediately after formation. This suggests that the darker the colour of the precipitate the larger the average crystal size. Once monoclinic precipitates were completely dry there was no further darkening of the colour.

As noted before, the transformation is acid-catalyzed. In experiments where dichromate was substituted for chromate ions in the synthesis, no orthorhombic lead chromate was observed in the powder X-ray trace. It was observed that, during the mixing and washing of the initial precipitate formed using dichromate, the solid was bright yellow, but quickly changed to the more orange yellow colour typical of the monoclinic phase. There was no further change in the precipitate colour regardless of when it was filtered or dried. Acid in this style of synthesis is generated during the reaction according to the following equation.
$2\text{Pb}^{2+}(aq) + \text{Cr}_2\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(l) \leftrightarrow 2\text{PbCrO}_4(s) + 2\text{H}^+(aq)$

These observations reconcile conflicting results in the literature concerning the synthesis of orthorhombic versus monoclinic lead chromate (Collotti et al., 1959; Quittner et al., 1932; Ryan and Williamson, 1959; Wagner et al., 1932). Most early workers did not recognize the effects of the acid catalysis and that source of chromate ions (chromate versus dichromate) was critical in slowing the transformation. Quittner et al. (1932) however, pointed out that in order to obtain the orthorhombic modification the lead salt solution used should be neutral, the synthesis should be carried out at room temperature and the product should be dried in vacuo below 25°C. Chromium(VI) is extensively hydrolysed in water (Baes and Mesmer, 1979). Under basic conditions the only significant aqueous species is CrO$_4^{2-}$. In acidic media HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ are the major Cr(VI) species present. When Cr (VI) concentrations are greater than 0.01 M, Cr$_2$O$_7^{2-}$ dominates.

Crystals that were synthesised using the method outlined by O’Connor and Buchanan (1952) did form deep red 5 mm equant crystals similar to the crystal form reported. Powder XRD showed these crystals, as expected, to be monoclinic. This was, as previously pointed out, due to the synthesis involving dichromate ions over an extended period of time. The suggestion by O’Connor and Buchanan (1952) that the crystals were orthorhombic was based solely on external crystal forms. In this study, crystals that formed in a sulfate/dichromate solution formed light-orange elongated prisms, and X-ray analysis showed that the crystals were also monoclinic and contained no sulfate (due to the excess of the chromate ions that precipitate out the more insoluble lead chromate). These crystals show a similar (if somewhat simpler) habit to natural crystals described from Dundas, Tasmania (Haupt, 1988) and elsewhere. There is some suggestion that small amounts of sulfate in solution may influence external crystal morphology. Variation of crocoite habits (particularly in the various Dundas mines) may reflect
variations in sulfate concentrations in the groundwater at time of formation. No method was found to synthesize large orthorhombic crystals under ambient conditions. When excess chromate rather than dichromate was used only large monoclinic crystals were formed.

3.2.2 SYNTHESIS OF ORTHORHOMBIC LEAD CHROMATE-LEAD SULFATE SERIES

Precipitates that formed from solutions with up to 20% sulfate in the initial mix had similar X-ray powder traces to that of pure orthorhombic lead chromate except for slight shifts in corresponding peak positions (Figure 3.5C). The greater the sulfate substitution the greater the peak shift. Increasing sulfate substitution in the lattice slowed the transformation to the monoclinic phase, however none of the compounds synthesized were thermodynamically stable at 298 K and no method was found to indefinitely stabilize any chromate dominant orthorhombic form. Once again synthesis using the dichromate ion accelerated the transformation so that no evidence of orthorhombic compounds was present in the X-ray traces.

However, solids initially formed from mixtures containing from 20 to 90 mol% sulfate contained a mixture of two orthorhombic phases. Powder X-ray traces showed a combination of both the orthorhombic chromate-rich lead chromate trace and the sulfate-rich orthorhombic lead sulfate trace. This is highlighted in the 60 mol% initial sulfate mix trace (Figure 3.5D). Emergence and disappearance of various peaks is proportional to the varying ratio of sulfate to chromate in the initial synthesis.

The pure lead sulfate that was prepared was white and the X-ray pattern was identical to anglesite (orthorhombic lead sulfate; Figure 3.5A). The refined unit cell parameters were calculated as $a = 8.483 \pm 0.002$, $b = 5.400 \pm 0.002$, $c = 6.962 \pm 0.002$ Å.
and a cell volume of 318.9 Å³, in good agreement with those reported by previous workers (Miyake et al., 1978; Jacobsen et al., 1998). Solids formed from 90-100 mol% initial sulfate mixes gave similar powder X-ray traces to anglesite with only very slight shifts in peak positions. These solids are stable indefinitely at 298 K. There is no monoclinic lead sulfate known to be stable at ambient temperatures. Only pure lead sulfate was white and even low concentrations of chromate in the compound gave a distinct yellow colouration.

3.2.3 SYNTHESIS OF MONOCLINIC LEAD CHROMATE- LEAD SULFATE SOLID SOLUTION SERIES

Given that all orthorhombic chromate-rich solid solution phases are thermodynamically unstable at room temperatures, the extent of solid solution in monoclinic chromate-rich analogues are not the same. Monoclinic lead chromate (crocoite) can accommodate somewhat more sulfate. X-ray traces of aged precipitates formed with up to 40 mol% sulfate in the initial mix were similar to that of pure monoclinic lead chromate (Figure 3.6A), with increasing shifts in peak positions being observed with increasing sulfate content. X-ray traces of aged precipitates formed from mixtures with initial sulfate contents of between 40 and 90 mol% showed a trace comprised of both monoclinic lead chromate and orthorhombic lead sulfate phases. Relative peak positions for the latter did not change to any significant extent with changing initial composition though relative peak heights did change in proportion to the total amount of sulfate present.

3.2.4 LIMITS OF THE TWO SOLID SOLUTION SERIES

Both orthorhombic and monoclinic solid solution series obey Vegard’s Law and
Figure 3.6  Powder X-ray diffraction traces for A: pure monoclinic PbCrO₄ (crocoite); B: the thermodynamically stable, single monoclinic phase formed when Cr:S equals 6:4; C: the thermodynamically stable mixture of monoclinic and orthorhombic phases formed when Cr:S equals 4:6.
Figure 3.7  Unit cell dimensions refined using LAPOD (Langford, 1973), of the monoclinic phase formed in the reaction of lead(II) sulfate and chromate ions at 298K. The approximate upper limit of sulfate substitution in crocoite is indicated by dashed lines. Maximum standard error from the least squares analyses are 0.002, 0.001 and 0.002 for $a$, $b$ and $c$, respectively,
limits in each can be conveniently defined using X-ray powder diffraction methods. For the monoclinic series, the presence of two phases in mixtures containing greater than 40 mol% sulfate, a monoclinic sulfatian lead chromate and an orthorhombic chromian lead sulfate, indicates that the monoclinic solid solution series at room temperature only exists between 0-40 mol% sulfate. Unit cell dimensions of aged monoclinic precipitates formed from 0-40 mol% initial sulfate mixtures all decrease in relation to the amount of sulfate in the structure (Figure 3.7). When more than 40 mol% sulfate is present in the initial reaction mixture there is no appreciable change in any of the unit cell dimensions coinciding with the thermodynamically stable two-phase region. These results are in good agreement with previous results of Suquet and Launay (1988), who report that the extent of solid solution is about 38 mol%, and the lower limits of the series proposed by Jaeger and Germs (1921) and Chernysheva et al., (1985), of 35 mol% and 40 mol% respectively. The limit of substitution of chromate in (orthorhombic) anglesite corresponds to about 10 mol%.

A plot of the unit cell dimensions of the dominant orthorhombic phase versus the composition of the initial mixture, when metastable, orthorhombic sulfatian lead chromate is formed is shown in Figure 3.8. The extent of the miscibility gap divisions between the one and two phases on the diagram have been taken from the observed one- and two-phase limits indicated on the X-ray traces. Absence of data at 40 mol% sulfate is due to the difficulty of calculating accurate unit cell parameters because of the presence of two phases in comparable proportions. Peak overlap made resolution of individual lines in many cases too difficult to resolve. Between 0 and 20 mol% sulfate in the one-phase region there is a definite and smooth proportional decrease in all three unit cell parameters as more sulfate is accommodated in the lattice. This decrease stops abruptly at the boundary of the one- and two-phase regions. Between 20-30 mol% sulfate there is no
Figure 3.8 Unit cell dimensions refined using LAPOD (Langford, 1973), of the dominant orthorhombic phases formed in the reaction of lead(II) sulfate and chromate ions at 298K. The two phase region lies between the dashed lines. Maximum standard error from the least squares analyses are 0.002, 0.001 and 0.002 for $a$, $b$ and $c$, respectively.
appreciable change in unit cell dimensions of the dominant orthorhombic phase
(orthorhombic sulfatian lead chromate). In the extended two-phase region, where data
can be conveniently measured, the composition of the solid remains the same. At 50
mol% total sulfate, the dominant orthorhombic phase corresponds closely with chromate-
saturated orthorhombic lead sulfate, anglesite, which can accommodate about 10 mol% chromate in the lattice at 298 K. Minor variations in unit cell parameters obey Vegard’s
Law from 90-100 mol% PbSO₄.

3.2.5 STABILITY OF ORTHORHOMBIC LEAD(II) CHROMATE AND ITS
CONGENERS

After the initial precipitation of the bright yellow orthorhombic lead chromate the
metastable equilibrium between orthorhombic lead(II) chromate is quickly established.
This was evident by constant pH readings in all samples. The precipitate maintained its
bright yellow colour during the temperature equilibration at 298 K.

Total lead concentrations for the experiments measured from the AAS are
presented in Table 3.3 and total chromium content was calculated from stoichiometric
relationships, since chromate was in slight excess in all experiments. Pb(II) and Cr(VI)
speciation was calculated using the program COMICS (Perrin and Sayce, 1967) which
gives free concentrations of Pb²⁺(aq) and CrO₄²⁻(aq), together with those of all other
species taken into account. Stability constant data for HCrO₄⁻, H₂CrO₄⁰, Cr₂O₇²⁻, PbOH⁺,
Pb(OH)₂⁰, Pb(OH)₃⁻, Pb(OH)₄²⁻, Pb₂OH³⁺, Pb₄(OH)₄⁴⁺ and Pb₆(OH)₈⁴⁺ (presented in
Appendix 1) were taken from the compilation of Smith and Martell (1976). A stability
constant for PbCrO₄⁰ was estimated to be equal to that of PbSO₄⁰ (Smith and Martell,
1976); speciation calculations showed that this was not a significant species in solution
under the experimental conditions employed. Data generated by COMICS (presented in

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Appendix 3) was used in turn to calculate ionic strengths of equilibrated solutions, and thus to estimate ionic activity coefficients using the same method that was used to calculate species concentrations for the stability of chrysocolla (see Section 2.2.4). Again all neutral species were assumed to have activity coefficients equal to unity.

Based on the following equation,

$$\text{PbCrO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$$

solubility data for orthorhombic lead chromate are given in Table 3.3. At 298.2 K, the solubility product is equal to $10^{-10.71(12)}$.

This value can be used in turn to derive the standard free energy of reaction (see Section 2.3.4.3 for the method) and the standard free energy formation of the compound.

### Table 3.3
Equilibrium data$^a$ for the solubility of orthorhombic lead(II) sulfate at 298.2 K.

<table>
<thead>
<tr>
<th>$[\text{Pb}^{2+}]_t$</th>
<th>$[\text{Pb}^{2+}]_e$</th>
<th>$[\text{CrO}_4^{2-}]_t$</th>
<th>$[\text{CrO}_4^{2-}]_e$</th>
<th>pH$^b$</th>
<th>I$^c$</th>
<th>$\log \delta^{2+}$</th>
<th>$\log K^d$</th>
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<tbody>
<tr>
<td>$3.50 \times 10^{-6}$</td>
<td>$3.32 \times 10^{-6}$</td>
<td>$4.84 \times 10^{-4}$</td>
<td>$7.57 \times 10^{-5}$</td>
<td>5.79</td>
<td>0.101</td>
<td>-0.43</td>
<td>-10.52</td>
</tr>
<tr>
<td>$2.82 \times 10^{-6}$</td>
<td>$2.69 \times 10^{-6}$</td>
<td>$4.83 \times 10^{-4}$</td>
<td>$6.98 \times 10^{-5}$</td>
<td>5.75</td>
<td>0.101</td>
<td>-0.43</td>
<td>-10.65</td>
</tr>
<tr>
<td>$3.79 \times 10^{-6}$</td>
<td>$3.68 \times 10^{-6}$</td>
<td>$4.84 \times 10^{-4}$</td>
<td>$4.38 \times 10^{-5}$</td>
<td>5.52</td>
<td>0.101</td>
<td>-0.43</td>
<td>-10.72</td>
</tr>
<tr>
<td>$4.41 \times 10^{-6}$</td>
<td>$4.33 \times 10^{-6}$</td>
<td>$4.84 \times 10^{-4}$</td>
<td>$2.86 \times 10^{-5}$</td>
<td>5.32</td>
<td>0.101</td>
<td>-0.43</td>
<td>-10.83</td>
</tr>
<tr>
<td>$2.24 \times 10^{-6}$</td>
<td>$2.15 \times 10^{-6}$</td>
<td>$4.82 \times 10^{-4}$</td>
<td>$5.71 \times 10^{-5}$</td>
<td>5.65</td>
<td>0.101</td>
<td>-0.43</td>
<td>-10.83</td>
</tr>
<tr>
<td>$2.13 \times 10^{-6}$</td>
<td>$2.03 \times 10^{-6}$</td>
<td>$4.82 \times 10^{-4}$</td>
<td>$6.31 \times 10^{-5}$</td>
<td>5.70</td>
<td>0.101</td>
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<tr>
<td>$3.18 \times 10^{-6}$</td>
<td>$3.01 \times 10^{-6}$</td>
<td>$4.90 \times 10^{-4}$</td>
<td>$7.13 \times 10^{-5}$</td>
<td>5.79</td>
<td>0.101</td>
<td>-0.43</td>
<td>-10.59</td>
</tr>
<tr>
<td>average $-10.71(12)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

$^a$Concentrations are given in molar units; subscripts t and e refer to total and free ion concentrations, respectively.

$^b$At metastable equilibrium. $^c$Ionic strength. $^d$For the reaction PbCrO₄(s) ⇌ Pb²⁺(aq) + CrO₄²⁻(aq).
The $\Delta G^\circ_{\text{reaction}}$ at 298.2K was calculated as $61.2 \pm 0.6$ kJ mol$^{-1}$ and $\Delta G^\circ_f$(PbCrO$_4$(s),orthorhombic, 298.2K) = $-813.0 \pm 0.9$ kJ mol$^{-1}$. Values for $\Delta G^\circ_f$ for Pb$^{2+}$(aq) and CrO$_4^{2-}$(aq) (presented in Appendix 1) were taken from Robie and Hemingway (1995) and Dellien et al. (1976), respectively. Thus, at this temperature, the monoclinic phase is more stable than the orthorhombic dimorph by some 11 kJ mol$^{-1}$. Since the orthorhombic to monoclinic lead chromate transformation is quite fast at ambient temperatures, it is unlikely that the former phase would be detected in Nature.

While it is acknowledged that neither of the solid solution series should be viewed as behaving ideally, it is worth reflecting on the formation of the solid solution series, given that the solubility product of anglesite at 298.2 K is $10^{-7.79}$ (Smith and Martell, 1976). If the effects of solid state and solution species’ activity coefficients are set aside, substitution of around 1 mol% sulfate in crocoite and orthorhombic lead chromate when Pb$^{2+}$(aq) concentrations are low compared to the anions, would require activity ratios $a$(SO$_4^{2-})/a$(CrO$_4^{2-}$) of around 7500 and 10, respectively (and the absence of other anions that would compete for lead). In other words, unless the activity of Pb$^{2+}$(aq) is equal to or greater than that of chromate, and sulfate is available, sulfate substitution in crocoite will be rarely observed. With respect to chromate substitution in anglesite, this would only be observed when restricted amounts of chromate are available compared to sulfate and lead ions; the differences in solubility products of the sulfate and the two chromates are simply too great. However, if conditions are optimal, the solid solution series might be found in appropriate, albeit rare, circumstances.

3.2.6 ANALYSIS OF CROCOITE AND CHROMIUM-BEARING ANGLESITE

Analyses of crocoite (Table 3.2) since Pfaff (1816) from different locations are remarkably consistent from specimen to specimen with compositions being close to the
theoretical value (ranging from 66-69 wt% PbO and 30-31 wt% CrO₃. There is no record in the literature of any substantial substitution of crocoite by other ions. Small amounts of impurities usually total less than 1%. Impurities reported include Si, Cu, As, P, Ca, Ag, Sb, Mo and W. Anglesite, associated with weathered galena from the Red Lead mine, Dundas, Tasmania, is distinctly yellow and contains 0.2-0.4% CrO₃. The analyses are listed in Table 3.4, together with similar data for crocoite associated with and in some cases in contact with the anglesite. In addition, traces of Ca, Cu and phosphate are present. While these chromate contents fall far short of the maximum that may substitute in the anglesite the observation of chromate substituted anglesite, made here for the first time, is significant. As far as sulfate substitution in crocoite is concerned, Williams (1974) makes no mention of sulfate in any reported analyses of crocoite. Analyses (Table 3.4) of crocoite adjacent to the chromate-substituted anglesite from the Red Lead mine failed to detect any sulfur and this is in accord with the predictions based on thermodynamic data in section 3.2.4, when sufficient chromate is available to satisfy all anionic sites. Very minor amounts of sulfate in the crocoite lattice have been reported in the literature (Bushmakin and Kainov, 1978; Southwood and Viljoen, 1986; Knight, 2000). Bushmakin and Kainov (1978) reported crocoite from the Tochil’naya Gora deposit in the Central Urals contained up to 0.3% sulfate. It is also interesting to note that the reported c axis for the crocoite is significantly shorter than for other crocoites (6.74 Å versus 6.79-6.80 Å for most crocoites). They reported that it was associated with anglesite and other secondary minerals. However no analysis of the anglesite was reported. Southwood and Viljoen (1986) reported crocoite associated with vauquelinite from the Argent mine, Republic of South Africa. From an average of 10 analyses it was found that the crocoite contained 0.05% SO₂ (sic). No anglesite was recorded from this deposit. Knight (2000) reported an average of 0.17% SO₃ (from 50 analyses of a sample from Dundas used in high
Table 3.4  Analytical data (%) for Cr-bearing anglesite and adjacent crocoite, Red Lead mine, Dundas, Tasmania.

<table>
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<th></th>
<th>1(^a)</th>
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<td>PbO</td>
<td>72.59</td>
<td>72.94</td>
<td>72.36</td>
<td>72.66</td>
<td>72.26</td>
<td>72.42</td>
<td>73.60</td>
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<tr>
<td>CaO</td>
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<td></td>
<td></td>
<td></td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>0.02</td>
<td></td>
<td>tr(^b)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CrO(_3)</td>
<td>0.21</td>
<td>0.27</td>
<td>0.26</td>
<td>0.23</td>
<td>0.30</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
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<td></td>
<td></td>
<td></td>
<td>0.01</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>As(_2)O(_5)</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>99.60</td>
<td>99.90</td>
<td>98.89</td>
<td>99.05</td>
<td>99.31</td>
<td>99.53</td>
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</table>

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<tr>
<td>PbO</td>
<td>69.09</td>
<td>69.69</td>
<td>69.49</td>
<td>69.05</td>
<td>69.73</td>
<td>69.09</td>
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<td>CaO</td>
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</tr>
<tr>
<td>CuO</td>
<td>0.01</td>
<td></td>
<td></td>
<td>0.03</td>
<td>0.01</td>
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</tr>
<tr>
<td>CrO(_3)</td>
<td>30.24</td>
<td>29.44</td>
<td>30.30</td>
<td>29.99</td>
<td>29.94</td>
<td>30.24</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
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<td>0.01</td>
<td></td>
<td>tr</td>
<td>0.02</td>
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</tr>
<tr>
<td>As(_2)O(_5)</td>
<td>0.02</td>
<td></td>
<td>0.03</td>
<td></td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Total</td>
<td>99.36</td>
<td>99.15</td>
<td>99.82</td>
<td>99.04</td>
<td>99.73</td>
<td>99.36</td>
</tr>
</tbody>
</table>

\(^a\)-6: chromian anglesite, Red Lead mine, Dundas, Tasmania; 7: PbSO\(_4\); 8-13: crocoite, adjacent to chromian anglesite, Red Lead mine, Dundas, Tasmania; 14: PbCrO\(_4\). \(^b\)Trace analyses are quoted to two decimal places to indicate the trace nature of substitution of all foreign species in the crocoite and anglesite lattices, save for chromate in the latter lattice.
temperature phase work) but no other details of the sample were reported. A search of material adjacent to oxidizing galena from crocoite deposits may provide examples of more significant sulfate substitution.

3.2.7 RAMAN SPECTROSCOPY OF NATURALLY OCCURRING CROCOITE AND CHROMIUM ANGLESITE.

3.2.7.1 Raman spectroscopy of naturally occurring crocoite

Raman spectroscopy is proving to be a useful tool in the study of minerals and geochemical systems. Griffith (1987) gave an excellent compilation of the literature pertaining to minerals studied using Raman spectroscopy. It was noted that minerals have been studied using both powder and single crystal work.

The Raman spectra of crocoite and artificial lead chromate have been investigated by a number of workers (Scheuermann et al., 1970; Wilkins, 1971). However no studies on different samples from different locations have been undertaken. Wilkins (1971) suggested that the small Cr – O distances in crocoite suggested a substantial amount of multiple-bonding character in the chromate ion which also led to strong Raman interactions. The Cr-O bonds in CrO$_4^{2-}$ tetrahedra involve a substantial degree of π-bonding, and are polarisable, giving rise to strong, well-defined Raman spectra (Griffith, 1987). In aqueous solutions the chromate ion has $T_d$ symmetry. All allowed vibrations ($1A_1 + 1E + 2T_d$) are Raman active (Stammreich et al., 1958).

The Raman spectrum for crocoite as expected gave a strong and diagnostic pattern based on the interactions of the chromate ion (Figure 3.9). Two sub-regions were readily identifiable in the 200-1000 cm$^{-1}$ range, the first between 300-400 cm$^{-1}$ ($v_2$ and $v_4$) and the second 800-900 cm$^{-1}$ ($v_1$ and $v_3$) dominated by an intense peak with a number of shoulders. The 800-900 cm$^{-1}$ ($v_1$ and $v_3$) region is dominated by a large peak centred on
Figure 3.9  Raman spectra of a crocoite crystal from the Adelaide mine, Dundas, Tasmania in different orientations: A: beam parallel to the c axis (note splitting of main peak); B and C: beam perpendicular to the c axis and parallel to the b axis and a axis respectively.
836-839 cm\(^{-1}\). It is made up of a number of smaller peaks that are indicated by the presence of shoulders at the edge of the main peak when the orientation of the crystal is approximately at right angles to the c-axis. When the orientation of crocoite crystal is changed so that the beam is parallel to the c axis, a distinct peak appears at 852 cm\(^{-1}\). The relative intensity of this peak compared to the 838 cm\(^{-1}\) peak increases to maximum relative intensity when the crystal is oriented parallel to the c axis.

The region between 300-400 cm\(^{-1}\) displays 6 distinct peaks at 328-31, 341-343, 349-352, 359-61, 378-79 and 400-402 cm\(^{-1}\). The relative intensities of these peaks particularly at 328, 339, 349 and 359 cm\(^{-1}\) show variation according to the orientation of the crystal (Figure 3.9) with the 359 cm\(^{-1}\) stretch showing the greatest variation with orientation.

Scheuermann et al. (1970) reported Raman spectra for single-crystal and powdered samples of crocoite at 300 and 77 K. Ten bands were observed at 300 K, six in the 300-410 cm\(^{-1}\) (\(v_2\) and \(v_4\)) and four in the 800-900 cm\(^{-1}\) (\(v_1\) and \(v_3\)) regions. However, at 77 K twelve bands were observed in the Raman; six bands in both the 300-410 cm\(^{-1}\) (\(v_2\) and \(v_4\)) and 800-900 cm\(^{-1}\) (\(v_1\) and \(v_3\)) regions, indicated a site symmetry lower than \(T_d\). For a powder pellet sample, the most intense absorption occurred at 358 and 839 cm\(^{-1}\) at 300 K, corresponding to \(E\) and \(A_1\) parentage (for \(T_d\) symmetry). With respect to single-crystal spectra, intensities in the 300-410 cm\(^{-1}\) region are dependent on crystal orientation, but the \(E\) transition remains most intense in all cases from 300 to 900 cm\(^{-1}\), in agreement with the current study. Wilkins (1971) only reported 8 bands, 3 bands in the 800 - 900 cm\(^{-1}\) (\(v_1\) and \(v_3\)) region and 5 in the 300 - 410 (\(v_2\) and \(v_4\)) range. It is assumed that the Raman spectrum was measured under ambient conditions and the missing bands were too much overlapped to be measured. However, Wilkins (1971) also included 4 Raman frequencies for \(\text{CrO}_4^{2-}\) in solution, 3 of which match (within in experimental error) the missing Raman bands. Both Wilkins (1971) and Scheuermann et al. (1970) note that because four oxygens in a distorted
tetrahedral configuration surround the chromium ion, all degeneracies are removed. The resulting 9A vibrational modes were all Raman active. The only significant difference between the monoclinic and orthorhombic Raman spectra reported by Scheuermann et al (1971) was a lower scattering efficiency in the orthorhombic phase.

3.2.7.2 Raman spectroscopy of naturally occurring chromium anglesite

Anglesite forms an isomorphous series in the barite group (Pnma) with the lead being twelve coordinated (Griffith 1987). In the 200-1000 cm\(^{-1}\) region, the strongest absorption bands for anglesite from the Red Lead mine Dundas are observed at 437-439 (B parentage), 447-50 (A + B), 601-602 (2A + 2B), 640-643 (2B), and 978-981 (B) cm\(^{-1}\). These values are in excellent agreement with values of 439, 450, 606, 640 and 978 cm\(^{-1}\) reported in the literature (Griffith, 1987). As with crocoite, variations occurred in the relatively peak intensities from grain to grain. It is assumed that this is a reflection of different crystal orientations. Unfortunately the crystals analysed were part of a matrix specimen set in resin and determination of accurate crystal orientation was not possible. The relative intensities of the peaks at 437 and 447 cm\(^{-1}\) showed the greatest variation. At one extreme the 447 cm\(^{-1}\) peak is present only as a shoulder of the 437 cm\(^{-1}\) peak (Figure 3.10A) and at the other extreme the 642 cm\(^{-1}\) band displayed a higher relative intensity (Figure 3.10C). Another variation in spectra is change in intensity of the shoulder at 614-620 cm\(^{-1}\) (Figure 3.10A and C) where both the 608 and 642 cm\(^{-1}\) bands were present as distinct peaks and absence of the shoulder (in Figure 3.10B).

A number of additional low intensity peaks occurring at 348-352, 844-848 and 884 cm\(^{-1}\) are present in all the spectra, which do not relate to anglesite (Figure 3.11A). These peaks suggest the present of another substituted ion in the anglesite. It has been shown that there is some limited chromate-substitution from electron microprobe analyses. It is useful
Figure 3.10 Variation in Raman spectra of Red Lead mine anglesite due to random crystal orientations.
that the main absorption bands for the chromate ion 348 $\nu_2(E)$, 847 $\nu_1(A_1)$ and 884 $\nu_3(F_2)$ cm$^{-1}$ (Nakamoto, 1964) are well separated from other modes arising from anglesite. These most intense chromate absorption bands are in excellent agreement with the additional peaks present in the Raman spectra of anglesite and correlate with the low levels of chromium detected (Cr 0.2%; Figure 3.11). Conversely, the main sulfate absorption bands occur at 450 $\nu_2(E)$, 611 $\nu_3(F_2)$, 983 $\nu_1(A_1)$ cm$^{-1}$ are easily distinguishable from the absorption bands in crocoite. Therefore it would be easy to discern sulfate substitution in crocoite to low levels (0.2%). In line with analytical results, no sulfate could be detected using Raman microprobe methods in crocoite adjacent to chromate-bearing anglesite from the Red Lead mine. The same situation applied to crocoite from the nearby Adelaide mine (Haupt, 1988) and the Happy Jack mine, Comet Vale, Western Australia (Simpson, 1951). The use of Raman microprobe has proven to be a fast, efficient and non-destructive method for screening material involved in solid solutions of the lead chromate-sulfate series.

3.3 CONCLUSIONS

Lead chromate forms two polymorphs under ambient conditions, a monoclinic phase (crocoite) and a metastable orthorhombic phase. No method was found to stabilise the orthorhombic phase. The transformation is acid-catalyzed, a fact not recognized by earlier workers and the observation reconciles the conflicting results in the literature concerning the synthesis of orthorhombic versus monoclinic lead chromate. Optimal conditions to prolong the orthorhombic phase involve the use of chromate rather than dichromate and immediately drying the compound after synthesis. Even under ideal conditions the transformation of orthorhombic to monoclinic lead chromate is quite fast,
Figure 3.11  Comparison of the Raman spectra of A: pure anglesite, from Broken Hill, NSW; B: chromium anglesite from the Red lead mine, Dundas, Tasmania; C: Crocoite from the Red Lead mine, Dundas Tasmania. Note the small extra band in chromian anglesite which corresponds to the main peak in crocoite.
and under ambient temperatures it is unlikely that the former phase would be detected in Nature due to its rapid transformation in the oxide zone environment.

At 298.2 K, the solubility product for orthorhombic lead chromate was calculated as $10^{-10.71(12)}$. $\Delta G^0_f (\text{PbCrO}_4(s), \text{orthorhombic}, 298.2 \text{ K})$ was calculated to be $-813.0 \pm 0.9$ kJ mol$^{-1}$. Both orthorhombic and monoclinic lead (II) chromate form a limited series with sulfate. Both solid solution series obey Vegard’s Law and limits in each can be conveniently defined using X-ray powder diffraction methods. A continuous solid solution series in the orthorhombic series exist between 0-20 mol% and 90-100 mol% $\text{SO}_4^{2-}$. Orthorhombic lead chromosulfate compounds with up to 20 mol% $\text{SO}_4^{2-}$ are metastable under ambient conditions but still transform to the monoclinic phase. The transformation is slower with increasing sulfate content. The monoclinic phase can accommodate up to 40 mol% $\text{SO}_4^{2-}$ into the structure. Between 40-90 mol% a mixed region of monoclinic and orthorhombic phases exists. Orthorhombic solid solution exists between 90–100 mol% $\text{SO}_4^{2-}$. In the oxide zone sulfate substitution in crocoite might be found if the activity of $\text{Pb}^{2+}(\text{aq})$ is equal to or greater than that of chromate and sulfate is available. Unless these conditions are optimal sulfate substitution in crocoite will rarely be observed though very limited substitution has been observed. Chromate substitution in anglesite would only occur when restricted amounts of chromate are available compared to sulfate and lead ions. Limited chromate substitution has been observed in anglesite from the Red Lead mine Dundas Tasmania. Raman spectroscopy was shown to be quite an efficient method for detecting chromate substitution in anglesite, even at the levels that were encountered in the material from the Red Lead mine Dundas Tasmania.
3.4 REFERENCES


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CHAPTER FOUR

THE SOLID SOLUTION PHENOMENON IN THE
WULFENITE (PbMoO$_4$) - STOLZITE (PbWO$_4$) SERIES.

4.0 INTRODUCTION

Lead(II) molybdate(VI) and lead(II) tungstate(VI) have attracted much scientific interest for more than two centuries as the naturally occurring minerals wulfenite, PbMoO$_4$, stolzite, PbWO$_4$ (Figures 1a and b respectively) and raspite, PbWO$_4$. Over the last forty years, the development of methods to synthesise large crystals of lead tungstate and molybdate from melts (particularly using the Czochralski method) has lead to artificial crystals being used as scintillators and acousto-optic light deflectors (Van Uitert et al., 1961; Loiacono et al., 1974; Van Loo, 1975).

Wulfenite occurs in oxidised zones of lead deposits and is commonly associated with other secondary lead minerals such as mimetite, Pb$_5$(AsO$_4$)$_3$Cl, vanadinite, Pb$_5$(VO$_4$)$_3$Cl, cerussite, PbCO$_3$, and anglesite, PbSO$_4$. Stolzite occurs in similar environments, commonly associated with the weathering of scheelite, CaWO$_4$.

Wulfenite is found in numerous locations around the world, some of the most notable being Bleiberg, Austria (its type locality), Tsumeb, Namibia and Los Lamentos, Mexico. However the state of Arizona in the United States of America is unsurpassed for its quantity, quality and variety of wulfenite. It has been recorded at more than 150 different locations in the state (Anthony et al., 1995) including such famous mines as Red Cloud, Tiger and the Glove. The most notable wulfenite localities in Australia are Broken
Figure 4.1a  Yellow wulfenite crystals from the San Francisco mine, Sonora, Mexico. Individual crystals are 1 cm across. Specimen from the Albert Chapman Collection, Australian Museum, Specimen No. 50583. (Photograph by Carl Bento supplied by the Australian Museum, Sydney).

Figure 4.1b  Orange stolzite crystals from the Proprietary mine, Broken Hill, NSW, Australia. Individual crystals are 0.5 cm across. (Albert Chapman Collection, Australian Museum, Specimen No. 549932. Photograph by David Barnes, courtesy of the NSW Department of Mineral Resources).
Hill, New South Wales, Whim Creek, Western Australia and the Christmas Gift North mine, Chillagoe, Queensland, which is the type locality for the tungstenian variety chillagite. Stolzite is much rarer than wulfenite and the most celebrated location is Broken Hill, New South Wales, where it occurs in a wide variety of colours and habits (Birch, 1999). At Broken Hill it is sometimes associated with the even rarer monoclinic PbWO₄ polymorph, raspite. Other notable stolzite locations include Tsumeb, Namibia, the Fat Jack mine, Arizona, the Clara mine, Germany and the Cordillera mine, New South Wales.

Pure lead molybdate and lead tungstate are white when precipitated out of solution and artificial crystals are usually colourless. Wulfenite occurs in an extremely wide range of colours. It is typically brown or yellow, but can range from tan through yellow to orange and deep red (Bideaux, 1990; Roberts et al., 1990). Bideaux also notes other wulfenite colours including colourless, white, grey, green, blue, and black. Stolzite is usually grey or tan through to brown in colour though it has been reported in a variety of other colours including yellow, orange and green (Roberts et al., 1990).

Wulfenite crystals have an extremely wide variety of habits, forms and modifications. However, Williams (1966) noted that five forms are most dominant. These are {001}, {011}, {112}, {013} and {114} and combinations of these five forms account for most habits commonly observed including tabular, prismatic and pyramidal forms. Williams (1966) attempted to correlate common wulfenite forms with Eh and pH conditions based on accessory mineral associations and concluded that the stability of {hkl} forms generally increases while stability of {0kl} forms decreases during normal oxidation. Vesselinov (1995, 1996a, b) synthesised wulfenite from solutions at ambient
conditions and observed patterns of crystal growth and morphology. He suggested that solution chemistry had a strong influence on the growth morphology of wulfenite and noted that chemical complexes in solutions had a significant and very sensitive response on crystal interfaces. He suggested that apart from the pH and Eh of the solutions (Williams, 1966) factors such as excess Pb$^{2+}$ or MoO$_4^{2-}$ ions influenced the development of different crystal morphologies.

Stolzite does not display as great a diversity of habits or forms as wulfenite. It commonly forms steep bipyramidal or thick tabular crystals, but has also been reported as flattened bipyramidal, prismatic and thin tabular crystals (Roberts et al., 1990; Birch, 1999). There have been no reported studies of growth effects and modifications.

Molybdates(VI) and tungstates(VI) with the formula ABO$_4$ (where A = Pb$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Cd$^{2+}$ and B = Mo$^{6+}$ or W$^{6+}$) generally form either the monoclinic wolframite structure or tetragonal scheelite structure (Figure 4.2). However at ambient conditions, CdWO$_4$ forms the wolframite structure, whereas CdMoO$_4$ forms the scheelite structure (Sleight, 1972; Jayaraman et al., 1995c, d; Shieh et al., 1996; Daturi et al., 1997). The tetragonal polymorphs of PbMoO$_4$ and PbWO$_4$ both belong to the scheelite group, space group I4$_1$/a, with four molecules per unit cell. The $d$-spacing, relative intensities and $hk$ assignments for powder X-ray patterns are presented in Table 4.1. The oxygen coordination of the A cation is eight while the W or Mo anion is a slightly distorted (flattened) tetrahedron with four oxygen atoms. Overall the structure maybe regarded as a cubic close packed array of A$^{2+}$ and BO$_4^{2-}$ ions (Sleight, 1972).

The $c$ axis in the scheelite group is always larger for a molybdate compared to the

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Table 4.1  X-ray diffraction $d$-spacings and $hkl$ assignments for wulfenite and stolzite (relative intensities in parentheses).

<table>
<thead>
<tr>
<th>stolzite(^a) PbWO(_4)</th>
<th>wulfenite(^b) PbMoO(_4)</th>
<th>$hkl$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.96 (12)</td>
<td>3.246 (100)</td>
<td>101</td>
</tr>
<tr>
<td>3.248 (100)</td>
<td>3.244 (100)</td>
<td>112</td>
</tr>
<tr>
<td>3.012 (20)</td>
<td>3.028 (20)</td>
<td>004</td>
</tr>
<tr>
<td>2.732 (30)</td>
<td>2.718 (25)</td>
<td>200</td>
</tr>
<tr>
<td>2.395 (2)</td>
<td>2.383 (8)</td>
<td>211</td>
</tr>
<tr>
<td>2.376 (2)</td>
<td></td>
<td>114</td>
</tr>
<tr>
<td>2.205 (2)</td>
<td>2.212 (6)</td>
<td>105</td>
</tr>
<tr>
<td>2.087 (2)</td>
<td>2.082 (8)</td>
<td>213</td>
</tr>
<tr>
<td>2.024 (35)</td>
<td>2.021 (30)</td>
<td>204</td>
</tr>
<tr>
<td>1.931 (16)</td>
<td>1.920 (14)</td>
<td>220</td>
</tr>
<tr>
<td>1.7820 (20)</td>
<td>1.787 (18)</td>
<td>116</td>
</tr>
<tr>
<td>1.6606 (35)</td>
<td></td>
<td>312</td>
</tr>
<tr>
<td>1.653 (25)</td>
<td></td>
<td>303</td>
</tr>
<tr>
<td>1.6258 (16)</td>
<td>1.622 (12)</td>
<td>224</td>
</tr>
<tr>
<td>1.5065 (4)</td>
<td>1.515 (4)</td>
<td>008</td>
</tr>
<tr>
<td>1.496 (2)</td>
<td></td>
<td>321</td>
</tr>
<tr>
<td>1.4175 (2)</td>
<td>1.411 (2)</td>
<td>323</td>
</tr>
<tr>
<td>1.3656 (4)</td>
<td>1.359 (4)</td>
<td>400</td>
</tr>
<tr>
<td>1.3187 (8)</td>
<td>1.3229 (8)</td>
<td>208</td>
</tr>
<tr>
<td>1.3093 (12)</td>
<td>1.3085 (12)</td>
<td>316</td>
</tr>
</tbody>
</table>

\(^a\) International Centre for Diffraction Data card number 19-708. \(^b\) International Centre for Diffraction Data card number 8-475
Figure 4.2 Structural representation of wulfenite (PbMoO₄) a member of the scheelite group.

corresponding tungstate, and the \( a \) axis is always smaller for the molybdate. However the \( c/a \) axis ratio is always larger for molybdates than for corresponding tungstates. A number of authors (Leciejewicz, 1965; Gürman et al., 1971; Sleight, 1972) noted that tetrahedral units in the scheelite structure are essentially the same for tungstates and corresponding molybdates. Sleight (1972) notes that consistent differences of the \( c/a \) ratio in the group were not due to differences in the bond distances (W,Mo-O) or bond angles (O-W,Mo-O) of the tetrahedra. Cell volumes of scheelite group molybdates are slightly smaller than corresponding tungstates. A number of workers (Sleight, 1972, Christofilos et al., 1996; Jayaraman et al., 1995a, b, d; Shieh et al., 1996; Daturi et al., 1997) have shown that many compounds with the scheelite structure transform to the wolframite structure at high pressures but revert back easily when the pressure is lowered.
The first investigation of the crystal structure of PbMoO$_4$ was carried out by Dickinson (1920). He deduced that the structure of wulfenite and scheelite were essentially the same and described the structure as interpenetrating diamond lattices formed by Pb and Mo atoms. Vegard (1925) proposed that scheelite and a number of other compounds form an isomorphous group AXO$_4$ (A= Ca, Pb, Ba; X=Mo, W) which crystallise in the same space group $I4_1/a$. However, the exact positions of the oxygen atoms in the structure were unclear. Sillen and Nylander (1943) revised the oxygen coordinates of a number of molybdates and tungstates in the scheelite group, including PbMoO$_4$ and PbWO$_4$, using stereochemical considerations supported by single-crystal and powder X-ray analyses. They revealed that the XO$_4^2$- tetrahedra were compressed but all X-O bonds were still equal as dictated by the space group symmetry. Araki (1957) determined the crystal structure of a wulfenite crystal from Bolivia using X-ray single crystal oscillation and rotation methods. The positions of the lead and molybdenum atoms were determined using Fourier syntheses and the oxygen positions using difference syntheses. The structure was refined in space group $I4_1/a$ with $Z=4$. Cell parameters were $a = 5.47 \pm 0.01$ and $c = 12.18 \pm 0.02$ Å with a $c/a$ ratio of 2.226. No analysis was given for this wulfenite sample. Araki (1957) confirmed that the molybdenum atom was situated at the centre of a tetrahedron surrounded by four oxygens, whereas eight oxygen atoms surrounded the lead atom. One molybdenum atom and two lead atoms shared each oxygen atom. The Mo-O bond length was given as 1.77 Å; the nearest Pb-O bond lengths were 2.49 and 2.82 Å. The closest O-O distances ranged from 2.88-2.94 Å.

Problems with early crystal structure determinations were that both lead and molybdenum atoms (due to high atomic numbers) dominated the scattering of X-rays.
causing inaccuracies in determining the position of the oxygen atoms. Leciejewicz (1965) provided the first accurate full structure refinement (including the oxygen positions) using neutron diffraction techniques. The advantage of neutron diffraction was that the scattering of neutrons was of the same order for lead, molybdenum and oxygen. Leciejewicz (1965) used a crystal from Los Lamentos and the refined cell parameters in space group \( I4_1/a \) were \( a = 5.4312 \pm 0.0016 \) and \( c = 12.1065 \pm 0.0039 \) Å with a \( c/a \) ratio of 2.229. Leciejewicz (1965) confirmed that the MoO\(_4\)\(^{2-}\) unit was a slightly compressed tetrahedron, and reported a Mo-O bond length of 1.772 Å and O-Mo-O bond angles of 112°50' and 107°40'. He observed that Mo-O bonds were shorter than the sum of the Pauling ionic radii (1.92 Å) after correction for tetrahedral coordination, which indicated the contribution of covalent bonding.

A recent crystal structure determination of a wulfenite from Italy by Lugli et al., (1999) refined the structure in space group \( I4_1/a \) and gave cell parameters very similar to those of Leciejewicz (1965). Cell parameters reported were \( a = 5.434(1) \) and \( c = 12.107(1) \) Å. The \( c/a \) ratio was 2.228 and the cell volume, 357.5 Å\(^3\). They reported full occupancies for the Mo atom in the tetrahedral sites and the Pb atom in the eight coordinate sites. There was no tungsten detected in the chemical analyses. They reported that the Mo-O bond length was 1.769(3) Å and the O-Mo-O bond angles were 107.8° and 112.8(2)°. The closest Pb-O bond lengths were 2.611 and 2.636 Å.

In the last forty years with the advent of reliable methods to manufacture large artificial crystals from melts (particularly using the Czochralski method) and the use of such crystals in industry, a number of studies using such crystals have reported cell parameters for pure lead molybdate. A summary of previously reported cell parameters
Table 4.2  Previously published unit cell parameters for pure natural and artificial PbMoO₄.

<table>
<thead>
<tr>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>V (Å³)</th>
<th>Material studied</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.414</td>
<td>12.079</td>
<td>2.231</td>
<td>354.0</td>
<td>artificial</td>
<td>Vegard and Refsum (1927)</td>
</tr>
<tr>
<td>5.41</td>
<td>12.08</td>
<td>2.23</td>
<td>353.6</td>
<td>natural</td>
<td>Quodling and Cohen (1938)</td>
</tr>
<tr>
<td>5.424</td>
<td>12.076</td>
<td>2.226</td>
<td>355.3</td>
<td>artificial</td>
<td>Sillen and Nylander (1943)</td>
</tr>
<tr>
<td>5.47</td>
<td>12.18</td>
<td>2.227</td>
<td>364.4</td>
<td>natural</td>
<td>Araki (1957)</td>
</tr>
<tr>
<td>5.4312</td>
<td>12.1065</td>
<td>2.230</td>
<td>357.1</td>
<td>natural</td>
<td>Leciejewicz (1965)</td>
</tr>
<tr>
<td>5.41</td>
<td>12.08</td>
<td>2.233</td>
<td>353.6</td>
<td>artificial</td>
<td>Bishop and Hanke (1961)</td>
</tr>
<tr>
<td>5.4355</td>
<td>12.108</td>
<td>2.228</td>
<td>357.7</td>
<td>artificial</td>
<td>Sleight (1972)</td>
</tr>
<tr>
<td>5.435</td>
<td>12.11</td>
<td>2.228</td>
<td>357.7</td>
<td>artificial</td>
<td>PDF No. 8-475*</td>
</tr>
<tr>
<td>5.44</td>
<td>12.13</td>
<td>2.230</td>
<td>359.0</td>
<td>artificial</td>
<td>Oeder et al. (1980)</td>
</tr>
<tr>
<td>5.436</td>
<td>12.10</td>
<td>2.226</td>
<td>357.6</td>
<td>artificial</td>
<td>Laishevtsева et al. (1989)</td>
</tr>
<tr>
<td>5.4268</td>
<td>12.1043</td>
<td>2.230</td>
<td>356.5</td>
<td>artificial</td>
<td>Rehim (1996)</td>
</tr>
<tr>
<td>5.434</td>
<td>12.107</td>
<td>2.228</td>
<td>357.5</td>
<td>natural</td>
<td>Lugli et al. (1999)</td>
</tr>
</tbody>
</table>

*International Centre for Diffraction Data card number 8-475

for lead molybdate are presented in Table 4.2.

Vegard and Refsum (1927) reported a crystal structure analysis for lead tungstate. They showed that the structure was the same as that of scheelite and was isomorphous with that of wulfenite. Sillen and Nylander (1943) revised the oxygen coordinates of lead tungstate, with cell parameters of a = 5.448 and b = 12.016 Å. There were no further reported detailed and reliable crystallographic studies of stolzite until that of Moreiras et al. (1991). They solved the structure of a stolzite from La Tala, Spain in space group I4₁/a, with a = 5.455(1) and c = 12.039(1) Å. Xu et al. (1994) reported the crystal
structure of a stolzite crystal from Hunan province, China, using Reitveld refinement methods of powder data. The unit cell in space group \( I4_1/a \) gave \( a = 5.44503(3) \) and \( c = 12.0495(1) \text{ Å} \). The W-O bond length was 1.7826 Å and the O-W-O bond angles were 123° and 105°. However, despite the apparent accuracies the refinement appears unreliable since the reported bond lengths and angles in the tungstate ion deviate significantly from those previously found. As with lead molybdate a number of studies have reported cell parameters for artificial lead tungstate. A summary of previously reported cell parameters for lead tungstate are presented in Table 4.3.

Substitution of various elements has been reported in both wulfenite and stolzite

<table>
<thead>
<tr>
<th>Table 4.3</th>
<th>Previously published unit cell parameters for pure natural and artificial PbWO₄.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a (\text{Å}) )</td>
<td>( c (\text{Å}) )</td>
</tr>
<tr>
<td>5.455</td>
<td>12.031</td>
</tr>
<tr>
<td>5.442</td>
<td>12.01</td>
</tr>
<tr>
<td>5.44</td>
<td>12.01</td>
</tr>
<tr>
<td>5.448</td>
<td>12.016</td>
</tr>
<tr>
<td>5.4619</td>
<td>12.049</td>
</tr>
<tr>
<td>5.4622</td>
<td>12.048</td>
</tr>
<tr>
<td>5.47</td>
<td>12.05</td>
</tr>
<tr>
<td>5.462</td>
<td>12.05</td>
</tr>
<tr>
<td>5.455</td>
<td>12.039</td>
</tr>
<tr>
<td>5.4450</td>
<td>12.0495</td>
</tr>
</tbody>
</table>

\(^a\) International Centre for Diffraction Data card number 19-708.
(Palache et al., 1951; Williams, 1990). The most common substitution is of tungsten for molybdenum in wulfenite or *vice versa* for stolzite. Often present as a minor impurity, significant concentrations of tungsten in wulfenite (greater than 5 wt%) have been reported from numerous localities (Ullman, 1912; Ahlfeld and Angelelli, 1948; Palache et al., 1951; Clark and Sillitoe, 1970; Arnaudov et al., 1979; Williams, 1990; Livingstone, 1992). Significant amounts of molybdenum have also been reported in stolzite (Faick and Hildebrand, 1958; Scovil and Wagner, 1991; Blaß and Graf, 1999). From these observations it has been suggested that a complete solid solution series may exist between wulfenite and stolzite (Palache et al., 1951; Clark and Sillitoe, 1970). In studies on artificial compounds synthesised at high temperatures, the extent of the series is unclear. Jaeger and Germs (1921) found a miscibility gap at 1355 K between 44 and 59 mol% PbWO₄ and Tkachenko et al. (1981) found a corresponding gap at 1343 K between 20 and 38 mol% PbWO₄. However, other workers have reported evidence for a complete solid solution series (Oeder et al., 1980; Efendiev et al., 1982, 1984; Laishevtseva et al., 1989).

Probably the most famous tungstenian wulfenite specimens reported are from the Christmas Gift North mine, Chillagoe, Queensland. Discovery and initial chemical analyses were reported by Ullman (1912). He described the crystals as varying from lemon yellow to light-orange, some having a brown tinge. His analysis of the material was PbO 53, WO₃ 28 and MoO₃ 17%. He commented that the sample was "not merely a mixture; it is a distinct mineral in well-marked crystals". Ullman (1912) declared it a new mineral, named it "chillagite", and reported its composition as PbO 54.25, WO₃ 28.22 and MoO₃ 17.52%. Smith and Cotton (1912) conducted crystal measurements and
Mingaye (1916) analysed a number of different samples from the same location including pure wulfenite and various "chillagite" samples which varied in WO$_3$ composition from 21.10 to 29.52 wt% and noted that the MoO$_3$ composition varied inversely to the WO$_3$ composition. Duggan (1989) reported that most "chillagite" samples were strongly zoned and contained up to wulfenite$_{40}$stolzite$_{60}$. "Chillagite" has been discredited as a distinct mineral, being termed a tungstenian variety of wulfenite. However the term "chillagite" is still commonly used to describe substituted wulfenite/stolzites with 20-80 mol% tungsten (Clark and Sillitoe, 1970).

Chromium(VI) has been detected as trace amounts (up to 1600 parts per million) in a number of wulfenites (Haberlandt and Schroll, 1949; Mir-Mohammedi, 1977; Edson, 1980; Bideaux, 1990) and has been suggested as being responsible for the bright red colour of these and many other wulfenites, because of the intense red colouration of pure lead chromate crystals (crocoite). Jaeger and Germs (1921) conducted high temperature melt experiments on the PbCrO$_4$-PbMoO$_4$ system and reported up to 44 mol% lead chromate could be substituted into lead molybdate. Bishop and Hanke (1961), in carrying out precipitation experiments at ambient conditions, noted that a single tetragonal form was present up to 60 mol% CrO$_4^-$ with maximum unit cell parameters of $a = 5.27$ and $c = 12.33$ Å. Two phases were present, a tetragonal and a monoclinic phase, at ratios greater than 60 mol% CrO$_4^-$. Other elements that have been reported as substituting in wulfenite include calcium for lead (Williams 1990). A number of analyses have reported the substitution of arsenate, vanadate and phosphate ions for molybdate (Williams, 1990; Bideaux, 1990). Williams (1990) points out that the presence of the AsO$_4^{3-}$, VO$_4^{3-}$ and PO$_4^{3-}$ ions would
produce a charge balance problem which might be accommodated by holes in the lattice or the presence of metallic cations of higher oxidation state. Embrey et al. (1977) reported unusual blue wulfenite from Tsumeb. They suggested that the blue colour was due to partial reduction of Mo$^{6+}$ to Mo$^{5+}$ in the structure. The most unusual report of substitution in wulfenite was that of by Chernikov et al. (1960), who found wulfenites containing up to 11.63 wt% UO$_3$. Williams (1966) found no relation between minor element content and morphology of crystals.

There are few X-ray studies on the structure of substituted wulfenite/stolzites (Table 4.4). Quodling and Cohen (1938) conducted an X-ray analysis on “chillagite” from Chillagoe with a composition of 3PbWO$_4$·5 PbMoO$_4$. They reported two separate cell dimensions based on powder and oscillation photographs. However, they concluded that chillagite had the same structure as wulfenite and stolzite and therefore was not a distinct mineral species. Clark and Sillitoe (1970) reported cell dimensions for some tungstenian wulfenites from Chile (presented in Table 4.4) and they proposed that the $a$ and $c$ axis of intermediate members of the natural PbWO$_4$-PbMoO$_4$ solid solution series displayed a linear relationship. They suggested that the values for “chillagite” quoted by Quodling and Cohen (1938) may be in error.

Single crystal refinements of two tungstenian wulfenites with different compositions were reported by Hibbs, et al. (2000) following the work of Jury (1997). The first, from the San Francisco mine Sonora, Mexico had a composition of wulfenite$_{90}$stolzite$_{10}$. The refinement was in good agreement with previous refinements for pure wulfenite though the $a$ axis showed a slight lengthening. The cell parameters for this wulfenite were $a = 5.436(2)$ and $c=12.068(8)$ Å with $c/a$ 2.220 and $V = 356.6(3)$ Å$^3$. 

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Table 4.4  Previously published unit cell parameters for substituted wulfenites and 'chillagites'.

<table>
<thead>
<tr>
<th>Mol% W</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>V (Å³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>5.44</td>
<td>12.10</td>
<td>2.224</td>
<td>358.1</td>
<td>Ullman (1912)</td>
</tr>
<tr>
<td>38&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.41</td>
<td>12.08</td>
<td>2.23</td>
<td>353.6</td>
<td>Quodling and Cohen (1938)</td>
</tr>
<tr>
<td>38&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.46</td>
<td>12.11</td>
<td>2.22</td>
<td>361.0</td>
<td>Quodling and Cohen (1938)</td>
</tr>
<tr>
<td>&lt;1</td>
<td>5.430</td>
<td>12.074</td>
<td>2.223</td>
<td>356.0</td>
<td>Clark and Sillitoe (1970)</td>
</tr>
<tr>
<td>14</td>
<td>5.428</td>
<td>12.064</td>
<td>2.223</td>
<td>355.4</td>
<td>Clark and Sillitoe (1970)</td>
</tr>
<tr>
<td>23</td>
<td>5.431</td>
<td>12.060</td>
<td>2.222</td>
<td>355.7</td>
<td>Clark and Sillitoe (1970)</td>
</tr>
<tr>
<td>10</td>
<td>5.436</td>
<td>12.068</td>
<td>2.220</td>
<td>356.6</td>
<td>Hibbs &lt;i&gt;et al.&lt;/i&gt; (2000)</td>
</tr>
<tr>
<td>40</td>
<td>5.441</td>
<td>12.068</td>
<td>2.218</td>
<td>357.3</td>
<td>Hibbs &lt;i&gt;et al.&lt;/i&gt; (2000)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Using powder photography;  <sup>b</sup> Using oscillation photography.

The bond lengths reported were (Mo,W)-O 1.775(5) Å, Pb-O 2.627(5) and 2.611(5) Å.

The O-(Mo,W)-O bond angles were 107.8(2)° and 112.9(3)°.

The second wulfenite, from Chillagoe, had a composition of wulfenite<sub>64</sub>stolzite<sub>36</sub>. Precession camera photographs of different reciprocal lattice levels revealed a small but significant number of symmetry-forbidden reflections for the space group <i>I4</i><sub>1</sub>/a. This included 9 symmetry-forbidden reflections in the <i>hk0</i> zone. These symmetry-forbidden reflections were however consistent with the space group <i>I4</i>. The structure was refined in
\( I \bar{4} \) and the reported cell parameters were \( a = 5.441(1) \) and \( c = 12.068(6) \) Å with \( \alpha = 2.220 \) and \( V = 357.3(2) \) Å\(^3\). The bond lengths reported were (Mo,W)-O 1.774(8) and 1.778(8) Å, Pb-O 2.637(9), 2.605(8), 2.633(8) and 2.606(8) Å. The O-(Mo,W)-O bond angles were 107.9(3), 107.8(3),112.8(5) and 112.6(6)°. Hibbs et al. (2000) reported that the refined site occupancy factors showed that Mo/W was not distributed equally over the two crystallographically independent Mo/W positions in space group \( I \bar{4} \). They also noted that despite the increased freedom of the \( I \bar{4} \) space group for the chillagite, the independent geometries of the MO\(_4\) and PbO\(_8\) groups remained equal within experimental error with the \( I4_1/a \) tungstenian wulfenite from Sonora and also with pure wulfenite.

Hemihedrism has been observed in wulfenite and commented on by various authors (Hurlbut, 1955; Kleber, 1956; Williams, 1966; Vessilinov, 1995, 1996b; Hibbs et al., 2000) and has been a problem for mineralogists for a century since most X-ray studies have established wulfenite in the \( I4_1/a \) space group (Dickinson, 1920; Sillen and Nylander, 1943; Leciejewicz, 1965). Vessilinov (1996b) suggested hemihedrism of wulfenite may be a growth-induced phenomenon rather than purely a structural one as suggested by Kleber (1956). He suggested that \( 4/m \) symmetry can be reduced to \( 4 \) if a large enough crystal is orientated with its four-fold axis parallel to the direction of chemical change so that one end is growing in excess-molybdate solutions. In this way the crystal will develop a larger pinacoid face. Hibbs et al. (2000) noted that the unequal Mo/W distributions in tungstenian wulfenite in the \( I \bar{4} \) space group may provide one explanation for hemihedrism in the wulfenite-stolzite group.
Raspite is the other naturally occurring polymorph of lead tungstate and is known only from a very few locations around the world. These include the Proprietary mine, Broken Hill (Birch, 1999) and the Cordillera Mine, Tuena (McColl, 1974), both in New South Wales, Australia, the Clara Mine, Germany (Blaβ and Graf, 1999) and a few locations elsewhere. Interestingly, raspite is nearly always associated with, or in close proximity to, stolzite.

Shaw and Claringbull (1955) were the first to reported a structural analysis for raspite. In their analysis they proposed a structure closely related to stolzite with space group of $P2_1/n$ and cell parameters $a = 5.58$, $b = 5.00$, $c = 13.64 \ \text{Å}$ and $\beta = 107.7^\circ$. Fujita et al. (1977) found subsequently that raspite has a unique structure that is not related to the monoclinic wolframite structure. The space group is $P2_1/a$ and the coordination number of the tungsten atom is six with bond lengths varying from 1.70(2) to 2.17(2) Å. Lead is coordinated to seven oxygen atoms with bond lengths ranging from 2.31(2)-2.85(2) Å. Distorted WO$_6$ octahedra forms kinked chains by edge sharing (Figure 4.3). The cell parameters reported by Fujita et al. (1977) were $a = 13.555(11)$, $b = 4.976(2)$, $c = 5.561(3) \ \text{Å}$ and $\beta = 107.63^\circ$ with $Z = 4$. They commented on the very different coordination geometry of atoms in raspite compared to stolzite, despite the similarity of the unit cell volume.

Raspite has never been prepared artificially; instead all attempts result in the formation of the tetragonal form, stolzite (Chang, 1971). Raspite irreversibly converts to stolzite at 400 °C (Shaw and Claringbull, 1955). Fujita et al. (1977) suggested a topotactic relationship with stolzite and that the irreversible phase transformation of raspite to stolzite may be of a displacive nature, with the displacement of oxygen being
Figure 4.3  Projection of the structure of raspite along the $a$ axis (from Fujita et al., 1977). Atoms between $-\frac{1}{4} < x < \frac{1}{4}$ are depicted. The large open circles represent oxygen, small open circles represent lead, and small solid circles represent tungsten atoms. Independent oxygens are identified by numbers in parenthesis.

small compared to a large displacement of lead atoms. Williams (1990) reported that the various analyses of raspite all closely correspond to the ideal stoichiometric composition. He suggested that this structure may not easily accommodate other cations and the molybdate ion may not be able to form a stable analogous structure. The conditions of formation of raspite and its the exact structural relationship to stolzite still remains unknown.

An artificial, high-pressure monoclinic polymorph of PbWO$_4$ has been reported by Ritcher et al. (1976). It is related to the monoclinic wolframite structure, space group
$P2_1/n$ with $Z=8$ and $a=12.709(5)$, $b=7.048$, $c=7.348(3)$ Å, $\beta=90.57^\circ$. They found that the high pressure form prepared at 32 Kbar was quenchable to normal pressure. It is isomorphous with the high pressure phase BaWO$_4$ II (Kawanda et al., 1974). The structure was described as a two-dimensional network of WO$_6$ octahedra linked by lead atoms with the lead coordinated by nine oxygen atoms. Ritcher et al. (1976) suggested other similar molybdate phases may exist.

Moreau et al. (1996) described a new lead tungstate phase occurring in lead deficient melts with tetragonal symmetry but with space group $P4/nnc$. Its formula was given as Pb$_7$W$_6$O$_{32-x}$ with $x=3.2(8)$ and had unit cell parameters of $a=7.719$ and $c=12.018(2)$ Å. The $a$ axis was found to be $\sqrt{2}$ greater than $a$ in the scheelite structure, and the new structure was hence a derivative of it.

Various synthetic tungstates and molybdates belonging to the scheelite and wolframite structural groups have been studied using Raman spectroscopy. This technique is often used to study the incorporation of a wide variety of metals in such compounds for the use as catalysts (Fomichev and Kondratov, 1994; Hanuza et al., 1995, 1996, 1997; Ono et al., 1996; Daturi et al., 1997). Numerous studies have investigated phase transitions of tungstates and molybdates with scheelite-type structures at high pressures (Jayaraman et al., 1995a, b, c, d; Shieh et al., 1996; Christofilos et al., 1995, 1996). Mixed phase studies of solid solution series of various tungstates and molybdates using artificial compounds belonging to the scheelite group have been reported (Karaptyan et al., 1976; Efendiev et al., 1982; Daturi et al., 1997). Most of these Raman studies have used artificial crystals made using the Czochralski method.

Raman spectra for natural and artificial stolzite and wulfenite end members have
been reported by a number of authors (Khanna et al., 1968; Griffith, 1970; Ross, 1972; Kloprogge and Frost, 1999). However no Raman spectra have been reported for substituted wulfenites or stolzites. Raman effects of the natural solid solution series of wulfenite-stolzite have not been investigated nor have any intermediate members such as chillagite.

Elvy (1999) studying the geochemistry of the groundwater at the North Mungana deposit at Chillagoe, Queensland, found that where tungsten and molybdenum were present in the groundwater, stolzite and wulfenite limited the Pb(II)(aq) concentration. This highlighted the importance of both these minerals in the oxide zone, particularly in understanding the dispersion of Pb(II) during oxidation of the ore deposit and the overall geochemical processes involved in the secondary zone. Few studies have been undertaken to relate the chemistry of the wulfenite-stolzite solid solution series to geochemical systems, including the recent report of an intermediate member occurring in the $I4$ space group (Hibbs et al., 2000).

Numerous studies have reported substitution of various elements in wulfenite and stolzite (Ullman, 1912; Ahlfeld and Angelelli, 1948; Haberlandt and Schroll, 1949; Palache et al., 1951; Faick and Hildebrand, 1958; Clark and Sillitoe, 1970; Mir-Mohammedi, 1977; Arnaudov et al., 1979; Williams, 1990; Livingstone, 1992; Scovil and Wagner, 1991; Blaß and Graf, 1999) and various authors have suggested the existence of a complete solid solution series between stolzite and wulfenite (Clark and Sillitoe, 1970; Williams 1990). There is still, however, much confusion to what extent the series is continuous in either the artificial or natural wulfenite-stolzite series. There is especially a lack of experimental evidence of the nature of the series under ambient conditions.
With advancing technology, Raman microprobe spectroscopy is able to provide a quick, non-destructive (or damaging) method for studying a wide range of specimens with minimal preparation. This allows a detailed study and documentation of Raman spectra of natural wulfenites and stolzites from various locations. In addition, the difference in characteristic Raman frequencies of various anionic groups, particularly MoO$_4^{2-}$, WO$_4^{2-}$, and CrO$_4^{2-}$, presents an excellent opportunity to study substitution in the wulfenite-stolzite series using a different form of analysis to more traditional techniques. Use of Raman spectroscopy in the study of this relatively straightforward natural solid solution series has provided an excellent benchmark in developing the potential of the Raman microprobe as a precise non-destructive alternative analytical tool in the study of minerals and geochemical systems.

**4.0.1 GEOLOGICAL SETTING OF DEPOSITS FROM WHICH VARIOUS WULFENITES AND STOLZITES WERE STUDIED**

Important wulfenite and stolzite location references include Palache *et al.* (1951), and Bideaux (1990). A comprehensive list with references of the numerous wulfenite localities in Arizona is presented by Anthony *et al.* (1995). An excellent source of individual articles (too numerous to list here) on specific wulfenite / stolzite localities is *the Mineralogical Record* (ISSN 0026-4628).

**4.0.1.1 Broken Hill, New South Wales, Australia**

The geology and history of the Broken Hill ore body have been well documented by numerous workers and an excellent overview is presented by Birch (1999); only a
brief description of this overview is presented here. Essentially the Broken Hill ore deposit occurs in an early Proterozoic highly metamorphosed sequence of gneisses, amphibolites, and migmatites. Later retrograde metamorphism and deformation have remobilised the orebody, originally thought to be a stratiform volcanic exhalative. The orebody is shaped into a broad crumpled arch with the crest eroded away. It is 7 km long, up to 850 metres deep and 120 metres wide, consisting of several conformable mixed lead-zinc ore lens. The original oxide zone at Broken Hill extended down, on average, to about 75 metres but isolated “oxidation channels” extend this zone in places to 100 metres and in one area to about 900 metres (Birch, 1999). Even though a number of mineral associations have been established in the oxide zone, no simple zonation exists. The long and complex history of the oxidation of the ore body is reflected in the diversity of minerals and assemblages that are present.

Broken Hill has undoubtedly produced the finest and greatest variety of stolzite crystals from any one location (Bywater, 1983; Birch, 1999). The habits range from thin tabular through equant crystals, square tabular crystals, steep sided tetrahedral bipyramidal prisms, blocky elongated prisms and flat tabular bipyramids. Colour ranges from yellow to orange brown, reddish brown, yellowish white, fawn and smokey grey. Grey varieties occur towards the base of the oxide zone close to the sulfide ore and are often associated with secondary sulfides. Stolzite is often associated with its polymorph raspite but the nature of this relationship is unclear.

Wulfenite at Broken Hill is much rarer than stolzite and prior to its discovery in the Kintore open cut in the 1980s it was only collected on the 45 metre level of the Junction mine (Birch, 1999). It occurred as small clusters and drusy masses with a waxy
to resinous lustre. Tetragonal prisms modified by steep bipyramidal faces range from 1 to 5 mm. Wulfenite from the Kintore open cut shows a much wider range of colours and habits. They range from colourless to yellow and orange in colour, forming tabular and bipyramidal crystals up to 8 mm in size (Elliot, 1996; Birch, 1999).

4.0.1.2 The Christmas Gift North mine, Chillagoe, Queensland, Australia

Chillagite, from the Christmas Gift North mine, is perhaps the best known natural example of substitution in the wulfenite-stolzite solid solution series. The Christmas Gift North mine is associated with a number of other similar deposits (including the Christmas Gift and Lyonite Hills deposits) south-east of the township of Chillagoe. These deposits consist of metasomatic lead-silver-zinc-copper deposits in calc-silicate rocks on the boundary between a Permo-Carboniferous granodiorite and recrystallised limestone (de Keyser and Wolff, 1964). Gangue mineralogy is diverse being either siliceous or sideritic. Jenson (1940) notes that lead lodes were not associated with garnet rock. However, there is very little information on the Christmas Gift North mine itself and its exact location remains a mystery. Little is known of associated secondary minerals apart from cerussite which was reported on the original specimen (Ullman, 1912). Little is known of the primary mineralisation apart from its genesis as a contact metasomatic deposit and the abundance of primary molybdenum and tungsten minerals associated with the granites of the district (de Keyser and Wolff, 1964). It is suggested that molybdenite and scheelite would more than likely have occurred in the deposit. The water table around Chillagoe lies at between 15-33 metres depth. However, in places a zone of oxidation extends well
below this level and de Keyser and Wolff (1964) suggests this is due to the freely circulating groundwaters through cavernous limestone masses.

4.0.1.3 Whim Creek, Western Australia, Australia

The Whim Creek mine, located in the Pilbara, Western Australia, was one of Australia’s most prolific wulfenite localities. It is a stratiform lead-copper-zinc-silver deposit restricted to a single mineralised horizon hosted in essentially unmetamorphosed Archean volcanics and sediments (Nickel, 1982). The oxide zone extends to about 25 metres depth, close to the present water table.

Downes et al. (1998) outlined the different habits of wulfenites and other secondary mineral associations. They noted eight morphology/colour combinations varying from tabular crystals modified by pyramidal faces and bipyramidal crystals to flat tabular crystals, ranging in colour from yellow to orange sometimes showing colour zoning. They also noted that some of the wulfenites contained significant amounts of chromium.

4.0.1.4 The Red Cloud mine, Yuma County, Arizona, United States of America

The Red Cloud mine is world famous for its large (up to 6 cm across) tabular, brilliant red wulfenite crystals. A full description of the deposit is outlined by Edson (1980). A system of faults between younger volcanics (andesites) and older schists and granites (quartz monzonite-biotite hornblende diorites) control the ore mineralisation. These faults acted as channel ways for original epithermal fluids to deposit sulfides. Later high angle fractures (tension gashes) intersect the main fault. These contain remnants of
galena and well crystallised wulfenite. Secondary minerals occur in brecciated wallrock
and vughy masses with limonite, hematite and wad cavity linings. Common secondary
minerals include anglesite, cerussite, smithsonite, vanadinite, and wulfenite, in places
associated with argentiferous galena.

4.0.1.5 The Fat Jack mine, Yavapai County, Arizona, United States of America

The Fat Jack mine, Yavapai County, Arizona, though not a world famous location
for stolzite or wulfenite, does contain stolzites with significant amounts of substituted
molybdenum (Scovil and Wagner, 1991). The mine is associated with a large schist
inclusion in a quartz monzonite. Mineralisation occurs in quartz veins that cut the
monzonite/schist contact and are concordant with the foliation of the enclosing schist.
The source of veins is from an associated breccia pipe. Stolzite is found sparingly in the
mineralised zone associated with limonite (often pseudomorphing pyrite), quartz,
pyromorphite, cerussite, jarosite, mottramite, and osarizawaite. Stolzite usually occurs as
pale yellow to transparent acute bipyramids and thin tabular crystals (some with pale
orange centres).

4.0.1.6 Tiger, Pinal County, Arizona, United States of America

The ore deposit at Tiger, Arizona more accurately refers to the Collins and
Mammoth mines and is famous for its highly unusual copper-lead mineral suites which
occurred in outstanding quality and richness rarely surpassed in other deposits. An
excellent article on Tiger by Bideaux (1980) details much of the mineralogy of the two
mines and contains numerous references.
The regional geology consists of Precambrian granodiorite basement rock overlaid by Tertiary arkose sandstones and conglomerates interbedded with basalts and tuffs. Near the deposit, fine-grained to porphyritic intrusive rhyolite has intruded along faults. In places, it appears as a breccia containing granite and basalt fragments. The orebody consists of series of mineralised veins (up to six metres wide) between the fault controlled boundary of the rhyolite and older granodiorite. Sulfide ores have been oxidised to great depth. A second period of faulting outset the main vein forming the upper (Mammoth) and a lower (Collins) orebodies. The later continued to oxidise to the water table, while unusually the oxide zone of the Mammoth orebody existed below it.

Immense quantities of wulfenite were recovered from Tiger and the Mammoth mine was the principal source of molybdenum (from wulfenite) in the U.S. until 1945 (Bideaux, 1980). Wulfenite typically formed masses of large tabular orange crystals up to 8 cm across, often thickly encrusted with mimetite. Earlier generations of wulfenite were often coated with clay on which later crystals of red wulfenite, cerussite and diopside formed. In places wulfenite crystals are partially dissolved. Bideaux (1980) mentions that chillagite has been mentioned in earlier work and that chemical analysis of wulfenite concentrates contained up to 2 wt% WO₃. Williams (1990) mentions that wulfenite crystals also contained trace amounts of chromium.

4.01.7 The Clara mine (Grube Clara), Oberwolfach, Black Forest, Germany

The Clara mine at Oberwolfach, Germany has been a significant silver and base metal producer since at least 1652 (Wendel and Wendel, 2001). It has a strikingly varied mineralogy, especially in the oxide zone, as a result of the polymetallic nature of the

Broad compositional ranges of tungstenian wulfenites/molybdenian stolzites have been reported from the Clara mine by Blaß and Graf (1999). They noted a range of compositions in zoned crystals from between 10 –60 mol% stolzite.

4.0.1.8 Tsumeb, Namibia

The Tsumeb ore body is world famous for the extensive range of minerals present in the deposit. Wilson (1977) presents an excellent review of the Tsumeb deposit. A brief description of the deposit is summarised from Weber and Wilson (1977). The Tsumeb ore body is an elliptical pipe-like structure, pinching and swelling to a depth of over 1400 metres. It has been developed by fracturing and brecciation associated with the intrusion of a rock termed pseudoaplite. This consists of a feldspathic quartzite like rock (70 % quartz, 15-20% orthoclase and microcline, 5-10 % plagioclase) emplaced before ore-bearing solutions entered the pipe hosted in a sequence of dolomitic units. The primary ore mineralogy consists of massive Cu-Pb-Zn sulfides which include a host of more exotic elements such as As, V, Ni, Ga, and Ge. The Tsumeb deposit is unusual in that it has two oxide zones, the first down to 300 metres and the second from 800 metres to below 1400 metres. The existence of this second oxide zone occurs where the ore pipe cuts a permeable horizon and fracture zone in the surrounding country rock. Groundwaters have migrated along this fracture then channeled down the ore-pipe, oxidising the primary minerals.
Wulfenite crystals up to 7 cm across range in colour from clear through white to grey but are more commonly various shades of brown and rarely yellow, sherry, orange and pinks. Rare blue wulfenites have also been recorded. Tabular and pyramidal habits are common. Stolzite, though much rarer has also been reported from Tsumeb.

4.1 METHODS

4.1.1 WULFENITE AND STOLZITE SAMPLES

Samples of wulfenites and stolzites were acquired from a number of sources. The Australian Museum provided a number of Broken Hill stolzites, wulfenites and Chillagoe “chillagite” specimens. The Museum of Victoria also provided a sample of Chillagoe “chillagite”. Stolzites from the Cordillera mine were provided from the collection of Professor Peter Williams. Numerous wulfenite specimens were selected from the author’s collection. The following people provided various specimens from overseas locations: Chris Auer, Bryan Colon, David Shannon, William Gardner, Jack Kelper and Eric Melchiorre.

4.1.2 SYNTHESIS AND IDENTIFICATION OF THE LEAD(II) MOLYBDATE-LEAD(II) TUNGSTATE SOILD SOLUTION SERIES

A range of solutions with tungstate to molybdate ratios varying from 0:100 to 100:0 were made up from aqueous 0.100 M Na₂WO₄ and 0.100 M Na₂MoO₄. The solutions were mixed in various proportions to a total volume of 25.0 cm³. Then, 25.0 cm³ of aqueous 0.100 M Pb(CH₃COO)₂ solution was added to the tungstate/molybdate solution with constant stirring. Pb(CH₃COO)₂ was used to maintain a slightly basic
solution to prevent polymerisation of $\text{WO}_4^{2-}$ and $\text{MoO}_4^{2-}$ groups. All solutions were digested for 2 hours at 358 K. After digestion, precipitates were filtered off using a porosity 4 pyrex glass sinter, washed with water then acetone, sucked dry at the pump and then oven dried for 24 hours at 373 K. After drying, precipitates were subjected to X-ray powder diffraction analysis.

X-ray powder diffraction measurements were carried out with a Philips PW1925-20 powder diffractometer using CuK\(\alpha\) radiation ($\lambda = 1.5418\text{Å}$) and pure silicon as standard. The Traces software package (Diffraction Technology Pty. Ltd.) was used to analyse the data. Unit cell parameters were refined using the least-squares program LAPOD (Langford, 1973). Various pure and tungstenian wulfenites and stolzite were also investigated, as above, and their unit cell parameters also refined using LAPOD.

4.1.3 ELECTRON MICROPROBE ANALYSIS

The same equipment and experimental conditions used for crocoite sample analysis was used for the various wulfenite analyses (see Section 3.1.5). Extra standards in the array were tungsten and molybdenum metal.

4.1.4 RAMAN MICROPROBE SPECTROSCOPY

The tungstate and molybdate crystals were orientated on a polished metal surface on the stage of an Olympus BHSM microscope, which was equipped with 10x, 20x, and 50x objectives. No further sample preparation was needed. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-
Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm\(^{-1}\) in the range 100 to 4000 cm\(^{-1}\). Repeated acquisitions using the highest magnification were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm\(^{-1}\) line of a silicon wafer.

Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd., Waterfield, Surrey, England). Samples were placed in a stainless steel cup fitted over the silver plate of the thermal stage. For spectra at 77 K, nitrogen gas from liquid nitrogen passed through a small hole in this plate immediately below the centre of the glass disc. It was found that the best method of obtaining 77 K was to cool rapidly at 50 K per minute. Spectra at 77K are noisier and require longer accumulation times because of the increased optics used in collecting data. Spectra were obtained using 12 second scans for 20 minutes using the special short 50X (ULWD) objective. The intensity of the wulfenite spectra were found to decease by 0.3 using the ULWD objective compared with use of the normal X50 objective. A lower Raman signal was obtained using this objective due to the low numerical aperture of the longer working distance objective. Combined with the spherical aberration of the stage window, it results in decreased signal. It should be noted that the use of the X50 objective collects scattered light over a much wider angle than the X20 or X10 objective. There is less “polarisation leakage” if X20 objectives are used, but the intensity of the scattered light diminishes, making the collection of spectra more difficult.
4.2 RESULTS AND DISCUSSION

4.2.1 X-RAY STUDIES

4.2.1.1 Synthesised pure end members

The precipitates resulting from the mixing of the lead acetate and sodium molybdate solutions yielded a fine white powder. The resulting pH of the reaction solution was about 7.5. This was ideal and prevented the polymerisation of molybdate ions, which occurs rapidly at room temperature, low pH and high molybdate concentration (Baes and Mesmer, 1979).

The powder X-ray diffraction pattern of pure lead molybdate (Figure 4.4a) gave d-spacing values in excellent agreement with published values. Refined cell parameters were $a = 5.436 \pm 0.001$ and $c = 12.117 \pm 0.003$ Å. The $c/a$ ratio was 2.229 and unit cell volume was $358.1 \pm 0.1$ Å³. Once again these values are in excellent agreement (within experimental error) with most of the modern values reported in the literature for both artificial and natural tetragonal lead molybdate-wulfenite.

The precipitate resulting from the mixing of the lead acetate and sodium tungstate solutions also yielded a fine white powder. The resulting pH of the reaction solution was similar to that of the lead molybdate solution. The powder X-ray diffraction pattern of digested precipitated pure lead tungstate (Figure 4.4b) gave refined cell parameters of $a = 5.466 \pm 0.001$, $c = 12.050 \pm 0.006$ Å; $c/a$ was 2.205 and the unit cell volume $360.12 \pm 0.05$ Å³. These values are also in excellent agreement within experimental error with most of the modern values reported in the literature for both artificial and natural tetragonal lead tungstate. From the refined cell parameters, the lead tungstate has a longer
Figure 4.4  X-ray powder diffraction traces between 17-60° 2θ for A: PbMoO₄ and B: PbWO₄ synthesised under ambient conditions (Si represents the silicon standard peak).
c axis and a shorter a axis compared to the lead molybdate. As expected, the cell volume of the two are very similar, with lead tungstate having a slightly larger unit cell volume. These differences are consistent with other tungstate-molybdate pairs that crystallise in the scheelite structural group (Sleight, 1972). The main difference between the two X-ray diffraction patterns was the absence of the (101) peak around 17.90° 2θ in lead tungstate. The following peaks: (211), (105), and (213) around 38, 42 and 45° 2θ respectively, were comparatively lower in intensity compared to the other peaks in lead tungstate.

4.2.1.2 Synthesis of intermediate members.

All intermediate members of the solid solution series were easily precipitated and formed fine white powder which were identical in appearance to the pure end members. Intermediate compounds all appear to be stable over time.

From the X-ray diffraction analyses, all the traces gave patterns similar to either pure end member. There was no indication of two phases (for example the presence of multiple peaks where one peak should occur) at any W:Mo ratio over the entire solid solution series. All peaks across the range showed, to varying degrees, a shift between the end member peak positions. The position and degree of shift was consistent with the composition. Intensities of some of the peaks especially (101) around 17.90° 2θ decreased with increasing tungsten content. There were no anomalous or absent peaks in any of the traces between 20 -50 mol% which might indicate differences in symmetry arrangements corresponding to any different space group to I41/a. However, the subtle differences in these space groups may not produce an obvious pattern. It may be that the
Figure 4.5a  MoO$_4^{2-}$ mol\% versus $a$ axis calculated from refined cell parameters using LAPOD (Langford, 1973).

Figure 4.5b  MoO$_4^{2-}$ mol\% versus $c$ axis calculated from refined cell parameters using LAPOD (Langford, 1973).
Figure 4.5c  MoO$_4^{2-}$ mol\% versus c/a ratio calculated from refined cell parameters using LAPOD (Langford, 1973).

Figure 4.5d  MoO$_4^{2-}$ mol\% versus unit cell volume calculated from refined cell parameters using LAPOD (Langford, 1973).
formation of wulfenite-$\tau$ is related to unknown environmental rather than compositional controls.

Refined cell parameters for the intermediate members were all within the end-member ranges. Parameters are plotted versus composition (mol%) in Figures 4.5a, b, c and d. All plots (within experimental error) show an overall linear trend of cell parameters for the intermediate members, particularly the $c/a$ plot (Figure 4.5c) and total volume plot (Figure 4.5d). When all plots are considered it is clear that the solid solution series is complete over the entire range. There is no indication of gaps in the series where previous authors have reported them at 44-59 mol% (Jaeger and Germs, 1921) and 20-39 mol% (Tkachenko et al., 1981). Furthermore, the complete PbWO$_4$-PbMoO$_4$ solid series formed at ambient temperatures is in good agreement with Vegard's law and is consistent with the observations reported by Laishevtseva et al. (1989) on the series synthesised at high temperature. Oeder et al. (1980) also reported that the PbWO$_4$-PbMoO$_4$ solid solution series formed at high temperatures from melts was continuous over the complete range. However they found that though lattice parameters changed continuously, this change was not linear but curved between both end members for both the $a$ and $c$ axes.

4.2.1.3 X-ray studies of natural wulfenites and stolzites

A number of different wulfenites and stolzites, some of which were variously substituted, were studied by X-ray powder diffraction. Refined cell parameters are presented in Table 4.5. Overall, the results were as expected with pure wulfenite and stolzite cell parameters being almost identical to the synthesised compounds (within experimental error) and most reported values in the literature (Tables 4.2 and 4.3).
Table 4.5  Cell parameters, refined using LAPOD (Langford, 1973), of natural wulfenites, stolzites, tungstenian wulfenites, and molybdenian stolzites.

<table>
<thead>
<tr>
<th>Location</th>
<th>Colour</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$V$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Los Lamentos, wulfenite</td>
<td>orange</td>
<td>5.435(2)</td>
<td>12.108(5)</td>
<td>2.228(1)</td>
<td>357.77(4)</td>
</tr>
<tr>
<td>San Francisco mine, wulfenite</td>
<td>yellow</td>
<td>5.439(2)</td>
<td>12.098(5)</td>
<td>2.224(1)</td>
<td>357.91(3)</td>
</tr>
<tr>
<td>Red Cloud mine, wulfenite</td>
<td>red</td>
<td>5.439(1)</td>
<td>12.119(3)</td>
<td>2.228(1)</td>
<td>358.46(2)</td>
</tr>
<tr>
<td>Whim Creek, wulfenite</td>
<td>yellow</td>
<td>5.439(1)</td>
<td>12.111(3)</td>
<td>2.226(1)</td>
<td>358.40(2)</td>
</tr>
<tr>
<td>Chillagoe, tungstenian wulfenite</td>
<td>orange</td>
<td>5.439(2)</td>
<td>12.103(6)</td>
<td>2.225(1)</td>
<td>358.03(4)</td>
</tr>
<tr>
<td>Chillagoe, tungstenian wulfenites</td>
<td>brown</td>
<td>5.445(2)</td>
<td>12.086(5)</td>
<td>2.220(1)</td>
<td>358.33(5)</td>
</tr>
<tr>
<td>Fat Jack mine, molybdenian stolzite</td>
<td>yellow</td>
<td>5.444(3)</td>
<td>12.113(9)</td>
<td>2.225(1)</td>
<td>359.07(2)</td>
</tr>
<tr>
<td>Fat Jack mine, molybdenian stolzite</td>
<td>tan</td>
<td>5.450(1)</td>
<td>12.061(5)</td>
<td>2.213(1)</td>
<td>358.26(8)</td>
</tr>
<tr>
<td>Fat Jack mine, molybdenian stolzite</td>
<td>cream</td>
<td>5.458(1)</td>
<td>12.038(4)</td>
<td>2.205(1)</td>
<td>358.63(7)</td>
</tr>
<tr>
<td>Broken Hill, stolzite</td>
<td>brown</td>
<td>5.464(1)</td>
<td>12.052(3)</td>
<td>2.205(1)</td>
<td>358.81(6)</td>
</tr>
</tbody>
</table>

A number of known natural intermediate members of the series were analysed using X-ray diffraction. The San Francisco wulfenite, which is known to contain about 10 mol% W, showed definite shifts in peak positions as compared to pure wulfenite. The calculated unit cell parameters were $a = 5.439 \pm 0.002$ and $c = 12.098 \pm 0.005$, $c/a = 2.224$, $V = 357.9 \pm 0.1$ Å$^3$. When these parameters are compared to the artificial series they suggest a composition of about 10 mol% W, consistent with the chemical analysis.

Yellow stolzite from the Fat Jack mine, Arizona showed two distinct phases, one is stolzite rich and the second wulfenite rich. Since the solid solution series is continuous
over the complete range, the two phases indicate two distinct and diverse chemical events in the crystal suggesting at least two stages of formation rather than a continuous change over time.

Two different “chillagite” crystals were also studied by X-ray powder diffraction. The first was an orange crystal fragment and the second a brown crystal fragment. Each gave a slightly different unit cell, although the orange crystal parameters were similar to near pure wulfenite. This is consistent with orange wulfenite from the Christmas Gift North mine and various analyses have reported it as being always pure or near pure wulfenite (Mingaye, 1916; Duggan, 1989). The brown “chillagite” X-ray trace displayed broader, less distinct peaks, and the cell refinement matched a tungstenian wulfenite with about 35 mol% W. The less well defined pattern could be due to zoning in the crystal with the resulting X-ray diffraction pattern being a composite of a number of the zones of varying composition. Unlike the yellow Fat Jack mine stolzite (showing two phases), the compositional zones in “chillagite” are very similar, varying by only a few mol percent of tungsten and molybdenum. The refined cell could only be taken as an average of the average composition of the crystal.

Wulfenites reported to contain small amounts of chromium from the Red Cloud and Whim Creek mine (Edson, 1980; Downes et al., 1998), showed no variation in the X-ray diffraction trace. This not was surprising as the concentration of chromium in these wulfenites is well below 1 mol%. It was suggested by experiments on artificial compounds that for noticeable shifting of peak positions in X-ray traces and changes in unit cell parameters, concentrations need to be greater than about 5 mol%.
4.2.2 THE CHEMISTRY OF NATURALLY OCCURRING WULFENITES AND STOLZITES

4.2.2.1 Molybdate/tungstate

The most commonly reported chemical variation in wulfenite is the substitution of tungsten for molybdenum and *vice versa* for stolzite. Tungstenian wulfenite (up to 20 mol\% W) has been reported from locations all over the world and, though rarer, molybdenian stolzite has been reported from a number of locations. In this current study it was found that a complete solid solution series between lead tungstate and lead molybdate could easily be synthesised under ambient conditions (see Section 4.1.2). For the following equation

\[
PbMoO_4 +WO_4^{2-} \leftrightarrow PbWO_4 +MoO_4^{2-}
\]

values of $\Delta G^\circ$ and the equilibrium constant are -3.3 kJ mol\(^{-1}\) and 0.26, respectively at 298.2 K (using thermodynamic data from Appendix 1). If excess Pb\(^{2+}\)(aq) is available, and the system behaves ideally, the activity of the tungstate ion need only to be a quarter of the molybdate activity to be incorporated on a 1:1 basis in wulfenite; for stolzite, molybdate ion activity needs to be only four times higher. These activities must be easily achievable in Nature, reflected in the numerous reports of various intermediate members from numerous locations. Variability in groundwater conditions and given the right activity ratios over time a complete solid solution series could be represented in a single crystal.

Examination of numerous wulfenite/stolzite crystals with different colours and habits from different locations revealed that a majority represented essentially pure end member compositions, in agreement with earlier studies (Williams, 1966; Livingstone,
Tungstate/molybdate ratios of substituted wulfenites/stolzites crystals commonly varied within the same deposit and individual crystals were nearly always zoned. Microprobe analysis of various tungstenian wulfenites and molybdenian stolzites from different deposits are given in Appendix 5.1. Apart from spot quantitative analysis, zonation patterns in crystals could easily be observed in backscattered electron (BSE) images from the electron microprobe.

BSE images show relative brightness (variations in greyscale) (Heinrich, 1966) with larger atomic number elements appearing brighter (white). Comparisons of X-ray intensities of both molybdenum and tungsten in zoned crystals always show that where there is an increase in tungsten content there is a corresponding decrease in molybdenum content. The Raman microprobe also provided an excellent method of qualitative analysis of zoned crystals based on the relatively intensities of WO$_4$ and MoO$_4$ $v_1(A_g)$ (see Section 4.2.2).

4.2.2.1 Chillagoe, Queensland, Australia.

One of the best examples of variations in solid solution series in natural crystals is in "chillagite” from Chillagoe. Earlier studies have noted the strongly zoned nature of "chillagite” (Duggan, 1989; Jury 1997). However not all crystals from Chillagoe are zoned. Quodling and Cohen (1938) reported stolzite from Chillagoe based on calculated unit cell parameters from X-ray diffraction analysis. Later authors (Duggan, 1989; Jury, 1997) reported a maximum composition 75 mol% stolzite. The current study found a maximum composition of only 60 mol% and the existence of pure stolzite from Chillagoe is doubtful.
The colour of the chillagite is variable, ranging from brown and tan through orange to lemon yellow and there is some correlation of colour with composition. Orange crystals display no zonation and contain virtually no tungsten (< 0.5 mol). Earlier analyses of orange crystals from Chillagoe (Mingaye, 1916; Duggan 1989) also found no tungsten. Duggan (1989) noted that orange crystals occurred as orange cores of larger chillagite crystals and as individual crystals. In these larger crystals colour zonation abruptly changes from orange to lemon yellow. Jury (1997) reported that the core of a yellow-orange crystal contained no tungsten.

Lemon yellow crystals are the typical colour of chillagite crystals reported in the literature (Ullman, 1912; Palache et al., 1951). Yellow crystals display the greatest compositional range (between 0-75 mol% stolzite). All yellow crystal fragments and sections (in orange-yellow crystals) are zoned. Brown and tan coloured crystals are also zoned displaying a range of compositions between 10-50 mol% stolzite.

Overall tungsten/molybdenum variation between the core and rim of zoned crystals can be seen in SEM elemental maps (Figures 4.6a and b) and detailed chemical zonation is clearly observed in BSE images (Figure 4.7). All yellow and tan crystal BSE images displayed a broad variation in greyscale between the core and edge with tungsten-rich rims being much lighter. At a smaller scale zoned crystals display fine alternating bright and dark lines bands parallel to crystal edges. Compositional differences between these bands are usually only a few mol% (typically 2-5 mol%). Closer examination of a BSE image and corresponding elemental concentration profile (ECP) for molybdenum and tungsten of an orange-yellow ‘chillagite’ reported by Jury (1997) (Figures 4.8a and b) revealed detailed aspects on the evolution of the crystal. Jury (1997) noted that
Figure 4.6a  Elemental map of molybdenum distribution in Chillagoe tungstenian wulfenite. Lighter areas indicate higher molybdenum concentrations. Field of view is 5 X 5 mm.

Figure 4.6b  Elemental map of tungsten distribution in Chillagoe tungstenian wulfenite. Lighter areas indicate higher tungsten concentrations. Field of view is 5 X 5 mm.
Figure 4.7 Backscattered electron image of fine alternating; A: tungsten-rich (light) and B: tungsten-poor (dark) bands in zoned Chillagoe, 'chillagite'.

The core of this crystal at point B gave only 1 mol% tungsten and the BSE image displays no zonation. Towards the edge of the crystal (between points A and B) there is a sharp increase in tungsten content with a corresponding drop in the molybdenum content (point C). This compositional boundary is very irregular and the tungstenian wulfenite fills irregularities surrounding the original crystal. There is then a narrow zone where the tungsten content gradually increases in zoned bands towards the edge. At point D there is sharp decrease in tungsten content where a second narrow molybdenum-rich zone abruptly appears as a black band in the BSE image, sub-parallel to the wulfenite core. This is not as ragged as the boundary at point C.

Beyond the molybdenum-rich band the tungsten content increases again. Between D and A the relative Mo/W content constantly fluctuates appearing as an alternating
**Figure 4.8a** Backscattered image of ‘Chillagite’ from Christmas Gift North mine (modified from Jury, 1997). A-B elemental concentration profile traverse (Figure 4.11b). C, D and E referred to in text.

**Figure 4.8b** Elemental concentration profile (X-ray intensity) traverse for Mo and W of ‘chillagite’ from Figure 4.11a modified from Jury (1997).
stripe pattern with sharp boundaries in the BSE image. Compositional changes are more gradual compared to sharp compositional boundaries near the core of the crystal.

Zonation is parallel to inner compositional boundaries and not to the external form of the crystal. Close to the rim of the crystal a very light band in the BSE image (point E) with a sharp boundaries has a correspondingly high tungsten content. Microprobe analyses by Jury (1997) at the edge of this crystal reported two analyses of 67 and 78 mol% stolzite (the latter probably corresponding to the high tungsten band at point E).

From the current work it has been found that all zoned “chillagite” crystals consistently have a higher tungsten content at the rim as compared to the core.

Weathering of local granitic bodies in the area which contain scheelite and molybdenite (de Keyser and Wolff, 1964) or the possible existence of primary scheelite and molybdenite in the deposit (the deposit being formed through metasomatic processes) will be the origin of molybdate and tungstate. Elvy (1999) reported low levels of both tungsten and molybdenum in the groundwaters (up to 0.048 and 0.008 mg L\(^{-1}\) respectively) from the nearby Mungana North deposit and found that both stolzite and wulfenite limited the Pb(II) concentrations in the groundwater. This suggests that tungstate and molybdate activities may be influenced by regional groundwaters.

Zonation patterns of Chillagoe ‘chillagite’ crystals suggests that they developed in complex and constantly changing geochemical environment. Near-pure wulfenite compositions at the core of many crystals indicate that tungsten activities in the initial groundwaters were negligible. Conditions then changed such that wulfenite was unstable.
and existing crystals corroded (possibly due to changes in pH). A limited influx of
groundwaters containing tungsten is reflected in the growth of tungstenian wulfenite
crystals on many of the corroded crystals. These fluctuations may have been caused by
slight shifts in pH controlling the release and absorption of MoO$_4^{2-}$(aq) and WO$_4^{2-}$(aq)
ions by iron(III) oxyhydroxides (Williams, 1990) or slow depletion of MoO$_4^{2-}$ in the
geochemical system. Tungsten-rich rims, probably represents a late-stage influx of
tungsten into the system.

4.2.2.1.2 Arizona, United States of America

Many wulfenites from numerous well known Arizona and Mexican locations
including Rawhide, Rowley, Tiger and San Francisco mine contain tungsten above trace
levels, often exceeding 5 mol%. It is interesting to note that many famous Arizona
wulfenite deposits do not have a direct primary source of molybdenum or tungsten
(Wilson and Miller, 1974; Bideaux, 1980) and therefore the role of regional groundwater
is crucial in the development of these extensive deposits of wulfenite (Tittley and
Anthony, 1961). A regional source of both molybdenum and tungsten would be from the
numerous large-scale acid igneous intrusive complexes and associated porphyry
copper deposits throughout the region (Kerr, 1946; Tittley and Anthony, 1961; Wilt and
Keith, 1980).

Variation in tungsten content is commonly observed in different crystals from the
same deposit, particularly the Rawhide and San Francisco mines (though rarely
exceeding a few mol%). Tungsten content of crystals in these latter deposits range from 0
to 15 mol%. Zoning in single crystals is extremely common feature of most Arizona
Figure 4.9 Backscattered electron image of a Rawhide mine, tungstenian wulfenite. Lighter bands (A and B) in the crystal indicate areas containing higher concentrations of tungsten.

Tungstenian wulfenites and was particularly evident in crystals from Rawhide and Tiger mines. Overall zonation trends are similar with little or no tungsten at the core and significant amounts of tungsten (generally up to 10 mol% stolzite though not exceeding 20% mol% stolzite) at the edge. From BSE images, zonation appears as sharp bands, parallel to the crystal edges (Figure 4.9) as with Chillagoe many Arizona tungstenian wulfenites show broad compositional changes between the core and rim with small-scale fluctuations imprinted over broad trends.

An excellent example of this is an orange crystal from Tiger. It exhibited no external colour variation though microprobe analyses revealed its tungsten content ranged from about 3 mol% at the core to about 12 mol% at the edge, as is obvious from the BSE
Figure 4.10a  Backscattered electron image of tungstenian wulfenite from Tiger, Arizona.

Figure 4.10b  Backscattered electron image close-up of zonation in tungstenian wulfenite from Tiger, Arizona. Note the change in preferred growth orientation of the crystal between A and B.
image (Figure 4.10a and b), with the centre of the crystal having a darker core (less tungsten) becoming much lighter towards the rim (greater tungsten). The crystal displays intense zonation (Figure 4.10b) of alternating dark and light bands representing small fluctuations in the relative W/Mo content from the core to the edge of the order of 2-5 mol%. Zonation patterns indicate a change in crystal morphology and dominant crystal faces in the growth history of the crystal (Figure 4.10b). This change corresponds to elevated tungsten levels in the mid-section of the crystal. This increase in tungsten, may favour a subtle change in crystal morphology, as has been noted for wulfenite (Vessilinov, 1995, 1996a, b). Near the rim of the crystal there are small included subhedral wulfenite grains (<50 microns) which are not zoned and contain up to 15 mol% tungsten. These may have formed elsewhere and then transported and incorporated into the larger crystal.

Stolzite is much rarer than wulfenite in Arizona and recorded from only a few localities (Anthony et al., 1995). Stolzite from the Fat Jack mine reported to contain between 3.0-45.0 wt% WO₃ and 3.0-15 wt% MoO₃ with an average composition of 75 mol% stolzite and no associated wulfenite (Scovil and Wagner, 1991). The current study analysed a variety of Fat Jack stolzites. Large rounded yellow tabular crystals (some with an orange spot) had a core composition of almost pure wulfenite (< 3 mol% W). Towards the edge of these crystals there was a slight increase in tungsten content (to a maximum of 5 mol%). Raman and electron microprobe analyses revealed that at the edge of some of these crystals a dramatic change in composition from near pure wulfenite to a tungstenian wulfenite/molybdenian stolzite occurs (between 45 and 80 mol% stolzite). The BSE image (Figure 4.11a) shows that the dramatic increase in tungsten change is not uniform and near the boundary irregular patches of tungstenian wulfenite/molybdenian
stolzite (45-60 mol% stolzite) fill voids in the original wulfenite (Figure 4.11b). Compositions in the tungsten-rich rim range from 60 mol% stolzite at the wulfenite boundary to a maximum of 80 mol% stolzite at the rim. As with other tungstenian wulfenites, these crystals indicate significant changes in circulating groundwater geochemistry during the development of the oxide zone. An initial change in solutions may have led to corrosion of the original crystal prior to an influx of tungsten-rich solutions. However, partial dissolution of the original wulfenite crystal may be related to a major increase in tungsten activity of different solutions rather than to a separate event.

Scovil and Wagner (1991) noted that some orange tabular crystals, associated with limonite pseudomorphs after pyrite, were rough, rounded and a few had a hole in the centre, suggesting that these wulfenites had grown around a previous mineral that had leached away. These holes may have formed at the same time as the outer edges of the wulfenites were corroded. Scovil and Wagner (1991) provided no analyses of these crystals.

A second generation of molybdenian stolzite, from the Fat Jack mine, commonly formed small bipyramids and square tabular crystals. These crystals are euhedral, exhibit no evidence of corrosion and probably formed later in the paragenetic sequence. Individual crystals vary in compositions from 65-80 mol% stolzite and are typical of the average composition reported by Scovil and Wagner (1991). Most of these crystals show a slight but gradual increase in tungsten towards the edge. Apart from yellow individual crystals, stolzite also forms white to tan tabular crystal aggregates. These generally consist of two separate habits on each side of the aggregate mass. On one side, the
Figure 4.11a  Backscattered electron image of yellow tabular wulfenite/stolzite from the Fat Jack mine, Arizona. A sharp compositional difference is indicated by the white (high tungsten) and grey (low tungsten) areas. Note the preservation of original wulfenite crystal shape.

Figure 4.11b  Backscattered electron image close-up of yellow tabular wulfenite/stolzite from the Fat Jack mine, Arizona. Close to the sharp compositional boundary. Note voids in original wulfenite have been filled with molybdenian stolzite, indicated by the white (high tungsten) areas.
crystals form individual square tabular plates up to 2 mm across; on the reverse side the crystals are smaller (< 1 mm) and form stacked, bipyramid crystal groups. These masses contain the highest percentage of tungsten observed at the Fat Jack mine (90-100 mol% stolzite). Between the core and the bipyramidal crystal side of the crystal aggregate the composition is almost pure stolzite (>98 mol% stolzite) and exhibits no zoning. However, between the core and the side with the square tabular crystals, the stolzite contains more molybdenum (90-95 mol% stolzite) and is zoned. Across the tabular crystals are alternating light and dark bands in the BSE image. The change in habit of these stolzite crystals may be related to levels of molybdenum substitution in the crystal.

Fat Jack mine stolzites display both dramatic compositional differentiation and subtle zonation indicating both major shifts in groundwater geochemistry and localised fluctuations. Different generations of crystal growth based on crystal chemistry can be identified. Initial groundwaters characterised by low tungsten activities are associated with the formation of near pure wulfenite in the oxide zone. Sudden influx of tungsten-rich groundwaters mixed with molybdate ions released from dissolving wulfenite formed an initial generation of molybdenian stolzite around the rim of pre-existing wulfenite crystals. As molybdenum activities further decreased individual molybdenian stolzite crystals grew. It is unclear where in the sequence the tan crystal aggregates occur but their high tungsten content suggest that they formed late in the sequence when nearly all of the molybdenum was exhausted.

Other samples of molybdenian stolzite have been reported from Arizona. From the Lost Gulch area, stolzite was reported to contain between 5.5 and 8.6 wt% MoO₃ (Faick and Hildebrand, 1958). It is unknown whether these samples were zoned. It is
possible that stolzite and molybdenanl stolzite are more widespread in Arizona than has been previously reported. More detailed geochemical investigations may reveal more zoned crystals and hence may sheds light on the evolution of groundwater in oxide zones of the region.

4.2.2.1.3 Tsumeb, Namibia

Many wulfenites from Tsumeb, Namibia contain small amounts of tungsten (Pinch and Wilson, 1977). There has been no reported compositional zonation in crystals though tungsten compositions do vary from crystal to crystal with compositions reported up to 12 wt%. The highest tungsten contents in wulfenites analysed in this study were in thin dark tabular crystals. These crystals had small compositional variations between crystals and displayed minor zonation. Deep brown flattened bipyramids crystals were also analysed but contained no significant amounts of tungsten. The relationship of different wulfenites to each other remains unknown.

4.2.2.1.4 Clara mine, Germany

Broad compositional ranges of tungstenian wulfenites/molybdenanl stolzites have also been reported from the Clara mine in Germany, with values between 10–60 mol% stolzite (Blaß and Graf, 1999). In the current study a single tabular wulfenite crystal was distinctly zoned (Figure 4.12a and b) with a number of broad compositional bands. At the core the composition is generally around 25-30 mol% stolzite. Between the core and the next broad compositional band towards the edge, the boundary is jagged and appears to
Figure 4.12a  Backscattered electron image of zoned tungstenian wulfenite/molybdenian stolzite from the Clara Mine, Germany.

Figure 4.12b  Backscattered electron image close-up of zone boundary of tungstenian wulfenite/molybdenian stolzite from the Clara Mine, Germany. Note the different types of compositional boundaries. A: concave; B: straight and C: irregular.
have been corroded. In places the boundary is rippled, being concave towards the core (Figure 4.12b point A), similar to the second corroded boundary in the Chillagoe wulfenite (Figure 4.8 point D). The composition of this outer core is about 35-40 mol%, with some alternating compositional bands being present. The outer boundary of this zone is sharp and parallel to the outer crystal form (Figure 4.12b point B) and beyond this boundary tungsten content increases. This third zone contains the highest proportion of tungsten to molybdenum (about 60 mol% stolzite) and is technically a molybdenum stolzite. Tungsten content sharply decreases beyond this boundary toward the rim with an irregular outer boundary (Figure 4.12b point C). However the mol% W is still greater at the rim than at the core. This crystal from Clara is unusual in that other wulfenites analysed in this study contained significantly lower amounts of tungsten at the core.

In places, compositional zones and boundaries are highly irregular suggesting that the crystal has undergone various stages of growth and partial dissolution with changing groundwater conditions. Smaller wulfenite crystals have also been incorporated into the larger crystal. However, with these numerous changes in the composition there does not appear to be any significant change in the crystal morphology during its formation.

4.2.2.1.5 Broken Hill, New South Wales, Australia

Pure stolzite dominates the wulfenite-stolzite series at Broken Hill with wulfenite being extremely rare in the oxide zone. Both stolzite and wulfenite have only been reported as pure end members with no observed intermediate members of the series and no substitution of other elements. Stolzite has not been recorded occurring with wulfenite. The paragenetic relationship of wulfenite to stolzite is unclear. It is clear that
the formation of wulfenite is very localised in the oxide zone. Analyses of both Junction mine and Kintore open cut wulfenites revealed that they are stoichiometric. Analyses of various stolzites showed that nearly all crystals with steep bipyramidal habits are essentially pure stolzite. However many stolzites with more tabular or flattened habits contained small amounts of molybdenum (up to about 5 mol%). Some orange tabular stolzites and zoned with a core of pure stolzite surrounded by a thin rim of about 1-2 mol% wulfenite. Grey flattened bipyramids contain significant amounts of molybdenum (up to 10 mol%). It has been suggested (Birch, 1999) that the colour of grey stolzite may be due to finely dispersed sulfide inclusions, though neither electron microprobe analyses nor Raman analysis support this suggestion.

An unusual specimen of stolzite from the author’s collection, associated with orange-red mimetite reported from the Junction mine was also analysed. These stolzite crystals were bright orange-red and formed very thin, square, tabular crystals with bevelled edges. One crystal exhibited a complex series of sharp zonation bands in the BSE image (Figures 4.13a and b). Bands of various thickness increased towards the edge and consisted of alternating Mo-rich/Mo-poor zones. Zonation occurs both as broad zones and finer alternating dark and light bands within these broad zones. The boundary between different compositional zones is sharp and regular with no evidence of corrosion. The composition of the crystal varied between a molybdenian stolzite and tungstenian wulfenite at one edge (about 50-90 mol% stolzite) and there is a great contrast in composition between some individual zones (often of the order of 20 mol% molybdate, though fluctuations on a scale of only a few mol% were also present). This zoning suggests that the groundwater conditions dramatically changed as molybdenum
Figure 4.13a  Backscattered electron image of a zoned Broken Hill, molybdenian stolzite.

Figure 4.13b  Close up backscattered electron image of a zonal pattern in Broken Hill, molybdenian stolzite. Note the sharp compositional boundaries.
activities rapidly rose and then decreased suggesting sudden influxes of molybdate-rich
groundwaters into a localised system. This is the first reported stolzite from Broken Hill
containing significant amounts of molybdenum and suggests that other of intermediate
members of the stolzite-wulfenite series may exist in the oxide zone.

Unlike Arizona, the source of the tungsten and molybdenum at Broken Hill is
from the breakdown of primary minerals within the deposit. Birch (1999) reports that
scheelite and wolframite were common locally in the Broken Hill orebody and would be
the primary source of the tungstate. These have been recorded in matrix specimens of
galena in cross cuts and seams in the ore body and in the garnet sandstone rim of the lead
lodes (Birch, 1999). Birch (1999) mentions that molybdenite occurs sparingly through the
Broken Hill deposit and weathered molybdenite has been observed associated with
secondary phosphate minerals from the Kintore open cut. The abundance of scheelite
compared to molybdenite is clearly related to the relative abundance of stolzite as
compared to wulfenite in this area.

Due to the highly complex nature of the Broken Hill oxide zone geochemistry and
structure, the extent of dispersion and migration of MoO$_4^{2-}$ and WO$_4^{2-}$ through the oxide
zone is unclear. However, the restricted occurrence of both minerals suggests that the
formation of these minerals was the result of highly localised (rather than regional)
groundwater conditions where the MoO$_4^{2-}$ and WO$_4^{2-}$ have been concentrated. It is
uncertain whether this is a reflection of a concentration of primary tungsten/molybdenum
minerals within the orebody or as the result of transport and concentration due to
chemical and/or structural factors. The increased molybdenum content of some stolzites
towards the edge of crystals and the absence of tungsten in wulfenites suggests that
wulfenite may have formed later than stolzite. However, the lack of direct paragenetic observations and the complex nature of the oxide zone may tempt an oversimplification of the true relationship.

4.2.2.1.6 Other locations

Livingstone (1992) reported two tabular crystals from Wanlockhead, Scotland that had a wide range of W and Mo compositions. These are from the same area, though from separate deposits, and had two separate (though broad) compositional ranges. The first, a tungstenian wulfenite, had a composition from 10 to 45 mol% stolzite. The second, a molybdenian stolzite, had a composition from 52 to 72 mol% stolzite. With regard to any zonation in the crystals, Livingstone (1992) only reported that the tungsten levels in the tungstenian wulfenite were higher around the edge as compared to the core, with no actual mention of zonation.

In agreement with synthetic studies, substitution of tungsten in wulfenite and vice versa is common in natural materials and a complete solid solution is represented in Nature, though no one deposit completely covers the entire series. Both pure stolzite and pure wulfenite have been reported from some deposits, although as expected neither occur together, indicating two distinct geochemical conditions during oxide zone evolution. Nearly all tungstenian wulfenites studied were zoned and it has been observed that the cores usually contained the lowest proportional of tungsten in the crystal. Nearly all examples that contained tungsten were thin tabular or platy crystals and no wulfenite with a pyramidal habit contained any significant amounts of tungsten. Molybdenum stolzites are fairly common in Nature and are also frequently zoned. Most stolzites that
contain significant amounts of molybdenum also form tabular crystals. Zonation in crystals can occur as both small fluctuations (of the order of a few mol%) or as dramatic compositional changes usually associated with irregular boundaries.

Changing groundwater geochemistry is crucial in developing zoned wulfenite/stolzite crystals. The simplest interpretation of changing groundwater conditions concerns the influx of various ions from external sources and/or the depletion of $\text{MoO}_4^{2-} \text{(aq)}$ and $\text{WO}_4^{2-} \text{(aq)}$ in the system. However, Williams (1990) suggests a more subtle explanation for the occurrence of wulfenite/ stolzite series in various oxide zones. Both ions are strongly absorbed on Fe(III) oxyhydroxides, where the latter are a feature of all base metal oxide zones. The mechanism of sorption has been studied by a number of workers, particularly with respect to the uptake of such ions in soils (Reinsauer et al., 1962; Barrow and Shaw, 1975; Vlek and Lindsay, 1977). It has been observed that sorption of $\text{MoO}_4^{2-}$ under ambient conditions is accompanied by the release of hydroxyl ions. Amounts of molybdate sorbed onto Fe(III) oxyhydroxides and released into solution is largely determined by pH (Reinsauer et al., 1962; Vlek and Lindsay, 1977), and the lower the pH the more molybdate that is sorbed. From the literature, a simplified equation for the process is as follows

$$\text{Fe(III) oxyhydroxide} + \text{MoO}_4^{2-} \text{(aq)} \leftrightarrow \text{Fe(III) oxyhydroxide} - \text{MoO}_4 + 2\text{OH}^{-} \text{(aq)}$$

This mechanism of concentrating and releasing anions under ambient conditions as the result of pH changes may provide controls on the formation of intermediate members of the solid solution series in the oxide zone, but it is unclear whether different proportions
of MoO$_4^{2-}$ versus WO$_4^{2-}$ are released under different pH conditions. If this is the case then it is possible that a range of wulfenite/stolzite compositions can form over time, controlled simply by fluctuations in pH rather than dramatic influxes of anions from external sources alone.

Williams (1990) suggests that sorption onto Fe(III) oxyhydroxides may also be an important mechanism in the concentrating of MoO$_4^{2-}$(aq) and WO$_4^{2-}$(aq) in the oxide zone where these anions have been derived from groundwaters outside the oxidising body, particularly in the case of many of the famous wulfenite locations in Arizona. Shifts in pH could lead to large releases of these ions which would react with the Pb(II) in the groundwaters (derived from weathered minerals such as galena in the deposit) to form the large masses of wulfenite commonly observed in many Arizona deposits.

The formation of wulfenite and stolzite is also controlled by the availability of MoO$_4^{2-}$(aq) and WO$_4^{2-}$(aq) ions. Polymerisation to form complex polytungstate and polymolybdate ions occurs with decreasing pH (< 4) and increasing molybdate and tungstate activities in solution (Baes and Mesmer, 1979). Under these conditions minerals such as betapakdalite would form in preference to wulfenite.

### 4.2.2.2 Chromate

#### 4.2.2.1 Chromate in wulfenite

Apart from tungsten, low levels of chromium have been reported substituting into wulfenite by previous authors (Haberlandt and Schroll, 1949; Mir-Mohammedi, 1977; Edson, 1980; Bideaux, 1990) and has been confirmed in a number of wulfenites in this study by Raman probe. Bishop and Hanke (1961) reported that, under ambient
conditions, up to 60 mol\% chromate could be doped into lead molybdate without a change in structure. However, in Nature substitution rarely exceeds 0.1%. Based on the following equation

$$\text{PbMoO}_4 + \text{CrO}_4^{2-} \rightarrow \text{PbCrO}_4 + \text{MoO}_4^{2-}$$

and using thermodynamic data from Appendix 1, the $\Delta G_{\text{reaction}}^\circ$ is 16.1 kJ mol$^{-1}$ and equilibrium constant (K) of $1.51 \times 10^3$ at 298.2K. Assuming ideality, for molybdate and chromate ions to be equally incorporated into the lattice of wulfenite, the activity of the chromate ion has to be about 700 times greater than that of the molybdate.

Trace element analyses of wulfenites from Whim Creek (Appendix 5.2) showed that chromium was the only significant substituted element. The habit of the wulfenite correlates with the amount of chromium. The tabular crystals contained up to 1400 ppm, with an average of 220 ppm Cr. Pyramidal crystals contained up to 390 ppm Cr with most below 50 ppm. Most crystals containing chromium exhibited a highly variable chromium content across the grain, though some displayed higher chromium contents at the core.

Only tabular wulfenites were observed with fornacite, $(\text{Pb,Cu}^{2+})_3[(\text{Cr}^{6+},\text{As})\text{O}_4]_2(\text{OH})$, in this study consistent with observations by Downes et al. (1998), and with the use of the Raman probe qualitative analysis was undertaken. All wulfenites associated with fornacite displayed the distinct Raman band at 818 cm$^{-1}$. Wulfenite always forms on the fornacite and therefore is later in the paragenetic sequence. Nickel and Hitchen (1994) reported the occurrence of an unnamed mineral which is the phosphate analogue of molybdoformacite, $(\text{Pb,Cu}^{2+})_3[(\text{P,As})\text{O}_4][(\text{Cr}^{6+},\text{Mo}^{6+})\text{O}_4](\text{OH})$. Its association with fornacite and chromium wulfenite is unclear but it may represent an intermediate in the paragenetic sequence between fornacite and wulfenite. It is interesting to note that even
though some Whim Creek wulfenites contain up to 1400 ppm chromium they are not red as is typical of other chromium wulfenites reported in the literature (Haberlandt and Schroll, 1949; Mir-Mohammed, 1977; Edson, 1980). Most of these red wulfenites often contain significantly lower amounts of chromium than those from Whim Creek and this suggests that the colouration may not simply be a reflection of internal chemical variation.

There is no primary molybdenum or chromium mineral reported from Whim Creek. However geochemical analysis of the deposit (Nickel, 1982) shows that small amounts of both molybdenum (maximum assay 500 ppm; average 70 ppm) and chromium (maximum 200 ppm; average 110 ppm) occur in the primary zone, Nickel (1982) notes that elemental concentrations are highly variable especially in the oxide zone. He reported that this zone had been enriched in lead and slightly in copper and there was a slight decrease in average molybdenum and chromium concentrations, however localised chromium content was up to 400 ppm.

Downes et al. (1998) note that the tabular and pyramidal wulfenite crystals from Whim Creek defined two separate but characteristic mineral associations. They suggested that this difference may simply reflect associations from different parts of the mine where different conditions prevailed rather than overall changes in oxide zone geochemistry. However, they also pointed out that the wulfenites have a complicated and multistage paragenetic history, with many showing colour zonation (not related to observed crystal chemistry) and various stages of overlapping crystal growth. The limited occurrence of secondary chromium minerals throughout the deposit (fornacite and vauquelinite) suggests that highly localised areas of the secondary zone, with extremely high reduct
potentials, may have generated abnormally high activities of chromium as soluble Cr(VI). Arsenate ion from the breakdown of primary arsenopyrite would have combined with the lead, copper and chromium (as chromate ion) to form fornacite. With continuing oxidation conditions and deposition of fornacite, geochemistry of the groundwater would have progressively changed. Initially very low concentrations of molybdenum in groundwaters resulted in the formation of molybdoformacite. With a continuing increase in molybdenum activities compared to chromium and increasing lead concentrations the formation of wulfenite would result. In localised areas of the oxide zone, where chromate activities were high, chromium substituted.

Red wulfenites from Anarak, Iran reported to contain chromium are also associated with yellow crystals (Bariand and Poullen, 1980). The latter were analysed and shown to contain no chromium. Wulfenites from Anarak are associated with a number of rare chromate minerals including fornacite (Bariand and Poullen, 1980) and there are at least two stages of wulfenite formation. Initial wulfenites that formed before the chromate minerals were flat, tabular yellow crystals and contained little or no chromium (similar to the crystals analysed in this study). A second generation of wulfenite that formed after the chromates contained significant amounts of chromium and crystallised as red bipyramids (similar to crystals analysed by Mir-Mohammed, 1977). This suggests that an influx of chromium rich groundwaters occurred sometime after the initial formation of wulfenite. The first minerals to form in the chromium rich environment were minerals such as fornacite (similar to the situation at Whim Creek) and as arsenate was exhausted, chromium-rich wulfenite resulted.
4.2.2.2 Chromate in stolzite

It is interesting to note that there have been no reports of chromium stolzites in the literature. Thermodynamic calculations based on the following equation

\[ \text{PbWO}_4 + \text{CrO}_4^{2-}(\text{aq}) \leftrightarrow \text{PbCrO}_4 + \text{WO}_4^{2-}(\text{aq}) \]

gave \( \Delta G^\circ_{\text{reaction}} = 13.1 \text{ kJ mol}^{-1} \) and \( \log K = -2.29 \) at 298.2K. Once again, assuming ideality, for tungstate and chromate ions to be equally incorporated into the lattice of stolzite the activity of the chromate ion has to be about 200 times greater. This indicates that chromate should dope into the stolzite lattice easier than into the wulfenite lattice, though no natural chromium stolzites have been reported. This may be a reflection of the rarity of groundwater conditions required for chromium substitution in stolzite or simply the lack of analyses for chromium in stolzites.

Microprobe analyses indicated that the zoned, orange-red stolzite crystals from Broken Hill contained significant amounts of chromium (up to 0.3 wt% CrO\textsubscript{3}) in places. The presence of chromium is also supported by the presence of a significant band at 818 cm\textsuperscript{-1} in the Raman spectrum of this specimen. This is the first reported occurrence of a chromium stolzite in Nature. At Broken Hill other chromium minerals such as fornacite, \( (\text{Pb, Cu}^{2+})_3[(\text{Cr}^{6+},\text{As})\text{O}_4]_2(\text{OH}) \), and vauquelinite, \( (\text{Pb, Cu}^{2+})_3[(\text{Cr}^{6+},\text{P})\text{O}_4]_2(\text{OH}) \), have been reported in the oxide zone from the Kintore open cut (Birch, 1999). Occurrence of chromium in this Broken Hill stolzite may be related to the supposed occurrence of crocoite at Broken Hill as reported by Marsh (1897). He cited crocoite occurring as red crystals below a crust of vanadinite in limonitic gossan from the Proprietary mine. No other specimens of crocoite have since been reported from Broken Hill and its occurrence has

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always been something of a mystery (Birch, 1999). The primary source of the chromium at Broken Hill has been suggested as being due to trace amounts of chromium substituted in magnetite, Fe₃O₄, gahnite, muscovite or garnet or other related minerals (L. J. Lawrence, pers. comm.) since no primary chromium minerals (such as chromite) have been reported from Broken Hill.

4.2.2.3 Arsenate, phosphate, vanadate

Of the various wulfenites and stolzites analysed, most did not contain significant amounts of AsO₄³⁻, VO₄³⁻ or PO₄³⁻ (<0.5 wt%). However, Clara mine wulfenite consistently contained small amounts of AsO₄³⁻ (up to 1 wt% As₂O₅). There are reports in the literature of these anions in wulfenite, particularly the vanadium variety ‘eosite’ (Palache et al., 1951). However, significant amounts of AsO₄³⁻, VO₄³⁻ and PO₄³⁻ above trace level in wulfenite should be viewed with caution, particularly in the older literature. It is well-known that minerals such as mimetite, vanadinite and pyromorphite are intimately associated with wulfenite from numerous deposits and often occur as inclusions. Therefore many chemical analyses in the older literature of such substituted wulfenite may simply reflect a mixture of wulfenite with such included minerals as impurities rare than a separate phase. This is supported by re-analyses of older samples reported as substituted wulfenites, which have been revealed to be mixtures. For example, Scottish ‘eosite’ reported by Heddle (1901) re-examined by Livingstone (1992) was revealed to be a mixture of vanadinite and wulfenite. This is not to say that substitution of such anions could not occur, Brugger et al. (1998) reported significant amounts of arsenate occurring in scheelite (up to 4 mol%). The charge difference is offset by a proportional doping of rare earth elements into the structure.
particularly $Y^{3+}$ for $Ca^{2+}$ (Brugger et al., 1998). An extreme case of this substitution is the mineral paraniite-(Y) with the formula $2CaWO_4.YAsO_4$ (Demartin et al., 1992, 1994). It has an overall scheelite structure consisting of two $CaWO_4$ layers and a $YAsO_4$ layer, compared to pure $YAsO_4$ (chernovite-(Y)) which has the zircon structure (space group $I4_1$). Demartin et al. (1992, 1994) state that the $YAsO_4$ in paraniite is not related to pressure effects but stabilised by structural effects. This structural arrangement may be possible in a lead arsено-
molybdate given that a suitable substituted cation could provide the charge compensation, some Pb be present as Pb(IV) or some anion sites remain vacant.

4.2.3 RAMAN SPECTROSCOPY OF THE WULFENITE-STOLZITE SERIES

4.2.3.1 Raman band assignment for stolzite and wulfenite

Both wulfenite and stolzite have group symmetry of $C_{4h}$ (Khanna et al., 1968). The unit cell has $Z = 4$ but since the molecules at the centre are related to those at the corners by simple translation, vibrational modes of the lattice correspond only to two molecules (Khanna et al., 1968). From group theory analysis (Wilson et al., 1955) the total vibrational modes for the point group $C_{4h}$ are

$$T = 3A_g + 5B_g + 5E_g + 4A_u + 4B_u + 4E_u$$

where $R_g$ represent Raman active-infrared inactive bonds and $R_u$ represent Raman inactive-infrared active bonds.

The 13 Raman active vibrations are further divided into two groups, internal modes and lattice (external) modes (Khanna et al., 1968). Table 4.6 gives the site and factor group splitting of all vibrational modes. This shows a maximum of 16 internal vibration peaks of which 7 are infrared inactive and 7 are Raman inactive. The scheelite
Table 4.6  Site and factor group splitting of the vibrational modes of the XO$_4^{2-}$ ions in the scheelite structure.

<table>
<thead>
<tr>
<th></th>
<th>$T_d$</th>
<th>$S_d$</th>
<th>$C_{4h}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-O symmetric stretch</td>
<td>$v_1 (A_g)$</td>
<td>A</td>
<td>$A_g$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A_u$</td>
</tr>
<tr>
<td>XO$_4$ def. bend</td>
<td>$v_2 (E)$</td>
<td>B</td>
<td>$A_u$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-O asymmetric bend</td>
<td>$v_3 (F_2)$</td>
<td>E</td>
<td>$E_u$</td>
</tr>
<tr>
<td>XO$_4$ asymmetric bend</td>
<td>$v_4 (F_2)$</td>
<td>E</td>
<td>$E_u$</td>
</tr>
</tbody>
</table>

structure has been shown to be one of the few for which correlation splitting of internal modes has been observed (Khanna et al., 1968). Table 4.7 shows the assignment of lattice and internal modes of the four main mineral members of the scheelite group by Khanna et al. (1968). It can be seen from Table 4.7 that variation in $v_1$ vibration modes between minerals is due to the nature of X in the XO$_4$ tetrahedra. Other mode variation is due largely to the nature of the cation, in this case lead versus calcium. Tables 4.8 and 4.9 lists previous Raman spectra data and assignments for wulfenite and stolzite.
Table 4.7  Internal vibrational modes and frequencies of minerals on the scheelite

<table>
<thead>
<tr>
<th>Isolated tetrahedron, $T_d$</th>
<th>tetrahedron in the lattice, $C_{4h}$</th>
<th>stolzite (PbWO$_4$)</th>
<th>wulfenite (PbMoO$_4$)</th>
<th>scheelite (CaWO$_4$)</th>
<th>powellite (CaMoO$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$ ($2A_1$)</td>
<td>$v_1$ ($A_g$)</td>
<td>900</td>
<td>868</td>
<td>911</td>
<td>878</td>
</tr>
<tr>
<td>$v_1$ ($B_u$)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$v_3$ ($2F_2$)</td>
<td>$v_3$ ($A_u$)</td>
<td></td>
<td></td>
<td>Raman inactive</td>
<td></td>
</tr>
<tr>
<td>$v_3$ ($B_g$)</td>
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<td>764</td>
<td>838</td>
<td>844</td>
</tr>
<tr>
<td>$v_3$ ($E_g$)</td>
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<td>744</td>
<td>795</td>
<td>794</td>
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<tr>
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<td></td>
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</tr>
<tr>
<td>$v_4$ ($2F_2$)</td>
<td>$v_4$ ($A_u$)</td>
<td></td>
<td></td>
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<tr>
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<td>348</td>
<td>397</td>
<td>390</td>
</tr>
<tr>
<td>$v_4$ ($E_g$)</td>
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<td>403</td>
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</tr>
<tr>
<td>$v_4$ ($E_u$)</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>$v_2$ ($2E$)</td>
<td>$v_2$ ($B_u$)</td>
<td></td>
<td></td>
<td>Raman inactive</td>
<td></td>
</tr>
<tr>
<td>$v_2$ ($A_g$)</td>
<td></td>
<td>322</td>
<td>314</td>
<td>333</td>
<td>322</td>
</tr>
<tr>
<td>$v_2$ ($B_g$)</td>
<td></td>
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<td>333</td>
<td>322</td>
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<tr>
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<td></td>
<td>Raman inactive</td>
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<tr>
<td>rotations</td>
<td>$E_u$</td>
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<td>189</td>
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<tr>
<td></td>
<td>$E_u$</td>
<td></td>
<td></td>
<td>Raman inactive</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.8  Internal MoO$_4^{2-}$ vibrational modes and frequencies in PbMoO$_4$.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
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<tr>
<td>$v_1$ ($2A_1$)</td>
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<td>870</td>
<td>868</td>
<td>872</td>
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<td>859$^a$</td>
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<td>770</td>
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<td>352</td>
<td>348</td>
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<td>$v_4$ ($E_g$)</td>
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<td>356</td>
<td>384</td>
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<tr>
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<td></td>
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<td>319</td>
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<td></td>
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<td>$A_g$</td>
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<td>171</td>
<td>164</td>
<td>n.r.</td>
<td>166</td>
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<tr>
<td></td>
<td>$E_g$</td>
<td>193</td>
<td>193</td>
<td>190</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

n.r.: not reported

$^a$ $v_1$ ($B_u$) and $v_2$ ($B_u$) bands should be Raman inactive, it has been suggested by Ross (1972) they are activated by stain in the sample and are visible as weak bands; $^b$ originally reported as the $v_2$ ($B_g$) band but correlated with $v_4$ ($B_g$) in other studies.
4.2.3.2 Raman spectroscopy of pure wulfenite

The various wulfenite spectra that have been studied were all typical of the scheelite structural group with the W atom being replaced by the slightly smaller Mo in the oxyanion, XO$_4^{2-}$, and the Ca$^{2+}$ ion being replaced by Pb$^{2+}$ ion as the cation. The isotyping of the crystal structure is clearly reflected in the Raman spectra (Figure 4.14). Assignment of the various bands in the region between 100 and 1000 cm$^{-1}$ closely follows the assignments valid for the scheelite spectrum as discussed above. Values for band assignments (Table 4.9) were in good agreement (within experiment error) of previously published values.

Orientation of wulfenite to the beam was important with intensities of various bands in each vibrational mode ($v_2$, $v_3$, and $v_4$) varying with orientation (Figure 4.14). The most intense band in all orientations was around 868-870 cm$^{-1}$ corresponding to $v_1(A_g)$. A very weak shoulder was present at 858 cm$^{-1}$. It varied slightly in intensity in different wulfenites, though still remained very weak. Ross (1972) and Klopogge and Frost (1999) suggested this shoulder was the $v_1(B_a)$ infrared band that is normally Raman inactive but becomes active due to strain.

The band occurring around 319 cm$^{-1}$ corresponds to $v_2(A_g)$ according to the literature (Khanna et al., 1968; Griffith, 1970; Efendiev et al., 1982). The second band at 351-353 cm$^{-1}$ has been assigned to the $v_4(B_g)$ (Khanna et al., 1968; Griffith, 1970; Efendiev et al., 1982). Klopogge and Frost (1999) and Ross (1972) reported that this band around the 348 cm$^{-1}$ corresponded instead to $v_2(B_g)$ which the other studies reported as overlapping the $v_2(A_g)$ band. Relative intensities of $v_2(A_g)$ and $v_4(B_g)$ vary with crystal orientation. The $v_4(B_g)$ band has greatest intensity when the beam is parallel to the c axis and the $v_2(A_g)$ band has greatest
Table 4.9  Internal $\text{WO}_4^{2-}$ vibrational modes and frequencies in PbWO$_4$.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
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<td>$v_1$ ($A_g$)</td>
<td>905</td>
<td>906</td>
<td>900</td>
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<tr>
<td></td>
<td>$v_1$ ($B_u$)</td>
<td>inactive</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_3$ ($2F_2$)</td>
<td>$v_3$ ($B_g$)</td>
<td>766</td>
<td>767</td>
<td>764</td>
</tr>
<tr>
<td></td>
<td>$v_3$ ($E_g$)</td>
<td>756</td>
<td>753</td>
<td>748</td>
</tr>
<tr>
<td>$v_4$ ($2F_2$)</td>
<td>$v_4$ ($B_g$)</td>
<td>358</td>
<td>337</td>
<td>348</td>
</tr>
<tr>
<td></td>
<td>$v_4$ ($E_g$)</td>
<td>358</td>
<td>360</td>
<td>353</td>
</tr>
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</tr>
<tr>
<td></td>
<td>$v_2$ ($A_g$)</td>
<td>328</td>
<td>329</td>
<td>322</td>
</tr>
<tr>
<td></td>
<td>$v_2$ ($B_g$)</td>
<td>328</td>
<td>329</td>
<td>322</td>
</tr>
<tr>
<td>rotations</td>
<td>$B_u$</td>
<td>inactive</td>
<td></td>
<td></td>
</tr>
<tr>
<td>($2F_1$)</td>
<td>$A_g$</td>
<td>179</td>
<td>158</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>$E_g$</td>
<td>194</td>
<td>187</td>
<td>n.r.</td>
</tr>
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</table>

n.r.: not reported.
Figure 4.14  Raman spectra of wulfenite from the Milford mine, Nevada, USA, showing variation in peak intensities with crystal orientation. A: beam parallel to the $c$ axis; B: beam at $45^\circ$ to $a$ and $c$ axis; C: beam parallel to the $a$ axis.
intensity (compared to the $v_1(A_g)$ band) when the crystal is orientated such that the beam is parallel to the $a$ axis and perpendicular to the $c$ axis. When the beam is orientated perpendicular to the $c$ axis the weak shoulder develops into a distinct peak at 354-356 cm$^{-1}$. This peak was not recorded by Ross (1972) or by Kloprogge and Frost (1999) in natural wulfenite but has been recorded by others in artificial material (Khanna et al., 1968; Efendiev et al., 1982). The band disappears when the beam is orientated parallel to the $c$ axis. Griffith (1970) and Khanna et al. (1968) assigned the band to $v_4(E_g)$, but Ross (1972) reported $v_4(E_g)$ around 384 cm$^{-1}$ in natural wulfenite. The existence of a band at 384 cm$^{-1}$ was not found in previous studies or in any of the wulfenites analysed in this study and hence its identity remains unknown.

Two bands at 748 and 768-770 cm$^{-1}$ are consistent with the literature values and correspond to $v_2(E_g)$ and $v_3(B_g)$ respectively. These bands show the greatest variation in intensity (with respect to each other) with varying crystal orientation (Figure 4.14). When the crystal is orientated such that the beam is parallel to $c$, $v_3(B_g)$ is the most intense band with $v_2(E_g)$ being observed only as a weak band or shoulder. However, when the beam is parallel to $a$ and perpendicular to $c$, $v_3(E_g)$ is the dominant $v_3$ band with the intensity of $v_2(B_g)$ less than half that of the $v_3(E_g)$ band.

Bands at 190 and 166 cm$^{-1}$ were not assigned by Ross (1972), but were assigned by Khanna et al. (1968) and Efendiev et al. (1982) as 2$F_I$ rotations $A_g$ and $E_g$. Similar bands were also observed for NaBi(MoO$_4$)$_2$ at 192 cm$^{-1}$ (Hanuza et al., 1995) and other compounds with the scheelite structure.
4.2.3.3 Raman spectroscopy of pure stolzite

The Raman spectra of stolzite was consistent with previous studies of pure lead tungstate and stolzites. The overall appearance of the spectra compared to the wulfenite spectra is very similar and hence the band assignments are the same for the lower wavenumbers. The most obvious difference between the spectra for stolzite and wulfenite is the position of \( v_1(A_g) \). In stolzite this occurs at 905 cm\(^{-1} \) rather than 870 cm\(^{-1} \). There is an overall shift in wavenumber with some of the lower frequency bands, particularly for \( v_2(B_g) \), \( v_4(E_g) \), and \( v_3(E_g) \) between stolzite and wulfenite. The \( v_2(B_g) \) mode shows the greatest displacement. There is no band or shoulder noted in any stolzite spectra that correspond to the wulfenite strain band at 859 cm\(^{-1} \). This suggests that there may be too little strain in most stolzite crystals to make this band active. As expected, sample orientation was again important. Overall influences on variations of band intensities due to orientation are the same as for wulfenite.

4.2.3.4 Raman spectroscopy of “chillagite” and other W/Mo substituted wulfenite/stolzites

It has been shown that wulfenite-stolzite forms a complete solid solution series (Section 4.2.1) and that numerous wulfenites and stolzite specimens lie somewhere between the two pure end members. This combination of tungstate and molybdate in the solid solution series was easily discernible in Raman spectra (Figure 4.15). A “chillagite” spectrum, in particular, resembles the combination of stolzite and wulfenite spectra. Two \( v_1 \) modes are observed; the \( v_1(A_g) \) band of the WO\(_4\) unit is observed at 906 cm\(^{-1} \) and the band at 870 cm\(^{-1} \) is \( v_1(A_g) \) of the MoO\(_4\) unit. These two bands make up 35 and 45%
Figure 4.15  Raman spectra of various tungstenian wulfenites and molybdenian stolzites: A: Red Cloud mine wulfenite; B: San Francisco mine tungstenian wulfenite; C: Chillagoe 'chillagite'; D: and E: Fat Jack mine molybdenian stolzite; F: Broken Hill stolzite.
relative intensity of the band profile in the 750 to 950 cm$^{-1}$ region. Thus it suggests that the “chillagite” sample contains about 56 mol% MoO$_3$ and 44 mol% WO$_3$. However the composition of this sample was only about 35-40 mol% WO$_3$. Thus the relative intensity percentages are not 1:1 where the MO$_4$ $v_1(A_g)$ band is more intense than the WO$_4$ $v_1(A_g)$ band for the same mol%.

Multiple low intensity bands are observed in the 740 to 780 cm$^{-1}$ region. Only two bands are observed at 767 and 747 cm$^{-1}$ and are assigned to $v_3(B_g)$ and $v_3(E_g)$ modes, respectively. Both $v_3(E_g)$ and $v_3(B_g)$ show a slight shift compared to the values for pure wulfenite and stolzite, such that the wavenumbers are between the values for the pure end members (Table 4.10) for each band. Two bands observed at 355 and 323 cm$^{-1}$ correspond to the $v_2(A_g)$ and $v_4(B_g)$ modes. The $v_2(A_g)$ frequency is also shifted and lies between the frequencies for the $v_2(A_g)$ modes of the pure end members.

Various wulfenites/stolzites with different Mo/W ratios were analysed using the Raman probe. It was found that, with changing Mo/W compositional ratios, the intensities of the MoO$_4$ $v_1(A_g)$ band versus WO$_4$ $v_1(A_g)$ band changed proportionally (Table 4.10 and Figure 4.15). For example wulfenite from the San Francisco mine, which contains a small amount of substituted WO$_3$ (about 10 mol%), displayed a typical wulfenite spectrum with a small peak centred at 905 cm$^{-1}$ and stolzite from the Fat Jack mine, which contains significant amounts of MoO$_3$ displayed a peak at 870 cm$^{-1}$. Once again, the actual intensity ratio was not directly proportional to the composition, with the MoO$_4$ $v_1(A_g)$ band being more intense than the WO$_4$ $v_1(A_g)$ band for the same composition. The positions of the WO$_4$ $v_1(A_g)$ (906 cm$^{-1}$) and the MoO$_4$ $v_1(A_g)$ bands (870 cm$^{-1}$) remained constant regardless of the varying intensities associated with
Table 4.10  The main measured Raman bands (cm$^{-1}$) in some natural intermediate members of the wulfenite-stolzite series.

<table>
<thead>
<tr>
<th></th>
<th>Los Lamentos wulfenite</th>
<th>San Francisco wulfenite</th>
<th>Chillagoe ‘chillagite’</th>
<th>Fat Jack stolzite</th>
<th>Fat Jack stolzite</th>
<th>Broken Hill stolzite</th>
<th>Cordillera stolzite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1 (A_g)^a$</td>
<td>no band</td>
<td>905</td>
<td>905</td>
<td>906</td>
<td>905</td>
<td>905</td>
<td>905</td>
</tr>
<tr>
<td>$v_1 (A_g)^b$</td>
<td>870</td>
<td>870</td>
<td>871</td>
<td>870</td>
<td>870</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$v_3 (B_g)$</td>
<td>768</td>
<td>765</td>
<td>767</td>
<td>765</td>
<td>767</td>
<td>766</td>
<td>766</td>
</tr>
<tr>
<td>$v_3 (E_g)$</td>
<td>745</td>
<td>746</td>
<td>749</td>
<td>sh</td>
<td>751</td>
<td>751</td>
<td>752</td>
</tr>
<tr>
<td>$v_4 (B_g)$</td>
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<td>355</td>
<td>356</td>
<td>358</td>
<td>357</td>
<td>358</td>
<td>360</td>
</tr>
<tr>
<td>$v_2 (A_g)$</td>
<td>319</td>
<td>323</td>
<td>325</td>
<td>325</td>
<td>328</td>
<td>328</td>
<td>330</td>
</tr>
</tbody>
</table>

$^a$WO$_4^{2-}$ $v_1$ band; $^b$MoO$_4^{2-}$ $v_1$ band.

compositional change of wulfenites/stolzites. Other vibrational modes ($v_2$, $v_3$ and $v_4$) between 200-800 cm$^{-1}$ showed a proportional shift between end member values depending on the sample’s relative W/Mo composition. This is highlighted by the $v_2(E_g)$ and $v_2(A_g)$ bands (Table 4.10).

From observations of changes in band positions and intensities of the intermediate members of the solid solution series it is concluded that the vibrational mode $v_1(A_g)$ has a dual behaviour in substituted specimens. The two separate $v_1(A_g)$ vibrations for WO$_4$ and MoO$_4$ groups can be interpreted as having localised independent vibrations for MoO$_4$/WO$_4$ substituted in the lattice. Other vibration frequencies are not independent in the lattice and show a single peak, which shifts according to the amount of substitution is seen rather than dual MoO$_4$/WO$_4$ peaks. A similar situation of the dual nature versus the
single nature of vibrational modes has been reported in artificial mixed crystals of the CaMo$_x$W$_{x-1}$O$_4$ solid solution series (Karaptyan et al., 1976).

### 4.2.3.5 Raman Spectroscopy of “chillagite” at 77K

The $v_1(A_g)$ band is observed at 906 cm$^{-1}$ for “chillagite” and shows a slight shift to 905 cm$^{-1}$ upon cooling to liquid nitrogen temperature. The bandwidth narrows from 7.0 to 4.9 cm$^{-1}$. By way of comparison, $v_1(A_g)$ bands for wulfenite and stolzite show no shift in frequencies at 77K. However, considerable band narrowing is observed for stolzite from 10.0 to 7.6 cm$^{-1}$. The $v_2(A_g)$ vibration is observed as a strong band at 323 cm$^{-1}$ for “chillagite”, at 319 cm$^{-1}$ for wulfenite and at 327 cm$^{-1}$ for stolzite. The bands show no shift in frequencies at 77K; however these minerals have bandwidths of 12.7, 10.4 and 12.5 cm$^{-1}$ which reduce to 9.4, 6.9 and 8.5 cm$^{-1}$ upon cooling to liquid nitrogen temperatures. The weak $v_4(B_g)$ band was observed at 355 cm$^{-1}$ for “chillagite” and at 351 cm$^{-1}$ for wulfenite. Again, no shift in position is observed upon cooling to 77K.

### 4.2.3.6 Raman spectroscopy of chromate-substituted wulfenite.

Limited substitution of chromate up to a few hundred parts per million has been observed in wulfenite from different locations (Haberlandt and Schroll, 1949; Mir-Mohammed, 1977; Edson, 1980; Bideaux, 1990). The low concentrations of chromate found in wulfenite are generally below the detection limits of most rapid quantitative non-destructive tests.

The chromate ion has a very distinct Raman spectrum with characteristic frequencies occurring between 350-500 and 800-950 cm$^{-1}$ (Gadsden, 1975). The main
\textbf{Figure 4.16} Raman spectra (700-950 cm$^{-1}$) of Whim Creek wulfenite showing the chromate band at 816-818 cm$^{-1}$. The blue line represents Whim creek wulfenite and the pink line represents Broken Hill molybdenian stolzite.

$v_1(A_g)$ band occurs around 820-850 cm$^{-1}$ in various compounds and this does not overlap any bands in the wulfenite spectrum. It was seen that small amounts (<0.2 mol\%) of substituted chromate could be easily be detected in anglesite (PbSO$_4$).

Significant amounts of chromium (up to 1200 parts per million) have been detected in some of the wulfenites from the Whim Creek mine Australia (see Section 4.2.2.2). Other wulfenites from the same location did not contain any chromium. Raman studies of both types of wulfenite found that all those that contained chromium had a distinct band around 818 cm$^{-1}$ (Figure 4.16). The intensity of this band varied slightly depending on the amount of chromium present. In an orange-red stolzite crystal from Broken Hill there is a very prominent band at 818 cm$^{-1}$ which varies in intensity across the crystal. It reaches a maximum intensity where both the MoO$_4$ and WO$_4$ $v_1(A_g)$ bands
are equal in intensity. Probe analyses of this crystal found significant amounts of chromium which varied across the crystal. A similar band was present in other red-orange wulfenites including an orange wulfenite from Tiger which is known to contain trace amounts of chromium (Williams, 1990). Chromium-bearing wulfenites from the Red Cloud mine, Arizona, did not show this extra band at 818 cm\(^{-1}\) at room temperature. However, its Raman spectrum at 77 K showed a weak but distinct band at 818 cm\(^{-1}\). Chromium contents of the Red Cloud wulfenites are generally much lower than those of Whim Creek wulfenite, being less than 0.01 wt % (Edson, 1980) and hence the band would be lost in background noise at room temperature. When background noise is greatly reduced (by lowering the temperature) the sensitivity of the instrument is greatly improved and thus low intensity peaks are easily discernible.

The occurrence of this extra band in wulfenites with chromium suggests that the band is related to a vibrational mode of substituted chromate in the lattice, probably \(v_J(A_g)\). In crocoite the \(v_1\) and \(v_3\) vibrational modes are centred at 836-838 cm\(^{-1}\). The MoO\(_4\) 818 cm\(^{-1}\) band is much more intense (particularly in the Broken Hill stolzite) than expected for its very low concentration relative to MoO\(_4\) and WO\(_4\) in wulfenite/stolzite. However, a similar situation occurs in chromium-substituted anglesite where very prominent additional bands are present in the spectra (particularly at 847 cm\(^{-1}\)). The main chromate band (\(v_J(A_g)\)) is shifted in anglesite (847 cm\(^{-1}\)) compared to crocoite (PbCrO\(_4\)) (836-838 cm\(^{-1}\)) due to different symmetries in the lattices of anglesite (barite structure, \(Pnma\)) and crocoite (monazite structure, \(P2_1/n\)). This also accounts for the shift in the chromate \(v_J(A_f)\) band in wulfenite (scheelite structure, \(I4/a\)) compared to crocoite or chromate substituted anglesite.

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The \( v_1(A_1) \) chromate band does not shift with varying compositions, and this vibrational band is thus localised. It is independent in the lattice as was the case for WO\(_4\) and MoO\(_4\) \( v_1(A_1) \) bands.

The significance of these observations in the Raman spectra of the wulfenite-stolzite solid solution series demonstrates that the Raman microprobe can provide a very quick, non-destructive method for analysing substitution in minerals down to quite low concentration levels.

4.3 REFERENCES


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CHAPTER FIVE

THE SINGLE-CRYSTAL X-RAY STRUCTURE OF POWELLITE-I\(^4\)
FROM TSUMEB, NAMIBIA AND THE SOLID SOLUTION PHENOMENON
IN THE POWELLITE (CaMoO\(_4\)) -SCHEELITE (CaWO\(_4\)) SERIES

5.0 INTRODUCTION

Powellite is the naturally occurring, tetragonal molybdate end-member of the CaWO\(_4\)-CaMoO\(_4\) solid solution series and scheelite the calcium tungstate end-member. There are no other reported naturally occurring polymorphs of either CaWO\(_4\) or CaMoO\(_4\) though monoclinic forms have been synthesised.

Powellite usually occurs as an alteration product after primary molybdenum minerals such as molybdenite (MoS\(_2\)), which powellite commonly pseudomorphs. It has also been reported as altered vugh fillings (Palache et al., 1951). Apart from massive alteration material it can also occur as pyramidal and tabular crystals in oxide zones (Figure 5.1) (Roberts et al., 1990). Scheelite is much more common than powellite, occurring in a variety of geological environments including granitic pegmatites, contact metasomotic rocks and hydrothermal veins (Palache et al., 1951; Hsu and Galli, 1973). It commonly occurs as bipyramidal crystals and more rarely in tabular habits (Roberts et al., 1990). Scheelite usually forms part of the primary mineralisation (usually forming at high temperatures). However, it has been reported as a secondary mineral occurring as an alteration product, forming pseudomorphs after wolframite (Palache et al., 1951) and on weathered material (P. A. Williams, pers. comm.). Identification of scheelite and powellite is often based on characteristic fluorescence properties with scheelite being blue under short wave ultraviolet light and powellite being yellow.
Figure 5.1  Powellite crystals from Tsumeb, Namibia (crystals are 0.5 mm across).

Both scheelite and powellite are structurally isomorphous with stolzite-wulfenite. They belong to the scheelite structure group, crystallizing in the tetragonal space group $I4_1/a$.

The arrangement of atoms and structural coordination of powellite and scheelite is essentially the same as wulfenite-stolzite which has been previously outlined in Section 4.0. Dickinson (1920) and Vegard (1925) conducted the first structural investigations on scheelite and powellite, respectively, and established both as being structurally isomorphous with wulfenite and stolzite. Sillen and Nylander (1943) reviewed the crystal structures of members of the scheelite group including scheelite and powellite. They attempted to resolve the positions of the oxygen atoms in the structure and concluded that the oxygen coordinates were nearly constant fractions of the $a$ and $c$ unit cell dimensions.
The first reliable single-crystal structure determination of powellite in space group $I4_1/a$ was reported by Aleksandrov et al. (1968) using X-ray diffraction techniques and hydrothermally grown crystals. They refined the structure with $Z = 4$ and cell parameters of $a = 5.224$ Å and $b = 11.430$ Å. Ca-O bond lengths were 2.45(4) and 2.48(4) Å. Mo-O was 1.76 Å and O-Mo-O bond angles were 114°50' and 107°. Aleksandrov et al. (1968) concluded that the structure was the same as that of scheelite and that the geometry of the MoO$_4^{2-}$ tetrahedron was nearly regular. Gürmen et al. (1971), using an artificially grown crystal, refined the structure of powellite using neutron diffraction methods and reported values similar to those of Aleksandrov et al. (1968) (Table 5.1). More recent studies on CaMoO$_4$ (Sleight, 1972; Oeder et al., 1980; Christofilos et al., 1995) have also reported cell parameters for the synthetic compound (Table 5.1). There have been no reports in the literature of a single crystal refinement for natural powellite though cell dimensions have been reported for a near pure powellite crystal from Nasik, India (Kothavada, 1982; Hurlbut, 1982) and a powellite with 10 wt% tungsten from Scotland (Battery and Moss, 1962).

Both Zalkin and Templeton (1964) and Kay et al. (1964) reported accurate cell refinements of synthetic CaWO$_4$ in space group $I4_1/a$. Zalkin and Templeton (1964) reported cell dimensions of $a = 5.243 \pm 0.002$ and $c = 11.376 \pm 0.003$ Å from X-ray data. Ca-O bond lengths were 2.44 and 2.46 Å. Mo-O was 1.78 Å and O-Mo-O bond angles were 113.4° and 107.5°. Using neutron diffraction data, Kay et al. (1964) reported similar values. As with CaMoO$_4$, other X-ray studies of the system have all reported similar cell parameters (Sleight, 1972; Oeder et al., 1980) (Table 5.2).

Substitution of tungsten/molybdenum in the natural powellite-scheelite series has been reported by various authors (Melville, 1891; Lacroix, 1940; Kerr, 1946; Palache et al., 1951; Vermaas, 1952; Konakov, 1967, 1972; Hsu and Galli, 1973;
Table 5.1  X-ray diffraction \( d \)-spacings and \( hkl \) assignments for scheelite and powellite (relative intensities in parentheses).

<table>
<thead>
<tr>
<th>scheelite(^a) CaWO(_4)</th>
<th>powellite(^b) CaMoO(_4)</th>
<th>( hkl )</th>
</tr>
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<tr>
<td>4.76 (55)</td>
<td>4.76 (25)</td>
<td>101</td>
</tr>
<tr>
<td>3.10 (100)</td>
<td>3.10 (100)</td>
<td>112</td>
</tr>
<tr>
<td>3.0072 (30)</td>
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<td>103</td>
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<tr>
<td>2.844 (14)</td>
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</tr>
<tr>
<td>2.622 (25)</td>
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<td>2.377 (4)</td>
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<tr>
<td>2.296 (20)</td>
<td>2.290 (10)</td>
<td>211</td>
</tr>
<tr>
<td>2.256 (4)</td>
<td>2.262 (6)</td>
<td>114</td>
</tr>
<tr>
<td>2.0864 (6)</td>
<td>2.094 (2)</td>
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</tr>
<tr>
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<td>1.993 (6)</td>
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<td>1.9278 (30)</td>
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<tr>
<td>1.2488 (14)</td>
<td>1.254 (8)</td>
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</tr>
</tbody>
</table>

\(^a\) International Centre for Diffraction Data card number 19-708; \(^b\) International Centre for Diffraction Data card number 8-475.
Brugger et al., 1998). However, the true extent of the solid solution series is unclear
and, in some respects, controversial. Palache et al. (1951) noted an apparent miscibility
gap together with frequent compositional zoning. The original powellite specimen
described by Melville (1891) contained about 10 wt% tungsten. Battery and Moss (1962)
also reported a tungstenian powellite with 10 wt% tungsten. Zoning, however, has not
been reported in the powellite-rich end members.

Lacroix (1940) described a mineral with a composition intermediate between
scheelite and powellite with a MoO₃ of 24.01 wt % and termed it “seyrigite”. “Seyrigite”,
like “chillagite” was not accepted as a valid mineral but rather a Mo-rich scheelite
variety. Homogeneous molybdenum substitution in scheelite (“molybdoscheelite”) has
been reported by various authors (Kerr, 1946; Palache et al., 1951; Vermaas, 1952;
Brugger et al., 1998). Kerr (1946) reported scheelite samples with MoO₃ compositions
ranging from 1.70 to 34.25 wt %. This suggests that the series may be continuous
between scheelite and powellite. However Konokov (1967, 1972) noted that this
substitution was limited to 1.62 mol% Mo, a result in accord with observations of Kempe
and Wolf (1989) concerning exsolution laths of molybdenian scheelite (“seyrigite”)
containing 44-46 mol% Mo found in “molybdoscheelite,” the latter containing 1.1-1.7
mol% Mo overall. Hsu and Galli (1973) analysed various scheelite-powellite samples
from numerous locations in the western United States of America. They found that
minerals in the series which occurred in contact-metasomatic rocks displayed the greatest
compositional range in terms of W:Mo ratios with compositions up to 20 mol% Mo (one
anomalous sample contained 60 mol% Mo). The majority of samples contained less than
5 mol% Mo. Nearly pure scheelite was associated with granite pegmatites and
hydrothermal veins with most containing molybdenum below
Table 5.2  Previously studied unit cell parameters for tetragonal CaMoO$_4$

<table>
<thead>
<tr>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>volume (Å$^3$)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.23</td>
<td>11.44</td>
<td>2.187</td>
<td>312.92</td>
<td>Vegard (1925)</td>
</tr>
<tr>
<td>5.213</td>
<td>11.426</td>
<td>2.192</td>
<td>310.51</td>
<td>Sillen and Nylander (1943)</td>
</tr>
<tr>
<td>5.20</td>
<td>11.43</td>
<td>2.198</td>
<td>309.07</td>
<td>Battery and Moss (1962)</td>
</tr>
<tr>
<td>5.224</td>
<td>11.430</td>
<td>2.188</td>
<td>311.93</td>
<td>Aleksandrov et al., (1968)</td>
</tr>
<tr>
<td>5.226</td>
<td>11.43</td>
<td>2.187</td>
<td>312.17</td>
<td>Güremen et al. (1971)</td>
</tr>
<tr>
<td>5.226</td>
<td>11.434</td>
<td>2.188</td>
<td>312.2</td>
<td>Sleight (1972)</td>
</tr>
<tr>
<td>5.21</td>
<td>11.43</td>
<td>2.194</td>
<td>310.26</td>
<td>Oeder et al. (1980)</td>
</tr>
<tr>
<td>5.23</td>
<td>11.44</td>
<td>2.187</td>
<td>312.92</td>
<td>Hurlbut (1982)</td>
</tr>
</tbody>
</table>

Table 5.3  Previously studied unit cell parameters for tetragonal CaWO$_4$.

<table>
<thead>
<tr>
<th>$a$ (Å)</th>
<th>$c$(Å)</th>
<th>$c/a$</th>
<th>volume (Å$^3$)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.246</td>
<td>11.349</td>
<td>2.165</td>
<td>312.33</td>
<td>Aanerud (1931)</td>
</tr>
<tr>
<td>5.26</td>
<td>11.35</td>
<td>2.158</td>
<td>314.03</td>
<td>Vegard (1925)</td>
</tr>
<tr>
<td>5.230</td>
<td>11.348</td>
<td>2.170</td>
<td>310.04</td>
<td>Sillen and Nylander (1943)</td>
</tr>
<tr>
<td>5.243</td>
<td>11.376</td>
<td>2.170</td>
<td>312.72</td>
<td>Zalkin and Templeton (1964)</td>
</tr>
<tr>
<td>5.242</td>
<td>11.376</td>
<td>2.170</td>
<td>312.60</td>
<td>Sleight (1972)</td>
</tr>
<tr>
<td>5.242</td>
<td>11.372</td>
<td>2.169</td>
<td>312.47</td>
<td>Powder diffraction File No. 7-210</td>
</tr>
</tbody>
</table>
detection limits; no sample exceeded 4 mol% Mo. Hsu and Galli (1973) also reported that pure powellite occurring as vugh fillings in altered rhyolite. Apart from powellite occurring as an alteration product of molybdenite, Hsu and Galli (1973) made no mention of the relationship of powellite and scheelite in the oxide zone. However, a molybdenum-bearing scheelite has recently been found in the oxide zone at Elsmore, New South Wales Australia (P. A. Williams, pers. comm.). Brugger et al. (1998) reported a continuous range of substituted scheelite-powellite grains in a regionally metamorphosed Fe-Mn exhalative deposit embedded in limestone ranging from 28-70 mol% Mo. The grains showed a two stage chemical zonation. Vermaas (1952) and Kukui et al. (1967) synthesised, from melts, a number of intermediate members of the CaWO$_4$-CaMoO$_4$ series and reported that these compounds were not mixtures. Oeder et al. (1980) synthesised a range of high temperature crystals in the CaWO$_4$-CaMoO$_4$ series using the Czochralski method and also reported that the series was complete. Studies by Gramenitskii et al. (1980) and Tobelko et al. (1983) reported that a miscibility gap existed in the series, which decreased with increasing temperature until 773 K, at which temperature the series was continuous. However, Shoji and Sasaki (1978) and Tyson et al. (1988) synthesised the series from hot aqueous solutions and reported that the series was complete.

It has been well established by various authors that substitution of less 0.5 mol% of Mo in both natural and artificial scheelite changes the fluorescence colour from blue to white-yellow (Greenwood, 1943; Vermaas, 1952; Konokov, 1967; Hsu and Galli, 1973; Shoji and Sasaki, 1978; Tyson et al., 1988; Kempe and Wolf, 1989). The changes in fluorescence colour with increasing Mo content continue to about 10 mol% CaMoO$_4$ when the colour (yellow) remains constant for the remainder of the series. Hsu and Galli (1973) suggest that many reports of powellite in the literature based solely on
fluorescence could be misleading and that rather than pure powellite the samples could be a Mo-rich scheelite. Occasionally in contact-metasomatic assemblages, scheelite grains fluoresce two separate colours: blue (scheelite) and white-yellow (Mo-rich scheelite) (Greenwood, 1943; Hsu and Galli, 1973; Crane, 1990). It has also been observed by various authors that compositional zonation occurs in individual scheelite grains based on observed variations in fluorescence (Konokov, 1967; Hsu and Galli, 1973; Kempe and Wolf, 1989; Crane, 1990).

In the natural powellite-scheelite series there are few reports of significant substitution of other elements above trace levels. It has been noted by various authors that scheelites can contain significant amounts of rare earth elements, particularly Y, substituting for Ca$^{2+}$ (Semenov, 1963; Hsu and Galli, 1973; Brugger et al., 1998). Brugger et al. (1998) reported significant amounts of As$_2$O$_5$ substitution (up to 4 wt%) in the scheelite-powellite minerals from the Fianel Fe-Mn deposit in the Swiss Alps. The charge difference was balanced by the equal amounts of Y$_2$O$_3$ substitution in the grains (up to 2.5 wt%).

In studies using artificial mixed crystals Chang (1967) and Hsu (1981) found large miscibility gaps in the various systems under ambient conditions. However the solid solution series generally became continuous at higher temperatures (greater than 950 K). The PbWO$_4$-CaWO$_4$ series was found to be continuous above 998 K (Hsu, 1981), but below 778 K a miscibility gap occurs between 10-90 mol% PbWO$_4$. Using Czochralski method to grow mixed crystals, Oeder et al. (1980) reported a large miscibility gap in the PbMoO$_4$-CaMoO$_4$ series between 10-50 mol% PbMoO$_4$. They did not report whether the size of the miscibility gap increased with decreasing temperature.

As part of the study of the natural wulfenite-stolzite series a crystal of powellite from the oxide zone of Tsumeb, Namibia was obtained. Since there had been no recent
reports of single-crystal structure refinement of powellite or reports of any single crystal refinement of natural powellite, an accurate single crystal refinement was undertaken on the crystal. The crystal studied was a plumbian tungstenian powellite from Tsumeb, Namibia. Hibbs et al. (2000) were the first to report a member of the scheelite group of minerals (“chillagite”, tungstenian wulfenite) occurring in the space group $\overline{4}$ rather than the accepted $I4_1/a$ (see section 3.0).

Most studies of the artificial scheelite-powellite series have involved crystals synthesised at high temperatures. Studies on the natural scheelite-powellite series have all involved crystals that have formed at high temperatures from igneous intrusions or contact-metasomatism. Substituted powellite/scheelite between 40 and 90 mol% Mo is extremely rare. With the occurrence of a tungstenian powellite from the Tsumeb oxide zone, the gap in the natural scheelite-powellite series and the conflicting reports of the extent of the PbMoO$_4$-CaMoO$_4$ solid solution series at ambient temperatures a reinvestigation of the series was undertaken to establish the extent of continuity. This will provide a better understanding of the role of the series in influencing mineral formation, groundwater geochemistry and the dispersion of tungsten and molybdenum throughout the oxide zone.

5.1 METHODS

5.1.1 EXPERIMENTAL DETAILS AND STRUCTURE SOLUTION

A few single crystals removed from a specimen of powellite from Tsumeb, Namibia, in the collection of the author were shown by X-ray precession photography to correspond to the dimensions of the powellite unit cell. However, total reflectance X-ray fluorescence (TRXRF) spectrometry, using a Diffraction Technology prototype instrument
equipped with an Amptek XR-CR100 Pellitier-type energy dispersive X-ray detection system and capable of analysing micro samples, found small amounts of both Pb and W in all these powellite crystals. Using pure PbWO₄, CaWO₄ and a tungstenian wulfenite of known composition as standards, an average of three analyses (%) gave CaO, 27.0; PbO, 1.7; MoO₃, 69.3; WO₃, 1.9; sum = 99.9, corresponding to a formula of (Ca₀.₉₈Pb₀.₀₂)(Mo₀.₉₈W₀.₀₂)O₄ which was in excellent agreement with the electron microprobe analysis (Appendix 5).

The crystal chosen for data collection was a yellow 0.35 x 0.30 x 0.20 mm prism showing reasonably well-developed faces, where this moderate sized crystal was selected in order to facilitate any subsequent SEM and microprobe analyses. The crystal was examined by SEM/EDS methods on a Jeol T330 SEM equipped with EDS and X-ray mapping facilities supported by Moran Scientific software. The presence of small amounts of Pb and W was confirmed but no evidence of zoning or inclusions was found. Rather, X-ray maps showed the two elements to be distributed uniformly on all the faces of the crystal. Initial unit cell parameters were refined by a least-squares fit to diffractometer data. X-ray intensity data were collected at 293 K on an Enraf-Nonius CAD-4 diffractometer with MoKα radiation (λ = 0.71073Å). Intensity data were corrected for Lorentz and polarization effects by the program XPREP (© Siemens Energy and Automation Inc., Analytical Instrumentation, Madison, WI, USA; now Bruker), and for absorption using the psi scan method. A total of 713 measured reflections were merged to give 325 independent reflections with I > 2σ(I) and these were used for the final structure refinement. Experimental details of the data collection and structure refinement are given in Table 5.4.

The program package SHELX-97 (Sheldrick, 1997) was used for the subsequent structure refinement using full-matrix least-squares techniques in which the function
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>Ca$<em>{0.98}$Pb$</em>{0.02}$Mo$<em>{0.98}$W$</em>{0.02}$O$_4$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>205.12</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>$Iar{4}$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 5.222(1)$ Å, $c = 11.428(2)$ Å</td>
</tr>
<tr>
<td>Volume</td>
<td>$311.6(1)$ Å³</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>4.372 Mg m$^{-3}$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>7.37 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>383.5</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.35 x 0.30 x 0.20 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.57 to 26.26°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-6≤h≤6, 0≤k≤6, -14≤l≤14</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>713</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>325 [R(int) = 0.0923]</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Psi scan</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>325 / 0 / 28</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>0.863</td>
</tr>
<tr>
<td>Final $R$ indices [I&gt;2σ(I)]</td>
<td>$R_1 = 0.0490$, $R_w = 0.1206$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.0495$, $R_w = 0.1221$</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.043(8)</td>
</tr>
</tbody>
</table>

$\Sigma w(F_o^2-F_c^2)^2$ was minimized and the weighting scheme used in the final cycles of refinement (as defined by SHELX-97) gave a uniform analysis of $F_c^2$. Although the space group was not $I4_1/a$ but $I\bar{4}$, as evidenced by a handful of 'extra' reflections, an initial isotropic structure refinement was performed in $I4_1/a$ using the well-established atomic coordinates for AMO$_4$ scheelite-type structures with the origin at $\bar{4}$ (Gürmen et al., 1971). With an extinction correction applied this gave an $R_1$ of 0.098 but the resulting somewhat low thermal parameters for both Ca and Mo clearly indicated the presence of a slightly greater electron density at each of these metal atom sites, as expected from the
Table 5.5.  Final atomic coordinates, site occupancy factors and equivalent isotropic displacement parameters (Å²) for Tsumeb powellite, with estimated standard deviations in parentheses. $U_{eq}$ is defined as one third of the trace of the orthogonalised $U_{ij}$ tensor.

(a) Tsumeb powellite refined in space group $I4_1/a$

<table>
<thead>
<tr>
<th>Atom</th>
<th>position</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>4b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.0114(14)</td>
</tr>
<tr>
<td>Mo</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0089(10)</td>
</tr>
<tr>
<td>O</td>
<td>16f</td>
<td>0.2421(5)</td>
<td>0.1482(5)</td>
<td>0.0825(2)</td>
<td>0.0143(12)</td>
</tr>
</tbody>
</table>

(b) Tsumeb powellite refined in space group $I4$

<table>
<thead>
<tr>
<th>Atom</th>
<th>position</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>2b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.0140(13)</td>
</tr>
<tr>
<td>Ca2</td>
<td>2d</td>
<td>0</td>
<td>0.5</td>
<td>0.75</td>
<td>0.0099(13)</td>
</tr>
<tr>
<td>Mo1</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0083(7)</td>
</tr>
<tr>
<td>Mo2</td>
<td>2c</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.0099(8)</td>
</tr>
<tr>
<td>O1</td>
<td>8g</td>
<td>0.2374(7)</td>
<td>0.1470(8)</td>
<td>0.0866(3)</td>
<td>0.0122(9)</td>
</tr>
<tr>
<td>O2</td>
<td>8g</td>
<td>0.2469(7)</td>
<td>0.6478(8)</td>
<td>0.1683(4)</td>
<td>0.0140(9)</td>
</tr>
</tbody>
</table>

Note: In the above tables the Ca-sites are occupied by 98% Ca and 2% Pb, and the Mo-sites are occupied by 98% Mo and 2% W.

Elemental analysis of the crystals. With occupancies of the metal atom sites set at Ca$_{0.98}$Pb$_{0.02}$ and Mo$_{0.98}$W$_{0.02}$, and after several low angle reflections (004, 024 and 112) which were still badly affected by extinction were omitted, an anisotropic refinement converged smoothly to an $R_1$ of 0.055. In order to take into account the small but significant number of symmetry-forbidden reflections in $I4_1/a$, viz:

00l: 002, 006, 00 10

hko: 110, 130, 130, 150, 150, 330, 350, 350
the structure was then finally refined in space group \( I\bar{4} \) and this converged to \( R_1 = 0.049 \) and \( R_w = 0.121 \) \([= \frac{\Sigma w(F_o^{2} - F_c^{2})^2}{\Sigma w(F_o^{2})^2}^{1/2}]\) with weighing factor \( (w) \) determined by SHELX-97 for the 325 observed data. Full details are given in Table 5.4 and final atomic parameters are given in Table 5.5. A full list of observed and calculated structure factors are presented in Appendix 4. It must be emphasised the symmetry-forbidden reflections for space group \( I4_1/\alpha \) that were observed in this case are not due to Renninger effects and there are a significant number of them. The fact is unambiguously established by virtue of the equivalents observed, with quite different orientations of the diffractometer circles, during the collection of a hemisphere of reflection data. These included the equivalents 002 and 00\( \bar{2} \), 006 and 00\( \bar{6} \), 00 10 and 00 \( \bar{1}0 \), and 110 and \( \bar{1}10 \). In addition, the reflections 130, \( \bar{1}30 \), 150 and \( \bar{1}50 \) were each measured twice, in different orientations, during the course of the data collection.

5.1.2 SYNTHESIS AND IDENTIFICATION OF THE CALCIUM (II)

MOLYBDATE- CALCIUM (II) TUNGSTATE SOILD SOLUTION SERIES

A range of solutions with tungstate to molybdate ratios varying from 0:100 to 100:0 were made up from aqueous 0.100 M Na\(_2\)WO\(_4\) and 0.100 M Na\(_2\)MoO\(_4\). The solutions were mixed in various proportions to a total volume of 25.0 cm\(^3\). Then, 25.0 cm\(^3\) of aqueous 0.100 M Ca(CH\(_3\)COO)\(_2\) solution was added to the tungstate/molybdate solution with constant stirring. Ca(CH\(_3\)COO)\(_2\) was used to maintain a slightly basic solution to prevent polymerisation of WO\(_4\)\(^{2-}\) and MoO\(_4\)\(^{2-}\) groups. All solutions were digested for 2 hours at 358 K. After digestion, precipitates were filtered off using a porosity 4 Pyrex glass sinter, washed with water then acetone, sucked dry at the pump and then oven dried for 24 hours at 373 K. After drying, precipitates were subjected to
powder X-ray diffraction analysis.

Powder X-ray diffraction measurements were carried out with a Philips PW1925-20 powder diffractometer using CuKα radiation (λ = 1.5418Å) and pure quartz (SiO₂) as internal standard. The Traces software package (Diffraction Technology Pty. Ltd.) was used to analyse the data. Unit cell parameters were refined using the least-squares program LAPOD (Langford, 1973).

5.2 DISCUSSION

5.2.1 CRYSTAL STRUCTURE

The AMO₄ scheelite-type structure adopted by powellite-I₄̅ is most simply described as a close packing of tetrahedral MO₄²⁻ anions (M = Mo or W) and A²⁺ cations (Ca or Pb). It may be assumed that the small amounts (2 mol%) of both W and Pb found to be present in the structure are disordered over the two types of metal atom site which are primarily occupied by Mo and Ca respectively. In the lattice the MO₄²⁻ anions are slightly distorted tetrahedra although the crystal symmetry constrains the four M-O bonds to be equal. These tetrahedra are then linked through A-O bonds, with each Ca (or Pb) atom having trisdisphenoidal 8-coordination. Relevant structural parameters for refinement in both I₄̅/a and I₄̅ are listed in Table 5.6 and 5.7, and not unexpectedly the structure as refined in I₄̅/a is in excellent agreement with that reported for CaMoO₄ by Gürmén et al. (1971). However, when refined in I₄̅ the additional crystallographic freedom allows the two independent tetrahedral MO₄²⁻ anions to adopt a subtly different angular geometry. The distortion in the tetrahedral angles for one of the anions (M1) is significantly reduced and has now moved closer to that found in PbMoO₄ (Hibbs et al., 2000) and CaWO₄ (Gürmén et al., 1971). With the other anion (M2) there is little
Table 5.6  Bond lengths (Å) and angles (°) for Tsumeb powellite with estimated standard deviations in parentheses.

(a) Tsumeb powellite refined in space group I41/a

\[
\begin{array}{ccc}
M - O & 1.757(2) & O - M - O & 106.75(6), 115.06(13) \\
A - O & 2.465(3) \\
& 2.465(2) \\
\end{array}
\]

(b) Tsumeb powellite refined in space group I\bar{4}

\[
\begin{array}{ccc}
M1 - O1 & 1.762(4) & O1 - M1 - O1 & 108.37(13), 111.7(3) \\
M2 - O2 & 1.769(4) & O2 - M2 - O2 & 106.18(13), 116.3(3) \\
A1 - O1 & 2.501(4) \\
A1 - O2 & 2.458(4) \\
A2 - O1 & 2.441(4) \\
A2 - O2 & 2.450(4) \\
\end{array}
\]

Note: In the above, the atom nomenclature refers to the AMO₄ general formula for a scheelite-type structure, where in the present study A has the composition Ca₀.₉₈Pb₀.₀₂ and M has the composition Mo₀.₉₈W₀.₀₂.

Table 5.7  Anisotropic displacement parameters (Å² x 10³) for Tsumeb powellite-I\bar{4}.
The anisotropic displacement factor exponent takes the form:
\[-2\pi^2 [ h^2 a^*^2 U_{11} + ... + 2 h k a^* b^* U_{12} ] \]

\[
\begin{array}{cccccc}
  & U_{11} & U_{22} & U_{33} & U_{23} & U_{13} & U_{12} \\
Mo(1) & 5(1) & 5(1) & 14(1) & 0 & 0 & 0 \\
Mo(2) & 3(1) & 3(1) & 22(1) & 0 & 0 & 0 \\
Ca(1) & 8(2) & 8(2) & 24(2) & 0 & 0 & 0 \\
Ca(2) & 7(2) & 7(2) & 13(2) & 0 & 0 & 0 \\
O(1) & 12(2) & 14(2) & 11(2) & -3(2) & -4(2) & 2(2) \\
O(2) & 5(2) & 7(2) & 29(2) & -3(2) & 1(2) & -2(2) \\
\end{array}
\]
change from the $I4_1/a$ situation. Finally, due primarily to the relatively small amount
(2 mol%) of W which replaces Mo in powellite-$I\bar{4}$ from Tsumeb, in the current
investigation it has not been possible to determine whether the Mo:W ratio in the two
independent $\text{MoO}_4^{2-}$ anion sites is significantly different, as was found in the tungstenian
wulfenite-$I\bar{4}$ from Chillagoe (which overall contained some 34 mol% W).

In terms of structural relationships, some of the differences in the series may be
due to the existence of some members in the alternative space group $I\bar{4}$. The present
study does not resolve these difficulties but attention is drawn to the study of Gürmen et
al. (1971). Their neutron diffraction studies of members of the scheelite group gave
results that were compatible with space group $I4_1/a$ “...except for a few very weak
reflections. These we have attributed to multiple scattering” (author’s italics). In the light
of the current findings concerning wulfenite-$I\bar{4}$ and powellite-$I\bar{4}$, it now seems unlikely
that these are not necessarily Renninger effects, and indeed it is probable that both
tetragonal space groups may be adopted for members of the scheelite group.

It is unknown whether phases crystallizing in the lower symmetry space group
($I\bar{4}$) are metastable under all conditions or whether certain patterns of substitution serve
to alter the precise symmetry of the thermodynamically stable phase.

5.2.2 SYNTHESIS AND IDENTIFICATION OF THE CALCIUM (II)
MOLYBDATE- CALCIUM (II) TUNGSTATE SOLID SOLUTION SERIES

5.2.2.1 Synthesised pure end members

The precipitate resulting from the mixing of calcium acetate and sodium
molybdate solutions yielded a white powder with the typical yellow fluorescence of
powellite under short wave ultraviolet light. The powder X-ray diffraction pattern of pure calcium molybdate (Figure 5.2a) gave d-spacing values in excellent agreement with previously published values. Refined cell parameters were $a = 5.227(1)$ and $c = 11.448(3)$ Å.

The precipitate resulting from the mixing of calcium acetate and sodium tungstate solutions yielded a very fine white powder. Fluorescence was a bluish-white colour typical of scheelite under short wave ultraviolet light. The powder X-ray diffraction pattern of digested precipitated pure calcium tungstate (Figure 5.2b) gave refined cell parameters of $a = 5.248(1)$, $c = 11.371(4)$ Å.

As expected, the artificial calcium tungstate/molybdate parameter trends were consistent with trends outlined by Sleight (1972) for the scheelite group. The $a$ axis is shorter in the molybdate than in the tungstate and vice versa for the $c$ axis. Except for cadmium molybdate, the pair has the smallest cell parameters in the scheelite group (Sleight, 1972). There is very little difference in the unit cell volume between calcium tungstate and calcium molybdate (0.3 Å$^3$) as compared to the difference between lead tungstate and lead molybdate (1.7 Å$^3$).

Apart from the minor displacement of the peak positions and intensities, the two X-ray diffraction patterns (Figure 5.2a, b) are very similar with only the (105) peak in calcium tungstate not being observed in calcium molybdate. Unlike the case with lead tungstate the (101) peak is present in calcium tungstate and does not vary very much in relative intensity with increasing molybdate content.

5.2.2.2 Synthesis of intermediate members.

All intermediate members of the solid solution series were easily precipitated and formed fine white powders which were identical in appearance to the pure end
Figure 5.2  X-ray powder diffraction traces between 17-60° 2θ for A: CaWO₄ and B: CaMoO₄ synthesised at under ambient conditions (Q indicates the quartz standard peaks).
members.

Intermediate compounds all appear to be stable over time. Blue fluorescence was only observed for 100 mol% WO$_4^{2-}$; it was replaced by a yellowish-white fluorescence at 90 mol% WO$_4^{2-}$ and became yellow at 80 mol% WO$_4^{2-}$, consistent with previous studies (Greenwood, 1943; Vermaas, 1952; Konokov, 1967; Hsu and Galli, 1973; Shoji and Sasaki, 1978; Tyson, et al., 1988; Kempe and Wolf, 1989).

From the powder X-ray diffraction analyses, all the traces gave similar patterns. All peaks across the entire compositional range showed, to varying degrees, a shift between the end-member peak positions. The degree of peak shift was consistent with the compositional ratios. There was no indication of two phases (for example the presence of multiple peaks, where one peak should occur) in any of the W:Mo ratio mixes over the entire solid solution range.

Refined cell parameters for intermediate members were all within the end-member ranges. Cell parameters versus composition were plotted (Figures 5.3a, b and 5.3c), where the $a$ axis, $c$ axis and the $c/a$ ratio plots each show linear trends. These linear trends in cell parameters and the lack of evidence for two phases in the traces suggest that solid solution series is complete over the entire range under ambient conditions and that the series obeys Vegard's Law.

It was noted for the Tsumeb powellite specimen that all the tabular crystals of powellite were uniform in composition (98 mol% powellite) no zoning was present in the crystal itself. However, it was found that some of the powellite crystals grow around a core of tungstenian powellite (Figures 5.4a and b) associated with copper sulfides. This tungstenian powellite forms euhedral bipyramidal crystals with a composition of about 45-50 mol% W and displays complex zonation patterns (Figure 5.4b). Chemical variation is up to 5 mol% W (see Appendix 5). There is a sharp compositional boundary
Figure 5.3a  MoO$_4^{2-}$ mol% versus $a$ calculated from refined cell parameters using LAPOD (Langford, 1973).

Figure 5.3b  MoO$_4^{2-}$ mol% versus $b$ calculated from refined cell parameters using LAPOD (Langford, 1973).
Figure 5.3c  MoO$_4^{2-}$ mol\% *versus* c/a calculated from refined cell parameters using LAPOD (Langford, 1973).

between the tungsten-rich powellite and surrounding near pure powellite (Figure 5.4b). It is not clear whether the tungsten-rich powellite is of primary or secondary origin, though its association with sulfides suggests it is probably primary but formed after the sulfides. This is the first report of molybdenum-rich scheelite from the Tsumeb deposit. There is no evidence of corrosion or reabsorption around the crystal boundary; thus the powellite crystals have not grown at its expense. This reflects a significant change in groundwater geochemistry.

The comparable sizes and geometries of the MoO$_4^{2-}$ and WO$_4^{2-}$ ions permits extensive solid solution in appropriate scheelite-type AMO$_4$ compounds (space group $I4_1/a$). Based on the following equation, at 298.2 K

$$\text{CaWO}_4(s) + \text{MoO}_4^{2-}(aq) \rightleftharpoons \text{WO}_4^{2-}(aq) + \text{CaMoO}_4(s)$$

the $\Delta G^\circ_{\text{reaction}}$ is 17.2 kJ mol$^{-1}$ and log K = -3.01 (from thermodynamic data in Appendix 1). While it is acknowledged that the solid solution series may not behave ideally, it is worth
Figure 5.4a  Backscattered electron image of a polished section of a Tsumeb powellite (P) with a core of W-rich powellite (WP) associated with manganese oxides (M) and sulfides (Sf).

Figure 5.4b  Close up of W-rich powellite crystal from Figure 5.4a. Note the sharp euhedral boundary and zonal variation crystal.
reflecting on the formation of intermediate members assuming the effects of solid state and species activity co-efficients are set aside. From the magnitude of the log K value, substitution of 1 mol% of MoO$_4^{2-}$ in scheelite would require an activity ratio $a$(MoO$_4^{2-}$)/$a$(WO$_4^{2-}$) of around 100 and the absence of other cations that would compete for WO$_4^{2-}$ or MoO$_4^{2-}$ such as Pb$^{2+}$. Therefore to form "molybdo-scheelite" under ambient conditions the Ca$^{2+}$ concentration has to be equal to or greater than the available WO$_4^{2-}$ and MoO$_4^{2-}$. The magnitude of the equilibrium constant means that even when MoO$_4^{2-}$ activities are 1000 times greater than WO$_4^{2-}$, tungsten will easily dope into powellite under ambient conditions. This is evident by the numerous reports of tungstenian powellite in Nature (Palache et al., 1951; Battery and Moss, 1962; Hurlbut, 1982; Brugger et al., 1998). Therefore it is not surprising that powellite from Tsumeb contains a small amount of tungsten since both stolzite and tungstenian wulfenite have been reported in the oxide zone (Pinch and Wilson, 1977; Foord and Conklin, 1982). Pure powellite will form in highly localised or closed environments where tungsten activities would be negligible, such as would be associated with vugh linings or alterations of molybdenite. The absence of intermediate members of the powellite-scheelite series in Nature simply reflects groundwater and environmental limits rather than a miscibility gap in the series. It is of course possible that the powellite crystals with a high tungsten content at the core of some of the near pure powellites may have formed as the result of secondary processes with the groundwater containing extremely high activities of MoO$_4^{2-}$ and significant activity of WO$_4^{2-}$.

As mentioned in Section 5.0, Mo substitution in various scheelites ("molybdo-scheelite") has been reported by various authors (Kerr, 1946; Palache et al., 1951; Vermaas, 1952; Konokov, 1967, 1972; Hsu and Galli, 1973; Kempe and Wolf, 1989; Crane, 1990; Brugger et al., 1998). All reported "molybdo-scheelites" in the
literature formed at high temperatures and/or pressure. They are generally associated with metasomatic or igneous rocks (though scheelites formed in igneous rocks rarely exceed 1 mol% Mo). There are no reports in the literature of ‘molybdoscheelite’ formed as a result of oxidation of primary minerals under ambient conditions. The general trend is that the molybdoscheelite with the highest molybdenum content generally forms first and decreases in the paragenetic sequence with the latter-formed scheelites being almost pure suggesting changes in conditions of formation (Hsu and Galli, 1973; Crane, 1990; Brugger et al., 1998). In metasomatic rocks, variation of the molybdenum content of “molybdoscheelite” has been observed in different grains in the same rock and as zoning in individual grains (Kerr, 1946; Hsu and Galli, 1973; Kempe and Wolf, 1989; Crane, 1990) including a wide range of scheelite-powellite compositions ranges reported in metasomatic deposits by Brugger et al. (1998), from 30-70 mol% powellite. These grains display two-stage chemical zoning.

Hsu and Galli (1973) indicated that the lack of powellite and powellite-rich members of the series in these rocks cannot be attributed to the lack of molybdenum in ore fluids. From thermodynamic calculations they suggested that the formation of molybdenite, MoS₂, was favoured over powellite under normal crustal conditions (not ambient conditions) and that the fugacities, fO₂ and fS₂, were important factors. Scheelite and molybdenite have a wide, overlapping fO₂ and fS₂ field whereas scheelite and powellite have a much narrower range, occurring together only under high fO₂ and relatively lower fS₂ values. The implications of this observation are that, when there is lower fO₂ and/or high fS₂, molybdenite and pure scheelite will coexist (such as in pegmatites and hydrothermal veins). Hsu and Galli (1973) suggested that metasomatic conditions, where higher fO₂ and/or low fS₂ would be expected, prevent the formation of molybdenite and cause the incorporation of molybdenum in scheelite if the activity of MoO₄²⁻ is sufficiently high.
Fluctuations in $f_{O_2}$ and $f_{S_2}$ conditions or in MoO$_4^{2-}$ activities would cause changes in molybdenum content of scheelite crystals as they formed. The observed increase in tungsten content around the rims of "molybdoscheelite" crystals would indicate an overall decrease in the molybdenum activity as ore fluids were depleted. It has been established, by various analyses from different locations, that almost the entire scheelite-powellite compositional range exists in Nature (0-70 and 90-100 mol% powellite) and this is supported by syntheses of the complete series under ambient conditions. The presence of intermediate members in the natural powellite-scheelite series is a reflection of particular chemical conditions rather than the existence of a miscibility gap in the series.

Under prevailing conditions in the oxidised zone where $f_{O_2}$ is high and $f_{S_2}$ correspondingly low, powellite and powellite-rich minerals would form in preference to molybdenite. This has been confirmed with a recent find of secondary molybdenum-rich scheelite from the oxide zone at Elsmore, New South Wales (P. A. Williams, pers. comm.).

The Tsumeb powellite analysed in this study is the first reported occurrence of lead substitution in powellite above trace levels. Analysis of the thermodynamic data provides a plausible explanation for this observation. Based on the following equation, at 298.2K

$$\text{PbMoO}_4(s) + \text{Ca}^{2+} (aq) \leftrightarrow \text{Pb}^{2+}(aq) + \text{CaMoO}_4(s)$$

the $\Delta G^\circ_{\text{reaction}}$ is 40.3 kJ mol$^{-1}$ and log $K = -7.05$ (from thermodynamic data in Appendix 1). It can be seen from the magnitude of the equilibrium constant that for powellite to form, the a(Ca$^{2+}$) compared to a(Pb$^{2+}$) has to be of the order of $1.14 \times 10^7$ greater. This means that wulfenite (PbMoO$_4$) is more likely to form. Oeder et al. (1980) reported that single crystals of Ca-rich Pb$_x$Ca$_{1-x}$MoO$_4$ grown by the Czochralski method were confined to compositions corresponding to $0 < x < 0.1$. They attributed the poor miscibility of
PbMoO₄ in CaMoO₄ in part to electronic effects. However, assuming that for compositions where the solid-solution series is continuous it behaves ideally, it can be seen from the magnitude of the equilibrium constant that Pb will easily be incorporated into powellite. However only a small amount of Pb will dope into the lattice, limited by the poor miscibility of PbMoO₄ in CaMoO₄.

A similar observation in the PbWO₄-CaWO₄ solution series was noted by Chang (1967) and Hsu (1981) who reported that the series was only continuous above 998 K. Below this temperature a large miscibility gap exists. Chang (1967) reported that this gap existed between 2 and 98 mol% Pb²⁺ below 973 K. Hsu (1981) reported that the gap was between 10 and 90 mol% below 573 K. Both these studies suggest that only very minor amounts of Pb are able to substitute into scheelite. From the thermodynamic data, at 298.2 K based on the following equation,

\[ \text{PbWO}_4(s) + \text{Ca}^{2+} (aq) \rightleftharpoons \text{Pb}^{2+} (aq) + \text{CaWO}_4(s) \]

\[ \Delta G^\circ_{\text{reaction}} \text{ is } 19.4 \text{ kJ mol}^{-1} \text{ and } \log K = -3.39 \text{ (from thermodynamic data in Appendix 1).} \]

For scheelite to form at ambient conditions in preference to stolzite, the \( a(\text{Ca}^{2+}) \) compared to \( a(\text{Pb}^{2+}) \) has to of the order of 2500 greater.

In terms of oxide zone geochemistry, a complete compositional range is possible between powellite and scheelite though this is unlikely since the limits of activities in groundwater and competition from other cations limit the formation of these minerals. In groundwaters associated with oxidising deposits which contain lead, an extremely large \( a(\text{Ca}^{2+})/a(\text{Pb}^{2+}) \) ratio with sufficient tungstate/molybdate concentrations is required to form plumbian powellite/scheelite under ambient conditions. Where the ratio is not large enough then wulfenite/stolzite will form instead. The large miscibility gap between the lead tungstate/molybdate and calcium tungstate/molybdate solid solution series limits the maximum observed substitution of Pb³⁺ in these minerals even if groundwater activities
are optimal. Therefore, conditions for powellite to form in oxide zones which contain lead would be extremely rare as compared to wulfenite/stolzite, an observation which is consistent with literature reports.

5.2.3 RAMAN SPECTROSCOPY OF TSUMEB POWELLITE

5.2.3.1 Raman spectroscopy of pure powellite.

Raman spectra of the Tsumeb powellite (Figure 5.5) were typical of scheelite group compounds. Assignment of the vibrational modes with band values is outlined in Section 4.2.3.1. Band values and their assignments from previous Raman studies of artificial powellite and the current study are outlined in Table 5.8.

The most intense band in all orientations was around 876-877 cm\(^{-1}\) corresponding to MoO\(_4\) \(v_1(A_g)\). A very weak shoulder was present at 864 cm\(^{-1}\) in some spectra. The shoulder varied slightly in intensity in different powellites, though still remained very weak. This shoulder is similar to the weak shoulder often present in wulfenite around 854 cm\(^{-1}\) (see Section 4.2.3.2) which was assigned by Ross (1972) and Kloprogge and Frost (1999) as the \(v_1(B_u)\) infrared band which becomes active due to strain.

The band occurring around 323-324 cm\(^{-1}\) corresponds to either \(v_2(A_g)\) or \(v_2(B_g)\) which according to the literature occur at the same frequency (Khanna et al., 1968; Griffith, 1970). Bands at 391-392 cm\(^{-1}\) and 402-404 cm\(^{-1}\) have been assigned to \(v_4(B_g)\) and \(v_4(E_g)\), respectively, based on the literature (Khanna et al., 1968; Griffith, 1970). Both these bands, as with wulfenite/stolzite, vary in relative intensity with different crystal orientations (Figure 5.5). The \(v_4(B_g)\) displays its greatest intensity with \(v_4(E_g)\) almost absent when the beam is parallel to the \(c\) axis. When the beam is parallel to the \(a\)
Table 5.8  MoO$_4^{2-}$ internal vibrational mode assignments and frequencies reported in various Raman studies on powellite (CaMoO$_4$).

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<th>tetrahedron in the lattice, $C_{4h}$</th>
<th>Khanna et al. (1968)</th>
<th>Tarte and Liegeois-Duyckaerts (1972)</th>
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<td>879</td>
<td>882</td>
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$^a$ $v_1$ ($B_u$) activated by strain.
Figure 5.5  Raman spectra of (300-1000 cm\(^{-1}\)) Tsumeb powellite in different orientations; A: beam between the \(a\)-axis and \(c\)-axis; B: beam parallel to the \(a\) axis; C: beam parallel to the \(c\) axis.
axis the reverse is true with \( \nu_4(E_g) \) being more dominant and \( \nu_4(B_g) \) being absent. An intense band occurs at 793 cm\(^{-1}\) in some spectra and corresponds to \( \nu_3(E_g) \) and a second band in the region occurring at 847 cm\(^{-1}\) corresponds to \( \nu_3(B_g) \). The relative intensity of these bands also varies with crystal orientation (Figure 5.5). The \( \nu_3(B_g) \) band is more intense and \( \nu_3(E_g) \) almost absent when the beam is parallel to the \( c \) axis and vice versa when the beam is parallel to the \( a \) axis.

Bands at 204-205 cm\(^{-1}\) and 189-191 cm\(^{-1}\) have been assigned by Khanna et al. (1968) as \( 2F_l \) rotations \( A_g \) and \( E_g \). Similar bands were also observed for CdMoO\(_4\) at 189 and 173 cm\(^{-1}\) (Daturi et al., 1997) and other compounds with the scheelite structure. In some powellite spectra a small band was present at 917 cm\(^{-1}\) corresponding to WO\(_4\) \( \nu_1(A_g) \), present because of small amounts of substituted tungstate in the powellite.

5.2.3.2 Raman spectroscopy of W-substituted powellite

It has been shown that, like wulfenite-stolzite, powellite-scheelite forms a complete solid solution series under ambient conditions and that numerous powellites/scheelites lie somewhere between the two pure end members. Some of the near pure powellite from Tsumeb have cores of tungsten rich powellite, which are easily discernable from their Raman spectra (Figure 5.6). Two \( \nu_1 \) modes are observed; the \( \nu_1(A_g) \) band of the WO\(_4\) ions observed at 915 cm\(^{-1}\) and the band at 879 cm\(^{-1}\) is \( \nu_1(A_g) \) of the MoO\(_4\) unit. Both modes show a slight shift in frequency from the values for the corresponding \( \nu_1(A_g) \) band in pure end members (912 cm\(^{-1}\) for scheelite and 876 cm\(^{-1}\) for powellite). The intensity of the two bands are not directly proportional to the composition of the tungstenian powellite. Even though the mol% of tungsten and molybdenum are about the same in the crystal (45-50 mol% W and 50-55 mol% Mo the MoO\(_4\) \( \nu_1(A_g) \)
Figure 5.6  Raman spectra of A: powellite from Tsumeb; B: tungstenian powellite from Tsumeb and C: scheelite from Nundle, N.S.W.
band has a significantly greater intensity than the corresponding \( \text{WO}_4 \) \( v_1(A_g) \) band (Figure 5.6).

Other bands in the spectra show some frequency displacement from positions in the pure powellite towards the corresponding frequencies for scheelite. These trends are identical to the trends in substituted wulfenite/stolzites (see Section 4.2.3.4). This is due to the dual nature versus the single nature of vibrational modes in the lattice which was reported in artificial mixed crystals of the \( \text{CaMo}_x\text{W}_{1-x}\text{O}_4 \) solid solution series (Karaptyan et al., 1976).

5.3 REFERENCES


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APPENDIX ONE

THERMODYNAMIC DATA TABLES

<table>
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<tr>
<th>Species</th>
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</tbody>
</table>

$^a$ Newberg (1967) gives a value of $-1206.7$ kJ mol$^{-1}$ and dioptase 11.7 kJ mol$^{-1}$ more negative. This dioptase value was used to represent 'aged' chrysocolla.
Table A1.2 Stability constant data for various aqueous species at 298.2 K used in COMICS (Perrin and Sayce, 1967) calculations for chrysocolla taken from the compilation of Smith and Martell (1976).

<table>
<thead>
<tr>
<th>Speciation equation</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{SiO}_4^{-(aq)} + \text{H}^+(aq) \rightleftharpoons \text{H}_3\text{SiO}_4^{-(aq)}$</td>
<td>13.1</td>
</tr>
<tr>
<td>$\text{H}_2\text{SiO}_4^{-(aq)} + 2\text{H}^+(aq) \rightleftharpoons \text{H}_4\text{SiO}_4^{0(aq)}$</td>
<td>9.86</td>
</tr>
<tr>
<td>$\text{H}^+(aq) + \text{SO}_4^{2-(aq)} \rightleftharpoons \text{HSO}_4^-(aq)$</td>
<td>1.99</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(aq) + \text{SO}_4^{2-(aq)} \rightleftharpoons \text{CuSO}_4^0(aq)$</td>
<td>2.36</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(aq) + \text{OH}^-(aq) \rightleftharpoons \text{Cu(OH)}^+(aq)$</td>
<td>6.5</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(aq) + 2\text{OH}^-,(aq) \rightleftharpoons \text{Cu(OH)}_2^0(aq)$</td>
<td>11.8</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(aq) + 3\text{OH}^-,(aq) \rightleftharpoons \text{Cu(OH)}_3^0(aq)$</td>
<td>14.5</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(aq) + 4\text{OH}^-,(aq) \rightleftharpoons \text{Cu(OH)}_4^0(aq)$</td>
<td>16.4</td>
</tr>
<tr>
<td>$2\text{Cu}^{2+}(aq) + \text{OH}^-,(aq) \rightleftharpoons \text{Cu}_2\text{(OH)}_2^{2+}(aq)$</td>
<td>8.2</td>
</tr>
<tr>
<td>$2\text{Cu}^{2+}(aq) + 2\text{OH}^-,(aq) \rightleftharpoons \text{Cu}_2\text{(OH)}_2^{2+}(aq)$</td>
<td>17.4</td>
</tr>
<tr>
<td>$3\text{Cu}^{2+}(aq) + 4\text{OH}^-,(aq) \rightleftharpoons \text{Cu}_3\text{(OH)}_4^{2+}(aq)$</td>
<td>35.2</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}(aq) + \text{OH}^-,(aq) \rightleftharpoons \text{Ca(OH)}^+(aq)$</td>
<td>-12.7</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}(aq) + \text{OH}^-,(aq) \rightleftharpoons \text{Mg(OH)}^+(aq)$</td>
<td>-11.42</td>
</tr>
<tr>
<td>$\text{K}^+(aq) + \text{OH}^-,(aq) \rightleftharpoons \text{K(OH)}^0(aq)$</td>
<td>-14.5</td>
</tr>
<tr>
<td>$\text{Na}^+(aq) + \text{OH}^-,(aq) \rightleftharpoons \text{Na(OH)}^0(aq)$</td>
<td>-14.2</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}(aq) + \text{SO}_4^{2-(aq)} \rightleftharpoons \text{CaSO}_4^0(aq)$</td>
<td>2.31</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}(aq) + \text{SO}_4^{2-(aq)} \rightleftharpoons \text{MgSO}_4^0(aq)$</td>
<td>2.23</td>
</tr>
<tr>
<td>$\text{Na}^+(aq) + \text{SO}_4^{2-(aq)} \rightleftharpoons \text{NaSO}_4^0(aq)$</td>
<td>0.70</td>
</tr>
<tr>
<td>$\text{K}^+(aq) + \text{SO}_4^{2-(aq)} \rightleftharpoons \text{KSO}_4^0(aq)$</td>
<td>0.85</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}(aq) + \text{H}_2\text{SiO}_4^{2-(aq)} \rightleftharpoons \text{Ca(H}_2\text{SiO}_4)^0(aq)$</td>
<td>14.36</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}(aq) + \text{H}_2\text{SiO}_4^{2-(aq)} \rightleftharpoons \text{Mg(H}_2\text{SiO}_4)^0(aq)$</td>
<td>14.11</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}(aq) + \text{H}^+(aq) + \text{SO}_4^{2-(aq)} \rightleftharpoons \text{CaHSO}_4^+(aq)$</td>
<td>2.29</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}(aq) + \text{H}^+(aq) + \text{SO}_4^{2-(aq)} \rightleftharpoons \text{MgHSO}_4^+(aq)$</td>
<td>2.39</td>
</tr>
<tr>
<td>$\text{Na}^+(aq) + \text{H}^+(aq) + \text{SO}_4^{2-(aq)} \rightleftharpoons \text{NaHSO}_4^0(aq)$</td>
<td>1.29</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}(aq) + \text{H}^+(aq) + \text{H}_2\text{SiO}_4^{2-(aq)} \rightleftharpoons \text{Ca(H}_2\text{SiO}_4)^+ (aq)$</td>
<td>4.59</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}(aq) + \text{H}^+(aq) + \text{H}_2\text{SiO}_4^{2-(aq)} \rightleftharpoons \text{Mg(H}_2\text{SiO}_4)^+ (aq)$</td>
<td>5.67</td>
</tr>
</tbody>
</table>

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Table A1.3 Stability constant data for aqueous lead and chromate species at 298.2 K used in COMICS (Perrin and Sayce, 1967) calculations of orthorhombic lead chromate taken from the compilation of Smith and Martell (1976).

<table>
<thead>
<tr>
<th>Speciation equation</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrO$_4^{2-}$(aq) + H$^+$(aq) $\rightleftharpoons$ HCrO$_4^-$ (aq)</td>
<td>6.51</td>
</tr>
<tr>
<td>CrO$_4^{2-}$(aq) + 2H$^+$(aq) $\rightleftharpoons$ H$_2$CrO$_4^0$(aq)</td>
<td>6.31</td>
</tr>
<tr>
<td>2CrO$_4^{2-}$(aq) + 2H$^+$(aq) $\rightleftharpoons$ Cr$_2$O$_7^{2-}$(aq) + H$_2$O(l)</td>
<td>14.55</td>
</tr>
<tr>
<td>Pb$^{2+}$(aq) + CrO$_4^{2-}$(aq) $\rightleftharpoons$ PbCrO$_4^0$(aq)</td>
<td>2.75$^a$</td>
</tr>
<tr>
<td>Pb$^{2+}$(aq) + OH$^-$ (aq) $\rightleftharpoons$ Pb(OH)$^+$(aq)</td>
<td>6.3</td>
</tr>
<tr>
<td>Pb$^{2+}$(aq) + 2OH$^-$ (aq) $\rightleftharpoons$ Pb(OH)$_2^0$(aq)</td>
<td>10.9</td>
</tr>
<tr>
<td>Pb$^{2+}$(aq) + 3OH$^-$ (aq) $\rightleftharpoons$ Pb(OH)$_3^-(aq)$</td>
<td>13.9</td>
</tr>
<tr>
<td>2Pb$^{2+}$(aq) + OH$^-$ (aq) $\rightleftharpoons$ Pb$_2$(OH)$_2^{2+}$(aq)</td>
<td>7.6</td>
</tr>
<tr>
<td>3Pb$^{2+}$(aq) + 4OH$^-$ (aq) $\rightleftharpoons$ Pb$_3$(OH)$_4^{3+}$(aq)</td>
<td>32.1</td>
</tr>
<tr>
<td>4Pb$^{2+}$(aq) + 4OH$^-$ (aq) $\rightleftharpoons$ Pb$_4$(OH)$_4^{4+}$(aq)</td>
<td>35.1</td>
</tr>
<tr>
<td>6Pb$^{2+}$(aq) + 8OH$^-$ (aq) $\rightleftharpoons$ Pb$_6$(OH)$_8^{4+}$(aq)</td>
<td>68.4</td>
</tr>
</tbody>
</table>

$^a$ stability constant for PbCrO$_4^0$ was estimated to be equal to that of PbSO$_4^0$.

REFERENCES


GEOCHEMICAL STUDIES OF SELECTED BASE METAL MINERALS FROM THE SUPERGENE ZONE

by

Martin John Crane MSc(Hons)

A thesis presented in accordance with the regulations governing the award of the degree of Doctor of Philosophy

University of Western Sydney

November 2001
PLEASE NOTE

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

and the best possible result has been obtained.
DECLARATION

I declare that this thesis is my own work, and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from published works of others has been fully acknowledged in the text, and listed in the reference section of the thesis.

----------------------------------
Martin Crane
Multimedia item accompanies print copy
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Above all, I am eternally grateful to my family for their support throughout my studies especially my Mum and Dad. Without their endless encouragement, generosity, and support (both financially and emotionally) the project would never have been possible.
LIST OF PUBLICATIONS


LIST OF CONFERENCE PAPERS


SUMMARY

Acid leaching of different natural chrysocolla (CuSiO₃·H₂O) samples under ambient conditions demonstrated that the chemical and crystallographic inhomogeneity significantly affects the rate and that it is virtually impossible to use the mineral as a model for the kinetics of hydrometallurgical processing of copper ores. From dissolution experiments the average ΔG°ₗ for natural chrysocolla was found to be $-1223.2 \pm 2.4$ kJ mol⁻¹ at 298.2 K which is more negative than previously reported values and is similar (within experimental error) to the calculated ΔG°ₗ value for the rare, stoichiometrically related mineral dioptase (CuSiO₃·H₂O). From stability diagrams, it was found that chrysocolla can readily replace malachite, but only under the most extreme activities. There is no achievable H₂SiO₄°(aq) activity such that libethenite (Cu₂PO₄·OH) or other basic copper phosphates can be directly replaced by natural chrysocolla.

X-ray powder diffraction studies have shown that solid solution in the orthorhombic lead(II) chromate – orthorhombic lead(II) sulfate system, space group *Pnma*, is lacunar at 298K, with the miscibility gap bounded by Pb(CrO₄)₀.₀₈(SO₄)₀.₂ and Pb(CrO₄)₀.₁(SO₄)₀.₉. All Cr-rich compositions are metastable with respect to the monoclinic polymorph, corresponding to crocoite, space group *P2₁/n*. The extent of solid solution of sulfate in crocoite at 298K is Pb(CrO₄)₀.₆(SO₄)₀.₄. Recrystallization at ambient temperatures is acid-catalyzed and these effects explain a number of disparate reports concerning the stabilities of the various series in the literature. A value for the solubility product of orthorhombic lead(II) chromate has been determined using solution methods as $\log K_{sp}(\text{PbCrO}_4\text{s,orthorhombic,298.2K}) = -10.71(12)$. Microprobe analyses of specimens of anglesite from the Red Lead mine, Dundas, Tasmania, show significant chromate substitution.

X-ray powder diffraction studies have shown that the artificial lead(II) molybdate -
lead(II) tungstate solid solution series is complete over the entire range at 298K and that it obeys Vegard's Law. X-ray studies on natural tungstenian wulfenites and molybdenian stolzites reinforce the same conclusion. A complete solid solution series exists in Nature with most tungstenian wulfenites and molybdenum stolzites containing a range of compositions. The first occurrence of a molybdenum stolzite from Broken Hill, Australia, which also contains small amounts of chromium is noted.

The single-crystal X-ray structure of powellite (CaMoO₄)- $I\overline{4}$ containing small amounts of lead and tungsten from Tsumeb, Namibia, has been determined. Powellite-$I\overline{4}$ is tetragonal, space group $I\overline{4}$, with $a = 5.222(1)$, $c = 11.428(2)$ Å and $Z = 4$. The structure was refined to $R = 0.049$ for 325 independent reflections with $I > 2\sigma (I)$. Ca (98%) and Pb (2%) are disordered in the lattice over special positions $2b$ (0,0,½) and $2d$ (0,½,3⁄4), and Mo (98%) and W (2%) are similarly disordered over special positions $2a$ (0,0,0) and $2c$ (0,½,½). X-ray powder diffraction studies have shown that solid solution in the calcium molybdate – calcium tungstate series is complete over the range at 298K and obeys Vegard's law.

Raman microprobe spectroscopy has proven to be a very quick and effective non-destructive method for semi-quantitative analysis of the wulfenite-stolzite and powellite-scheelite solid-solution series and in detecting very small amounts (<0.5 wt%) of substituted chromate in wulfenite, stolzite and anglesite.
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* Appendices store on CD-rom format supplied in back cover of this thesis