Colour and Cash: The Exquisite Minerals of the Oxidized Zone

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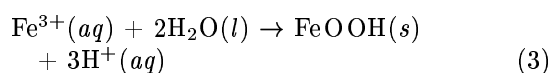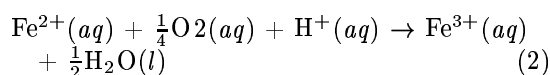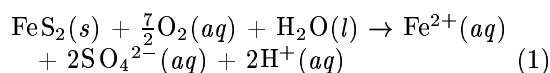
Abstract: The geochemistry and chemical mineralogy of the oxidized zones of orebodies are extraordinarily complex, much more so than the primary deposits from which they are derived. The zones themselves are of great economic importance, especially to Australia. Many of the free-milling gold ores exploited over the last two decades are of supergene origin (secondary gold) and cobalt, nickel and copper deposits of the same kind are of increasing importance. We know much of the equilibrium chemistry of such mineral settings for some elements and something of the general processes that play a part in the development of ore grades in the oxidized zone. For other elements the situation is somewhat more sketchy and of certain aspects, including kinetics of crystallization, temperatures of mineral formation and solid-solution phenomena, we know very little indeed. Oxidized zone mineralization, some of which is exquisitely beautiful, is described in terms of its origin and the associated chemistry necessary to extract metals from these sorts of deposits. Further research directions are highlighted, together with problems that remain to be solved.

INTRODUCTION

The oxidized zone of an orebody is that part of it that lies above the water table. Its lower limit is not definite, but fluctuates with the seasons and local climatic influences. This is important for the chemistry of the oxidized zone in that ions in groundwaters can be introduced by these fluctuations (or drawn upwards by capillary action) causing local redox conditions to vary at the base of the zone. As its name implies, the oxidized zone carries the oxidized equivalents of primary materials generally formed deep in the earth when prevailing conditions were much different. These conditions would typically be characterized by relatively high temperatures and pressures, a lack of oxygen and high activities of sulfur and sulfide. Naturally, it is to be expected that minerals stable in this environment are thermodynamically unstable in the near-surface environment, which is characterized by abundant oxygen dissolved in water, lower temperatures, ambient pressures and sulfur species dominated by sulfate (Williams, 1990).

In general, elements reach higher or their highest oxidation states in the oxidation zone. For example, pyrite (iron(II) disulfide, $Fe^{2+}S_2{}^{2-}$) is oxidized as shown in (1). Subsequent oxidation of Fe(II) and hydrolysis leads to goethite ($FeOOH$), a characteristic iron mineral of the oxidized zone, according to (2) and (3).

$$FeS_2(s) + \tfrac{7}{2}O_2(aq) + H_2O(l) \rightarrow Fe^{2+}(aq) + 2SO_4{}^{2-}(aq) + 2H^+(aq) \tag{1}$$

$$Fe^{2+}(aq) + \tfrac{1}{4}O_2(aq) + H^+(aq) \rightarrow Fe^{3+}(aq) + \tfrac{1}{2}H_2O(l) \tag{2}$$

$$Fe^{3+}(aq) + 2H_2O(l) \rightarrow FeOOH(s) + 3H^+(aq) \tag{3}$$

A weathered sulfide orebody exposed at the surface most frequently shows a characteristic zoning pattern with increasing depth. At the surface, chemically resistant minerals (e.g., quartz, SiO_2) remain, together with oxides and oxyhydroxides of certain metals. Notable among these are iron and manganese minerals. These constitute the weathered remnants of the orebody known as a gossan. Since pyrite and other iron- bearing phases are so common in sulfide ores, these gossans are usually reddish brown in colour and contain goethite, and sometimes its polymorphs lepidocrocite and akaganéite, and hematite (Fe_2O_3), together with a large number of rarer iron-bearing minerals.

2   WILLIAMS

When primary iron minerals are less abundant, a conspicuous gossan may not be formed. Alternatively, the gossan may manifest itself in other ways depending on the mineralogy of the primary ore from which it was derived. A notable example is the gossan associated with the Broken Hill, New South Wales lode which formed from ores lean in iron but very rich in manganese. Here, a black coronadite ($PbMn_8O_{16}$) gossan was extensively developed on the Number 2 and 3 Lead lenses (Birch, 1999). Beneath the gossan, a leached zone is often developed. Most transition and other heavy metals are leached and transported away from this zone in solution. Still deeper, the oxidized zone (*sensu stricto*) is encountered; this is a zone where the classical and aesthetically beautiful secondary minerals of the base and other metals are found. Finally, near the water table and the redox boundary between oxidizing and reducing conditions, a supergene enriched zone may be developed for certain elements. This is particularly important in many copper deposits and rich to bonanza grades comprised of native copper, chalcocite (Cu_2S) and its congeners such as digenite (Cu_9S_5) and djurleite ($Cu_{31}S_{16}$) have long been exploited in numerous and economically very important deposits, notably in the Americas (see, for example, Anthony et al., 1995), but also in Australia. Current examples for the latter include Girilambone, New South Wales (Fogarty, 1998) and Gunpowder in northwest Queensland (Richardson and Moy, 1998).

Aside from copper, the other coinage metals too can be supergene enriched. Silver has been won from many such deposits, but today these are largely exhausted. One example worth mentioning is the Chañarcillo field in Chile (Segerstrom, 1962), which produced 2,500 tonnes of silver between 1860 and 1885 from ores carrying native silver, chlorargyrite (AgCl), bromargyrite (AgBr), iodargyrite (AgI), together with solid-solutions of the three halides, dyscrasite (Ag_3Sb), acanthite (Ag_2S), stromeyerite (AgCuS), stephanite (Ag_5SbS_4), pearceite ($Ag_{16}As_2S_{11}$) and polybasite ($Ag_{16}Sb_2S_{11}$). The fabulous Consols mine

at Broken Hill NSW presented a similar wealth of these and related phases (Birch, 1999). Enrichment of gold remains an important economic process. Emmons (1917) provided an early summary of gold enrichment in various deposits and speculated on a mechanism for it. A more recent publication (Berkman and Mackenzie, 1998) lists no fewer than 18 Australian gold deposits that involve significant supergene enrichment of gold to an economically important degree. This enrichment is not solely due to removal of more reactive material from the oxidized zone. Spectacular examples are known of deposits that have bonanza grades of gold near the water table as a result of transport and redeposition due to solution chemistry at ambient temperatures and weathering. Hannon South stands out in this respect (Lawrance, 1994). Gold was leached from the weathered profile to a depth of about 30 metres with grades of less than 0.1 ppm Au remaining. At the base of the oxidized zone secondary gold of very high fineness (> 999) was deposited in a supergene enriched blanket with grades of over 100 ppm Au in places. Truly, the latest golden era of mining in Australia, contributing to a very significant level of export earnings, relied on the chemical processes responsible for the transport of gold in aqueous solution under ambient conditions in the oxidized zone.

Given the above, a thorough knowledge of the geochemistry and chemical mineralogy of the oxidized zone is desirable. Unfortunately, our knowledge is imperfect in many pertinent areas and in others virtually non-existent. The chemical mechanisms for the transport of gold in the supergene environment remain contentious for instance. Ligands that may be involved include chloride ion, thiosulfate ion and organic species; some have suggested that colloids are involved. In similar vein, the chemistry of the formation of many of the minerals in supergene enriched silver deposits is entirely unknown, other than for the overall stoichiometric equations that can be all too readily chalked on the board.

On the other hand, the geochemistry and

secondary mineralogy of the base metals is much better understood. This situation arises in part because of a better chemical understanding of these elements, a wealth of chemical data concerning a few of them and a serendipitous delight in their mineralogy. Concentration is now particularly focussed on copper, lead and zinc.

$PbSO_4$	anglesite	$PbWO_4$	stolzite
$PbCO_3$	cerussite	$Pb_5(PO_4)_3Cl$	pyromorphite
$PbCrO_4$	crocoite	$Pb_5(AsO_4)_3Cl$	mimetite
$PbMoO_4$	wulfenite	$Pb_5(VO_4)_3Cl$	vanadinite

Table 1: Some simple oxyanion minerals of Pb(II).

PARTICULAR SUITES

A chemical curiosity of the "simple" inorganic chemistry of these elements is the formation of basic double salts. For Pb(II) and Zn(II) examples include hydrocerussite ($Pb_2(CO_3)_2(OH)_2$) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$). However, both these ions tend to form simple salts in Nature. For Zn(II), smithsonite ($ZnCO_3$) is a reasonably common phase in oxidized zones, but the solubility of other simple zinc salts leads to a limited mineralogy of the element in such settings. This is so much the better in that equilibrium models for secondary zinc mineralization are that much easier to construct (Williams, 1990). On the other hand, Pb(II) forms a number of insoluble salts with a variety of oxyanions and these are reflected in oxidation zone mineralogy. Table 1 lists some of these phases; note that double salts with ions other than hydroxide are featured. Again, fortunately, reliable thermodynamic data are available for these species and they can simply be incorporated into models that describe their behaviour in the oxidized zone. Regrettably, we come unstuck (chemically speaking) with copper(II).

Copper is an element for chemical and mineralogical connoisseurs. Its propensity to form basic double salts is unparalleled in the Periodic Table and almost any ion imaginable will form a solid found in Nature (or the laboratory). Some mineral examples are given in Table 2. The situation is seen to be even more complex when it is realized that many of the species form solid-solution series; this is particularly true for the arsenate and phosphate examples listed. Further, other metals may enter into solid- solution. Thus, in the libethenite-olivenite series, Zn(II) and Co(II) may enter the lattice in all proportions (Hawthorne, 1976; Hill, 1976; Kato and Miura, 1977; Keller et al., 1979; Toman, 1978). In the adelite group of minerals, with formula $ABAsO_4(OH)$, end-member species have been named for A = Ca, B = Mg, Co, Cu (also for a vanadate analogue), Ni, Zn and A = Pb, B = Cu, Fe.

If other cations and anions can be present in the same lattice, the stoichiometries of known secondary Cu(II) minerals may become extremely complicated. Two examples involving multiple cations and multiple anions will suffice to illustrate the point. BolĆite has the formula $Pb_{26}Cu_{24}Ag_9Cl_{62}(OH)_{47}\cdot H_2O$; it crystallizes in the cubic system, space group $Pm3m$, with $Z = 1$ and with a proton disordered over the hydroxide sites. It is a rare mineral, but has been reported from a number of localities including various mines at BolĆo in Baja California, the South mine at Broken Hill, New South Wales, in ancient lead slags that had been immersed in sea water at Laurion, Greece, and as a corrosion product of debased silver coins recovered from the wreck of the Batavia off Western Australia (Williams, 1990). The much more common solid-solution series connellite-buttgenbachite, c. $Cu_{36}Cl_8(NO_3)_x(SO_4)_y(OH)_{64-(x+2y)}\cdot 5H_2O$, contains four different anions with an extremely complicated pattern of mutual substitution over several sites in the lattice (Hibbs et al., 2001).

4 WILLIAMS

Anion			Anion		
Cl^-	$CuCl_2 \cdot 2H_2O$	eriochalcite	$SO_4{}^{2-}$	$CuSO_4 \cdot 5H_2O$	chalcanthite
	$CuCl(OH)_3$	atacamite		$Cu_3SO_4(OH)_4$	antlerite
		botallackite		$Cu_4SO_4(OH)_6$	brochantite
		paratacamite	$CO_3{}^{2-}$	$Cu_2CO_3(OH)_2$	malachite
		clinoatacamite		$Cu_3(CO_3)_2(OH)_2$	azurite
$PO_4{}^{3-}$	Cu_2PO_4OH	libethenite	$H_2SiO_4{}^{2-}$	$CuSiO_3 \cdot nH_2O$	chrysocolla
	$Cu_5(PO_4)_2(OH)_4$	pseudomalachite	$NO_3{}^-$	$Cu_2NO_3(OH)_3$	gerhardtite
		ludjibaite			
		reichenbachite			
	$Cu_3PO_4(OH)_3$	cornetite			
$AsO_4{}^{3-}$	Cu_2AsO_4OH	olivenite			
	$Cu_5(AsO_4)_2(OH)_4$	cornwallite			
		cornubite			
	$Cu_3AsO_4(OH)_3$	clinoclase			

Table 2: Secondary mineral diversity for copper(II). Minerals with extra cations are excluded. When several names are given, these refer to polymorphs of the same composition. Only a few examples are given here for illustration.
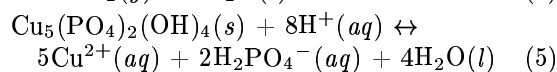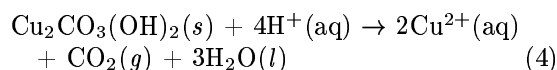
CHEMICAL AND PARAGENETIC RELATIONSHIPS

Comparatively simple primary metalliferous mineral suites of base metal orebodies in arid Australia (pyrite, chalcopyrite, galena, and sphalerite, with minor accessory phases) are accompanied by a bewildering array of secondary minerals in their supergene zones. This is as a consequence of saline (chloride, sulfate, carbonate) groundwater anion geochemistry with periodic fluctuations of the water table and capillary action contributing to a recharge of anions in the weathering zone. Arsenate, molybdate, tungstate and chromate are contributed by the breakdown of (usually) minor primary minerals. Silicic acid and phosphate species form through acid decomposition of gangue and host rock. Nitrate is common in groundwaters of Australian arid regions, due in part to formation of nitrogen oxides via electrical discharge during thunderstorms, but to some extent by leaching of nitrate formed in soils through biological action associated with termite mounds (Barnes et al., 1992).

Chlorides, especially those of Cu(II), are abundant in these settings. Atacamite and paratacamite are most common but the so-called rare species nantokite, CuCl, claringbullite, $Cu_4Cl(OH)_7$, and connellite are frequently encountered. Silver halides are common, being particularly abundant in the giant Broken Hill orebodies and surrounding deposits as noted above. Exotic secondary nitrates including gerhardtite, likasite, $Cu_3NO_3(OH)_5 \cdot 2H_2O$, and connellite-buttgenbachite are sometimes associated with the copper chlorides (Sharpe and Williams, 1999). Basic copper phosphates such as cornetite, and particularly libethenite and pseudomalachite, are common, associated with arsenate analogues clinoclase, olivenite, cornubite, cornwallite and other members of the adelite group, when arsenic-bearing sulfosalts are present in primary ores. Many other base metal arsenates and phosphates are found in more complex oxidized zones. Wulfenite, stolzite and crocoite, aside from the more commonly known localities, are present in many deposits of arid Australia. Chrysocolla is conspicuous in nearly all oxidized copper ores. More common sulfates (anglesite, brochantite, antlerite) and carbonates (mala-

chite, azurite, smithsonite, cerussite) contribute to very complicated assemblages of astonishing mineralogical diversity. These are, however, not randomly distributed throughout the oxidized zone. Rather, there are noticeably distinct patterns of distribution related to depth, redox potential and pH conditions (Sharpe, 1998; Williams, 1990).

Naturally, it would be desirable to gain an understanding of the chemical conditions that give rise to these assemblages. This is evident for a number of important reasons, not just because of the intrinsic interest that the minerals of the oxidized zone engender. First, it can be said that the chemistry associated with dissolution of secondary minerals in heap-leach operations is just the reverse of that responsible for their formation. Behaviour in acid conditions and kinetic phenomena are of special importance here.

$$Cu_2CO_3(OH)_2(s) + 4H^+(aq) \rightarrow 2Cu^{2+}(aq)$$
$$+ CO_2(g) + 3H_2O(l) \tag{4}$$
$$Cu_5(PO_4)_2(OH)_4(s) + 8H^+(aq) \leftrightarrow$$
$$5Cu^{2+}(aq) + 2H_2PO_4^-(aq) + 4H_2O(l) \tag{5}$$

Furthermore, many acid leach reactions are not strictly analogous. For example, reaction of malachite (4) with acid is essentially irreversible because of the loss of carbon dioxide to the atmosphere. However, reaction of pseudomalachite (5) is reversible and, with recycling of leach liquors, phosphoric acid will build up and indeed inhibit further reaction at the same pH unless the circuit is bled. A second reason concerns the application of the aqueous mineral chemistry to hydrogeochemical methods used in the exploration for new orebodies that are blind or very deeply or intensely weathered. Related to this, in that secondary minerals act as metal ion buffers, are strategies to avoid transition and heavy metal pollution associated with mining and manufacturing activities. This includes the dispersion of toxic species in acid mine drainage settings.

Fortunately, reliable thermochemical data for many of the minerals referred to above are available in the literature and a number of ex-

amples are given by Williams (1990). Incorporation of the data in equilibrium models has led to explanations of associations, paragenetic sequences and modes of formation of complex suites. A couple of recent examples will illustrate the utility of the approach. Field observations over the last decade have revealed just how widespread are the secondary phosphates of Cu(II) in the oxidized zones of copper orebodies in arid Australia. Examples include deposits at Girilambone (Gilligan and Byrnes, 1994) and Goonumbla or Northparkes in New South Wales (Heithersay et al., 1990; Crane et al., 1998) and several smaller deposits in the Mt. Isa Block in northwest Queensland (Ball, 1908; Day and Beyer, 1995; Carter et al., 1961; Sharpe, 1998). All of these deposits are characterized by an abundance of the secondary copper phosphates libethenite and pseudomalachite associated with smaller amounts of cornetite and turquoise, $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$. Secondary mineral distributions in these deposits vary, but a number of recurring paragenetic relationships are evident. Characteristic zoning of the phosphate minerals has also been noted, with libethenite invariably being found nearer the surface. Rhythmically banded, botryoidal malachite- pseudomalachite composites comprised of individual layers up to a few tenths of a millimetre thick are commonly found near the surface and sometimes in the outcrop. It has been shown that this material simply reflects the fluctuating availability of $H_2PO_4^-(aq)$ or $HPO_4^{2-}(aq)$ versus $HCO_3^-(aq)$ or $CO_3^{2-}(aq)$ in mineralizing solutions. The rare occurrence of cornetite, confined to the Great Australia, Cloncurry, Queensland, Main Lode outcrop (Day and Beyer, 1995) and the Crusader mine, north of Kajabbi, Queensland, is due to its formation under somewhat more unusual chemical conditions (relatively higher pH, higher copper and lower phosphate ion activities). The equilibrium models also show that libethenite-pseudomalachite zoning with depth depends on intensity of weathering with most intense weathering at the surface leading to higher phosphate concentrations in downward-

6   WILLIAMS

percolating groundwater, thus making the formation of libethenite more likely (Crane et al., 2001a). Related studies have shown that basic copper phosphates and arsenates control the dispersion of copper in groundwaters adjacent to the Great Australia, Girilambone and Mungana North, Chillagoe, Queensland, orebodies (Elvy, 1999).

A second example concerns the simplest of the copper chlorides, nantokite, CuCl. Nantokite was first reported in 1867 from the Carmen Bajo mine a few kilometres west of Nantoko, Chile (Palache et al., 1951). A second report was made by Liversidge (1894), regarding specimens found in a matrix of cuprite associated with native copper and cerussite from the Broken Hill South mine, New South Wales. A few other occurrences of nantokite have appeared since the early reports (Anthony et al., 1997). Complex crystals have been reported from the Southwest mine, Bisbee, Arizona (Graeme, 1993). It also has been found as a volcanic sublimate (Vergasova, 1983), but has continued to be regarded as being quite rare, until recently. Attention was drawn to the mode of formation of this comparatively rare mineral because of its discovery in considerable quantities in the oxidized zone of the Great Australia mine, near Cloncurry, Queensland, and its occurrence in a number of other Australian base metal deposits (Sharpe and Williams, 1999). Freshly broken specimens from Great Australia showed nantokite as colourless, water-clear masses, superficially resembling quartz, and showing a conchoidal fracture. The mineral is, however, thixotropic and is readily identified by its sectile nature, with a hardness of 2.5, similar to that of candle wax. On exposure to moist air, it oxidizes and hydrates within a few weeks to form a pale-green, crumbly powder consisting of atacamite or its dimorph, paratacamite. The abundance of nantokite at the Great Australia is noteworthy and tonnes of the mineral were mined and heap-leached to recover contained copper, even though its presence was unsuspected at the time. Nantokite altering to atacamite actually was observed first, but not rec-

ognized, in specimens from Cloncurry as early as 1887 when Lindon (1887) wrote:

> "I find that specimens of massive cuprite, or native copper changing to cuprite, from Cloncurry are very liable to be encrusted with malachite after keeping for a short time in the atmosphere of Brisbane."

Stability relationships between copper, nantokite, paratacamite and cuprite, Cu_2O, could be deduced using data taken from Robie et al., (1978), together with a value for the solubility product of paratacamite (Smith and Martell, 1976). These could be used to explain the fact that nantokite is the result of the alteration of native copper in a saline environment (Sharpe and Williams, 1999).

For Pb(II) and Zn(II), equilibrium modelling of secondary mineral assemblages is much simpler because of the fact that these ions usually form normal or simple salts with oxyanions. Reliable data are available for many of them (Robie et al., 1978; Smith and Martell, 1976). Nevertheless, much work remains to be done in this area so that a comprehensive database of stability constants is readily to hand; aside from known species, new minerals are reported at the rate of perhaps twenty per year.
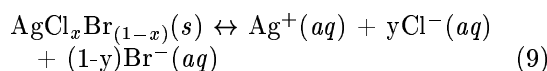
AREAS IN NEED OF FURTHER STUDY

Less than satisfactory knowledge attends several aspects of oxidized zone mineralogy and geochemistry. One concerns structural and thermodynamic properties of the many solid-solution systems that exist in Nature. Few of these behave ideally or regularly and, in order to include them rigorously in equilibrium models, solid-state activity coefficients need to be taken into account. This is because the activities of the components in a solid-solution are not in principle equal to unity. By way of example, the AgCl–AgBr solid-solution may be examined. For (6), the equilibrium constant expres-

sion is that given in (7), reducing to (8) since $a_{AgCl(s)}$ is equal to 1 by definition.
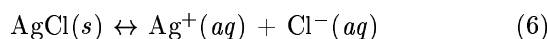
$$AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq) \qquad (6)$$

$$K_{sp} = a_{Ag^+(aq)}a_{Cl^-(aq)}/a_{AgCl(s)} \qquad (7)$$

$$K_{sp} = a_{Ag^+(aq)}a_{Cl^-(aq)} \qquad (8)$$

$$AgCl_xBr_{(1-x)}(s) \leftrightarrow Ag^+(aq) + yCl^-(aq)$$
$$+ (1\text{-}y)Br^-(aq) \qquad (9)$$

$$K_{sp}(AgCl) = m_{Ag^+(aq)}\gamma_{Ag^+(aq)}m_{Cl^-(aq)}$$
$$\gamma_{Cl^-(aq)}/N_{AgCl(s)}\gamma_{AgCl(s)};$$

$$K_{sp}(AgBr) = m_{Ag^+(aq)}\gamma_{Ag^+(aq)}m_{Br^-(aq)}$$
$$\gamma_{Br^-(aq)}/N_{AgBr(s)}\gamma_{AgBr(s)} \qquad (10)$$

For the solid-solution process (9), irrespective of whether the dissolution is congruent or not, activities of AgCl(s) and AgBr(s) are not equal to one (although they tend to unity for the major component as it approaches stoichiometric purity). Solutions and solids can be analyzed in any given case, but values of γ in the solid state need to be known to solve the expressions given in (10); m_i is the molality of the dissolved species and N_i is the mole fraction of the component in the solid-solution at equilibrium (γ_i for dissolved ions can be calculated from the Debye-Hückel or Pitzer formalisms). In the particular example chosen, values for solid-state activity coefficients are known as a result of the technical importance of it in the photographic industry. However, for most systems, including those mentioned earlier, the dearth of data is a serious shortcoming in our knowledge of secondary mineral chemistry.

Solid-solutions present other chemical surprises and it is evident that even the simplest of systems are sometimes not as well understood as might first be thought. One such system is that involving wulfenite, $PbMoO_4$, and stolzite, $PbWO_4$. In the study of groundwater geochemistry associated with the North Mungana orebody mentioned above, wulfenite and stolzite were found to limit the dispersion of Pb, Mo and W in solution. This discovery prompted a re-investigation of the variety "chillagite" ($Pb(Mo,W)O_4$, Mo $\sim$ W) from the Christmas Gift mine, Chillagoe, Queens-

land, and which was described as a new mineral nearly a century ago (Ullman, 1912; Smith and Cotton, 1912). Later workers concluded that it was merely a member of the solid-solution series extending between the end-members wulfenite, $PbMoO_4$, and stolzite, $PbWO_4$ (Quodling and Cohen, 1938). Both end-members crystallize in the tetragonal space group $I4_1/a$, and have been grouped with $CaWO_4$ (scheelite) and $CaMoO_4$ (powellite) in the Scheelite Group. Crystals from Chillagoe are frequently zoned, some crystals displaying rhythmic banding of Mo and W-rich material, which reflect the compositions of the solutions from which the specimens formed. Recently, however, single-crystal X-ray structure of a "chillagite" specimen from Chillagoe of approximately constant composition corresponding to wulfenite$_{60}$stolzite$_{40}$ was carried out. While the structure could be refined in space group $I4_1/a$, a significant number of symmetry-forbidden reflections was present in the diffraction record. These included 9 symmetry-forbidden reflections in the ($hk0$) zone and, significantly, the reflections 002, 006, 00$\overline{10}$ and 00$\overline{14}$ were observed in the [00l] axial direction; thus symmetry operations 4_1 and a could not be present. "Chillagite" actually crystallizes in the closely related space group $I\overline{4}$, as does a specimen of powellite from Tsumeb, Namibia (Crane et al., 2000b; Hibbs et al., 2001). Just what is responsible for the space group change is not completely understood, but such structural variations are common in solid-solutions and much systematic structural characterization, even for "simple" mineral cases, remains to be completed.

The temperatures at which secondary minerals form vary considerably and this fact is often overlooked. Most modelling has used data at 25°C and this is acceptable for most cases. On the other hand, subtle temperature variations serve to stabilize certain phases in preference to others. This is true of the hydrate posnjakite, $Cu_4SO_4(OH)_6 \cdot H_2O$, versus brochantite, $Cu_4SO_4(OH)_6$, the former being stable at about 10°C. Antlerite will crystallize directly from solution under appropriate pH conditions only

WILLIAMS

above about 35°C (Williams, 1990). It is difficult to estimate temperatures of crystallization in the oxidized zone. Recently, however, stable isotope methods have been applied to develop malachite, azurite and cerussite geothermometers (Melchiorre et al., 1999, 2000, 2001). Some surprising results have been obtained including that which shows significant amounts of cerussite in the Broken Hill, New South Wales ores to have formed at up to 50°C. Further applications of these kinds of studies will permit the "fine-tuning" of chemical models in the oxidized zone.

Finally, it must be stated that despite of the success of the equilibrium approach in explaining secondary mineral parageneses and stabilities in a wide variety of settings, other assemblages are subject to kinetic control. Some good examples of this added complexity concern a few of the secondary copper(II) chlorides and carbonate mentioned above. The three basic chlorides of stoichiometry $Cu_2Cl(OH)_3$ have standard free energies of formation at 298.2K in the order paratacamite < atacamite < botallackite, but are inter-related by a series of complicated kinetic phenomena. A fourth polymorph, clinoatacamite, is not as well characterized in this respect (Pollard et al., 1989, 1992a). Botallackite is a rare species, but atacamite and paratacamite are very widespread in oxidized zones of copper ore bodies. In the laboratory, precipitation of aqueous copper(II) chloride solutions with aqueous base first gives rise to claringbullite, which in time recrystallizes in turn to botallackite then atacamite then paratacamite. The last step can be almost completely inhibited by addition of excess chloride ion, while the addition of aqueous copper(II) chloride solutions to aqueous base gives rise to spertiniite, $Cu(OH)_2$, again under kinetic control, in a kind of "non-commutative" chemical reaction. This cascade towards compounds of increasing thermodynamic stability is a manifestation of the Ostwald Step Rule (Ostwald, 1897), which states

> "...if a reaction can result in several products, it is not the stablest

state with the least amount of free energy that is initially obtained but the least stable one, lying nearest to the original state in free energy."

Similar considerations apply to the formation of georgeite prior to recrystallization to malachite (Pollard et al., 1991, 1992b).

While our understanding of the details of these kinds of processes is poor, kinetic phenomena are very important in particular cases. In acid mine drainage settings (Parker and Robertson, 1999), control of metal ion dispersion most frequently depends on metastable phases. These include, for copper and zinc, the various hydrates of the brochantite stoichiometry, $Cu_4SO_4(OH)_6$, devilline, $CaCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$, and serpierite and orthoserpierite, $Ca(Cu,Zn)_4(SO_4)_2(OH)_6 \cdot 3H_2O$ (Krause and Täuber, 1992; Popov, 1999). Much remains to be done in this area.

CONCLUSIONS

Much is known of the mineral chemistry of the oxidized zone. Applications of this knowledge range from processing of ores to the search for new deposits and control of heavy metal pollution. Yet our knowledge is far from perfect and obvious gaps require many further detailed studies. In view of the importance of the oxidized zone in an economic sense, appropriate efforts will certainly be directed towards filling those gaps and helping to solve the problems that remain for geochemists and metallurgists.

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