

# Supergene Oxidation of Copper Deposits: Zoning and Distribution of Copper Oxide Minerals

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## ABSTRACT

Copper oxides represent an attractive exploration target because even low-grade prospects have the potential to produce low-cost copper in an environmentally friendly fashion. Derived from hypogene and/or supergene sulfides, copper oxides comprise a series of distinct assemblages that characterize a variable pH, oxidizing geochemical environment known as “the oxide zone.” Development of oxide copper minerals is a function of source-rock and host-rock mineralogy, pyrite and other (copper) sulfide abundance and distribution, fracture density and distribution, phreatic and/or vadose zone occurrence and stability, and maturity of the weathering profile.

The paragenesis of copper oxide mineral formation reflects local, dynamic changes in supergene solution composition attributable to reaction between host-rock mineral components and dissolved species. Especially important are the concentrations of  $\text{Fe}^{+++}$  (vs.  $\text{Fe}^{++}$ ),  $\text{SO}_4^{=}$ ,  $\text{H}^+$ , and  $\text{Cu}^{++}$  (vs.  $\text{Cu}^+$ ). Because mineral assemblages, even those that are metastable, represent the geochemical environment in which they formed, identification and mapping of copper oxides is useful in interpreting the geochemical history of an oxide zone. Furthermore, practical application of oxide zone geochemistry is significant in the recognition and solution of problems associated with weathering-engendered metals oxidation and transport from mine wastes.

**SPECIAL NOTE:** Readers will find more information about the copper oxide minerals mentioned in this article by referring to the SEG web site [<http://www.segweb.org>]. Photographs showing mineral relationships and paragenetic associations allow readers to further understand the nature of copper oxide assemblages and their geochemical and physical settings.

## RESUMEN

Oxidos de cobre comprenden una fuente importante del metal rojo, especialmente en yacimientos aptos para tratamiento del tipo “lixiviación—recuperación por solventes—electrowinning.” Este artículo describe la zonación y ocurrencia de los óxidos de cobre derivados por procesos supérgenos afectando a un protolito con sulfuros de cobre y hierro, hospedado por varias asociaciones mineralógicas de alteración. Los yacimientos considerados son principalmente pórfidos de cobre y molibdeno, y sistemas tipo skarn.

Geoquímicamente, el mineral más importante que influye la distribución de los productos de meteorización de un yacimiento metalífero del tipo pórfido de cobre es la pirita. Este mineral genera, en cantidades importantes, ácido sulfúrico ( $\text{SO}_4^{=}$  y  $\text{H}^+$ ) y hierro ( $\text{Fe}^{+++}$  y  $\text{Fe}^{++}$ ). Estos componentes de soluciones meteóricas (supérgenas) funcionan como lixiviantes, produciendo movilización de cobre y otros metales básicos desde el volumen de la roca lixiviada y resultando en la formación de la “capa lixiviada” (leached capping; véase Figura 1). Estos componentes acumulan, influido por la geoquímica de la roca huésped y de las soluciones que transportan estos componentes, en forma de óxidos y/o sulfuros, formando un volumen de roca enriquecida en metales y azufre.

En la *zona de óxidos*, minerales que contienen cobre oxidado ( $\text{Cu}^{++}$ , con menor  $\text{Cu}^+$  y cobre nativo) comprenden la fuente principal de cobre. La paragénesis de los óxidos refleja los cambios geoquímicos en las soluciones que proveen el cobre con respeto al tiempo. Así, la precipitación de los óxidos sigue, por lo general, la secuencia detallada en las figuras 3 y 4. Desarrollo de la secuencia vertical y/o lateral de óxidos de cobre es una función de (1) el tiempo disponible para meteorización e acumulación (maturity of supply and storage) de metales derivados de los sulfuros (madurez del perfil de meteorización), (2) composición y reactividad de la roca(s) fuente y de la roca(s) huésped (3) pH de soluciones transportadores de metales, (4) distribución y densidad de estructuras (fracturas, zonas de fracturamiento), y (5) estabilidad tectónica y fluctuación vertical del nivel freático. Aplicaciones de la geoquímica de la zona de óxidos es importante en la solución de problemas ambientales asociados con desechos de minas, especialmente oxidación y lixiviación desde relaves, desmontes, y pilas de lixiviación abandonadas.

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## SUPERGENE OXIDATION OF COPPER SULFIDE DEPOSITS, CONT.

### INTRODUCTION AND BACKGROUND

Despite low metal prices, mining and exploration for copper continue at a significant pace. Recovery of copper by leaching methods is economically more attractive than by conventional ore milling, so many companies are concentrating their mining and exploration efforts on copper oxide minerals. This article describes the nature and distribution of copper minerals occurring in oxide accumulations associated with weathering of copper sulfide deposits, with emphasis on minerals that occur in the supergene oxide zones of porphyry copper and skarn ore deposits. "Copper oxides" are defined as those copper minerals containing oxidized anions, especially copper oxides, *sensu strictu*, sulfates, phosphates, carbonates, and arsenates.

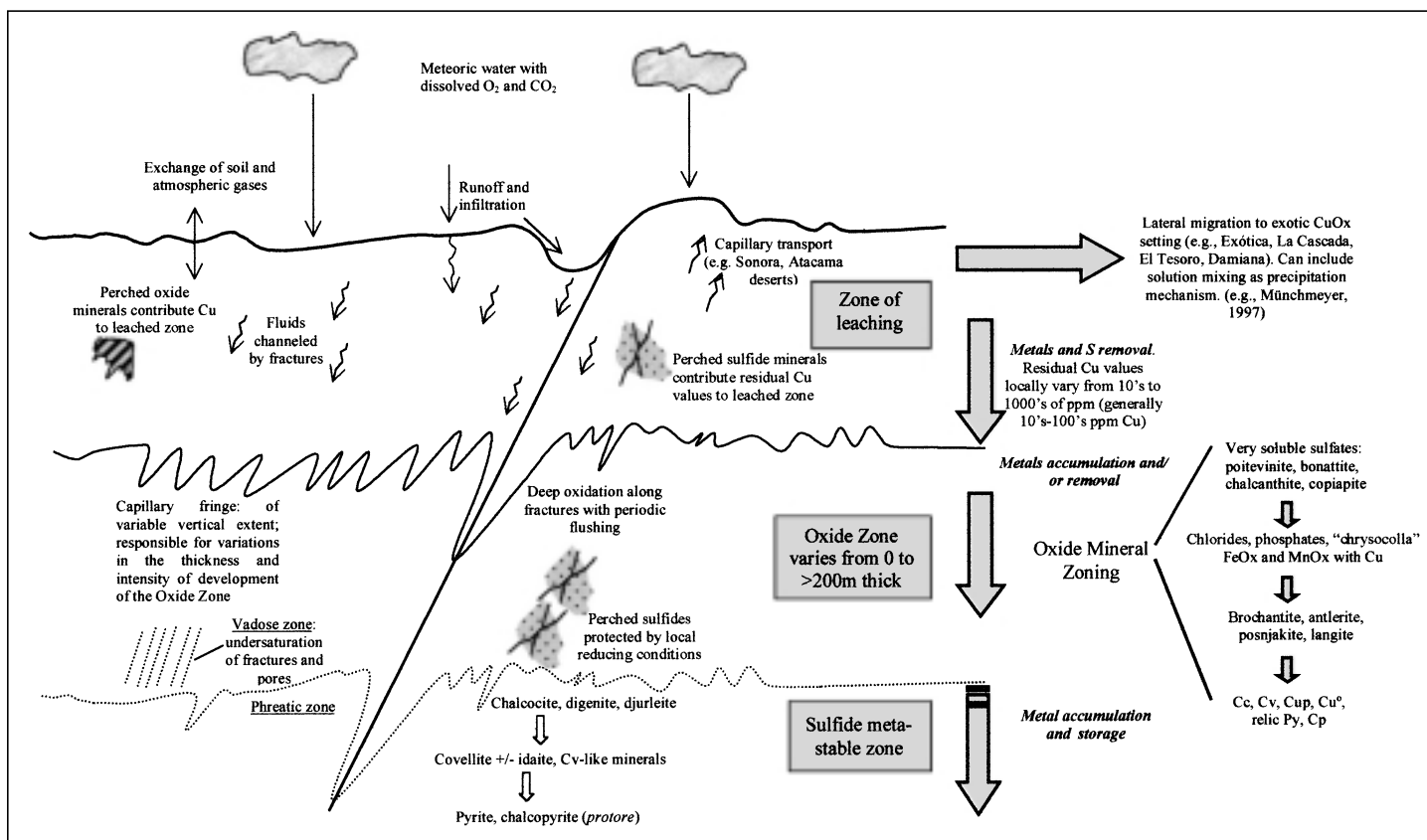
The oxidation of sulfide minerals, especially pyrite, is critical in determining the geochemical environment that characterizes a weathering sulfide-bearing rock volume. Sulfide destruction creates solutions containing hydrogen ions, metal ions, and sulfate; these solutions must be at least partially neutralized if the metals of economic significance are to be redeposited. One of the most important factors influencing the generation of the acid sulfate-bearing solutions is the ratio of reduced sulfur to metal in sulfide minerals before oxidation.

Weathering results in significant geochemical changes in the oxidation state of a sulfide-bearing mineral deposit because most ore

deposits are characterized by minerals containing base metals and reduced Fe and S. Figure 1 shows a schematic model of the components of an oxidizing rock volume containing sulfides and the location of the "oxide zone." In examples considered in this article, the pre-oxidation sulfide assemblage (protore) consists of pyrite and chalcocite, and contains sufficient pyrite to overcome at least some neutralizing capacity of host-rock minerals. The "oxide zone" consists of the rock volume in which copper oxide minerals are stable and are the dominant copper minerals.

### THE WEATHERING ENVIRONMENT

The weathering environment may be considered to have three principal geochemical domains. Although the contacts between these domains are gradational, each is characterized by distinct conditions of oxidation state and pH. These three domains are (1) a source region, comprising the volume of rock undergoing oxidation and mass loss; (2) a sink region(s), where mass from the source region accumulates and which includes residual (unreacted) hypogene minerals—the oxide zone discussed in this paper comprises part of this geochemical sink; and (3) protolith, the essentially unreacted material comprising pre-oxidation mineral assemblages. In some cases, if warranted by the metal concentrations, the protolith is termed protore or quasiprotore (Alpers and Brimhall, 1989). The mineralogy of the source, sink, and protolith rock volumes varies according to whether mass transport from the source region to the sink region is geochemically significant or minor. These geochemical domains are summarized in Table 1.



**Figure 1:** Schematic diagram showing the weathering environment of a sulfide-bearing mineral occurrence. Three component zones comprising the simplified weathering profile are shown, with mineral assemblages characteristic of the oxide zone displayed to the right of the diagram. See Table 2 for ranges of copper values in the zone of leaching.

**Table 1.** Mineral Assemblages in Geochemical Domains in High and Low Mass Flux Conditions

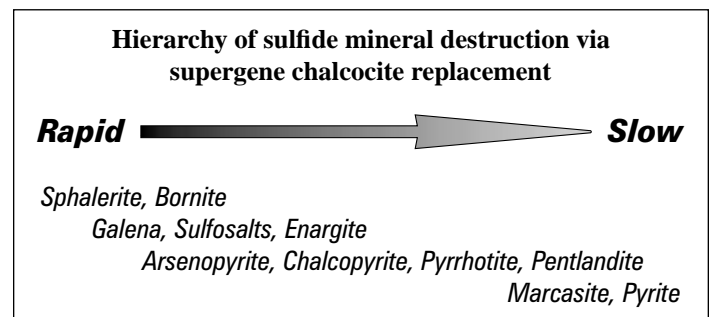
	Dominantly Transported Fe and Cu	Dominantly In Situ Oxidation
<b>Source</b>	Reactive sulfides with jarosite, goethite » hematite; Residual pyrite, chalcocopyrite; alunite, Al-Fe sulfates	Low total sulfide volumes or low S/metal sulfides Quasi-in situ oxidation and precipitation of hematite; hematite > to » goethite, jarosite
<b>Sink</b>	Chalcanthite, bonattite, antlerite, brochantite, posnjakite; local native copper Chalcocite, covellite, pyrite, chalcocopyrite Also: alunite, As-Fe oxides, arsenates	Atacamite, brochantite, native copper, chalcocite, cuprite, tenorite, paramelaconite, malachite, phosphates; local alunite; residual chalcocopyrite, bornite, pyrite
<b>Protolith</b>	Pyrite, chalcocopyrite; traces of bornite, pyrrhotite	Bornite, hypogene chalcocite, chalcocopyrite, ±pyrite

Well-developed copper oxide zones appear to form through two distinct mechanisms: (1) via substantial copper addition to a volume being oxidized, including the formation of exotic copper deposits, and (2) through in situ oxidation of a copper-bearing sulfide resource. Importantly, the first type of copper oxide system requires copper transportation from a source region, but the protore does not need to have high copper content if leaching and precipitation are efficient. Conversely, the second type requires substantial protolith copper content if the copper oxide zone developed is to be of potential ore grade, and requires also that removal of copper be minimal.

Distinction between these protore environments is significant in exploration for copper oxide and supergene sulfide enrichment targets because prospects dominated by reactive rock units are likely to display only incipient copper enrichment unless an adjacent or eroded non-reactive source-rock volume was available to provide transported copper. For example, an eroding phyllic or argillic alteration zone of a porphyry system may provide copper to a sink comprising a reactive (K silicate or propylitic) rock mass, whether in situ or exotic. This is why in situ copper occurs at El Abra (see below), Lomas Bayas, Mantos Blancos, and Radomiro Tomic, and exotic copper occurs at Mina Sur (Exótica), Huiniquintipa, El Tesoro, Ichuno, and La Cascada, Chile (Münchmeyer, 1997).

To generate the first type of copper oxide occurrence, a source region must be available to supply copper via oxidation and leaching. Pyrite is the most significant source of oxidized S and, indirectly, hydrogen ions, in a sulfide-bearing rock volume undergoing weathering. It is also a substantial, if not dominant, source of oxidized iron. As these components are intimately involved with copper mobilization from the source region, oxidation of pyrite is important to generate a well-developed copper oxide ore deposit via copper addition.

Oxidation of pyrite involves a series of stepwise processes resulting in the generation of “protominerals” such as schwertmannite and ferrihydrite, the solubility of which is a function of the production of Fe<sup>+++</sup> and Fe<sup>++</sup>, pH, and SO<sub>4</sub><sup>-</sup> activity (Murad et al., 1994). The combination of sulfate as a complexing anion, hydrogen ions (i.e., acid conditions), and atmospheric oxygen to enhance and maintain an oxidizing environment results in destruction of sulfides, oxides, and silicate minerals (Titley, 1982; Titley and Marozas, 1995). Importantly, the relative susceptibility to oxidation of sulfide minerals determines the sequence of sulfide mineral destruction, the consequent availability of metals for supergene transport, and the nature and zoning of resulting minerals (Bladh, 1982). Figure 2 shows the general succession of sulfide mineral destruction by chalcocite replacement, as observed from paragenetic relationships shown by oxide-sulfide zone assemblages. Boyle (1994) shows a similar sequence for sulfide replacement within sulfidic tailings undergoing oxidation.



**Figure 2:** Paragenetic diagram showing the general succession of sulfide mineral destruction by chalcocite replacement, as observed from paragenetic relationships shown by oxide-sulfide zone assemblages. Boyle (1994) shows a similar sequence for sulfide replacement within sulfidic tailings undergoing oxidation.

The oxidation of sulfides other than those of iron produces only modest quantities of acid sulfate-bearing solutions (Anderson, 1982; Williams, 1990), a factor which is significant in determining the types and distribution of oxide minerals developed within a zone of weathering (see below). Therefore, pyrite oxidation is generally the most important source of the acidic solutions responsible for mineral destruction during the weathering of a rock volume. This means that pyrite quantity is critical in determining oxide zone mineralogy.

Pyrite is a relatively refractory mineral in the replacement sequence; marcasite oxidizes more quickly than pyrite (Mason and Berry, 1968), and pyrrhotite oxidation is as much as two orders of magnitude faster than oxidation of pyrite (Nicholson and Scharer, 1994). Laboratory observations of Fe sulfide oxidation are corroborated by the parageneses of oxide and sulfide minerals reported from oxide zones: it is observed that pyrite shows incipient or no significant corrosion-replacement even when other sulfides in the same oxide volume display substantial oxidation, as in leached caps or gossans, or variable replacement by oxides or sulfides—as seen at Chuquicamata (Flores, 1985; G. Ossandón et al., unpub data<sup>1</sup>) and Mantos Blancos (Chávez, 1983), Chile; and Lakeshore, Arizona (Cook, 1988; Huyck, 1990). Therefore, for pyrite to provide a significant source of acid sulfate-bearing solutions, weathering conditions must be strongly oxidizing.

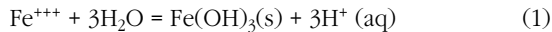
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<sup>1</sup> Ossandón, G., Fréaut, R., Rojas, J., and Gustafson, L.B., in review, Geology of Chuquicamata Revisited: Economic Geology.

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Other sources of acidic solutions, albeit generally minor compared to sulfides, include magnetite and Fe-bearing silicates. Silicate minerals that contain Fe<sup>2+</sup> are susceptible to oxidation, and minerals such as biotite, Fe amphiboles, Fe pyroxenes, and Fe-bearing garnets (e.g., the La Democrata skarn system in the Cananea district, México) may contribute to the generation of acid solutions during weathering. This is because ferric iron, produced during mafic mineral oxidation, generates goethite plus hydrogen ions via reactions such as:



The same type of reaction explains why magnetite, a common component of ore deposits, is capable of producing acid solutions even from mineralized rocks having scant or no sulfide minerals.

### LEACHED CAPPINGS: SOURCES OF METALS

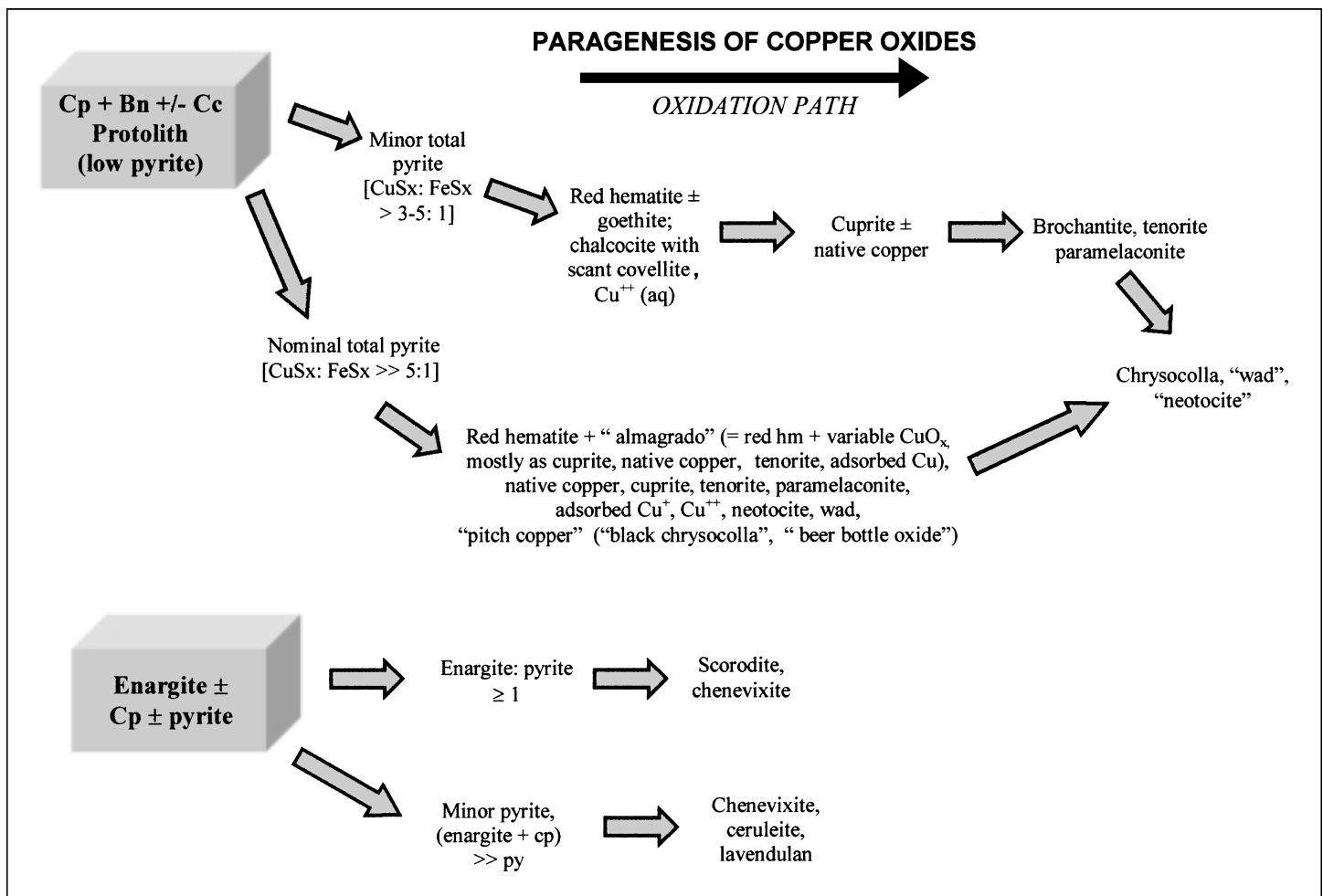
The metals that ultimately accumulate in the oxide or sulfide enrichment zone are derived from the volume of rock that has undergone oxidation and metal removal, referred to as the leached capping (developed from disseminated and fracture-controlled

sulfides; Locke, 1926) or gossan (developed from massive sulfide bodies, including skarn-hosted sulfides).

The extent to which the leached capping, oxide volume, and sulfide enrichment volume are developed depends on the amount of acid-producing sulfides in the rock volume, the neutralizing capacity of the minerals in the host rocks, the density and extent of host-rock fracturing, and the nature and duration of local and regional weathering conditions (López and Titley, 1995). Although removal of metals from the leached capping may be very efficient, residual copper and iron are always present in detectable quantities and comprise the geochemical anomalies—both positive and negative—important to minerals exploration and to environmental considerations of waste-rock disposal.

Table 2 provides examples of the residual copper values reported from leached rock volumes over porphyry copper deposits. Copper contributed from rock masses undergoing oxidation and removal of metals and sulfate is transported by acid solutions, dominantly as cupric copper. Figure 3 shows the general parageneses for copper phases related to different protolith sulfide assemblages for relatively reactive protoliths.

Copper is mobile at low pH, so copper occurrence in some environments may be represented by cupric ion as well as by minerals. Although copper oxide minerals display a wide range of



**Figure 3:** Oxidation path diagram showing paragenesis of copper oxides derived from low to moderate total pyrite protoliths. Note that the ending paragenesis, developed in geochemically mature copper oxide zones, comprises a series of Cu + Fe ± Mn oxides, dominated by hematite (rather than goethite or jarosite).

**Table 2.** Copper Content of Leached Cap Volumes

DISTRICT	LEACHED CAP COPPER CONTENT
Cananea, México	X0 to low X00 ppm Cu derived from pyritic protolith with jarositic-goethite dominant capping
Cerro Colorado, Chile	Up to 2,000 ppm, as contamination from relic hypogene sulfides and residual supergene chalcocite ± Cu oxides
Quebrada Blanca, Chile	700 to 1,500 ppm in a hematitic leached cap, probably derived from the incomplete oxidation of former chalcocite
La Escondida, Chile	Less than ~100 ppm in "superleached" cap, enhanced through chloride activity and essentially inert host rocks
El Abra, Chile	No leached cap in well-developed K silicate stable protolith with cp + bn + cc protore (~0.65% Cu) and in situ chrysocolla + brochantite + pseudomalachite + neotocite Cu-oxide zone (avg ~0.55% Cu)
Morenci, Arizona	X0 to 800 ppm Cu; protore Cu concentration approximately 1,200–1,500 ppm
Tyrone, New Mexico	200 to 400 ppm in jarositic to goethitic leached cap developed from pyritic protolith containing 700–1,200 ppm copper
Santa Rita, New Mexico	X0 to low X00 ppm Cu in hematitic to goethitic leached cap developed over phyllic-argillic alteration of monzonitic hosts; local native copper
Radomiro Tomic, Chile	Up to 1,000 ppm in poorly developed leached volumes derived from K silicate protolith
Lomas Bayas, Chile	Leached and oxidized rock volumes contain X00 ppm copper with residual Cu values to >1,000 ppm as sulfates, chlorides
Cerro Colorado, Panamá	No significant leached cap in humid, high-rainfall (>4,000 mm/year), steep terrain; protolith copper concentrations 4,000–9,000 ppm

stability, specific suites of copper oxides are useful in limiting the interpretations concerning weathering environments and the genesis of copper oxide minerals (Locke, 1926; Schwartz, 1934). This indicates that copper oxide minerals represent broad conditions of oxidation and pH; nonetheless, the mineralogy of a given oxide assemblage is very useful in assessing the Eh-pH conditions of copper oxide formation, including those conditions responsible for copper transportation and deposition. The following section describes the formation of copper oxides and associated minerals in the oxide zone of a weathering mineral deposit containing disseminated and fracture-controlled sulfides.

## COPPER OXIDE ZONE DEVELOPMENT

The oxide zone is defined as the rock volume representing a redox environment transitional between the very oxidized conditions present in the leached capping and the reduced conditions characterizing the supergene sulfide zone. Oxide zone mineralogy reflects variably oxidized and reduced conditions, with mineral zoning exhibited on both large and small scale. Table 3 lists minerals commonly found in the oxide zone and leached capping of porphyry copper deposits.

**Table 3.** Minerals Commonly Found in the Oxide Zone of Copper Deposits

Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$
Antlerite	$\text{Cu}_3\text{SO}_4(\text{OH})_4$
Atacamite (paratacamite, botallackite)	$\text{Cu}_2\text{Cl}(\text{OH})_3$
Bonattite	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
Brochantite	$\text{Cu}_4\text{SO}_4(\text{OH})_6$
Ceruleite	$\text{Cu}_2\text{Al}_7(\text{AsO}_4)_4(\text{OH})_{13} \cdot 12\text{H}_2\text{O}$
Chalcanthite (compare to kröhnkite)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Chalcosiderite (compare to turquoise)	$\text{CuFe}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$
Chenevixite	$\text{Cu}_2\text{Fe}^{++}\text{AsO}_4 \cdot 2\text{H}_2\text{O}$
Chrysocolla (mineraloid)	$\text{Cu}(\text{Fe},\text{Mn})\text{Ox} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ , with copper content varying from ~20-40 wt-% Cu
Copiapite	$\text{Fe}_5(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
Goethite	$\alpha\text{-FeOOH}$
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$
Kröhnkite	$\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$
Lavendulan	$\text{NaCaCu}^{++}_5(\text{AsO}_4)_4\text{Cl} \cdot 5\text{H}_2\text{O}$
Libethenite	$\text{Cu}_2\text{PO}_4(\text{OH})$
Paramelaconite	$\text{Cu}_4\text{O}_3$ (see tenorite (CuO) and cuprite (Cu <sub>2</sub> O))
Poitevinite	$(\text{Cu},\text{Fe},\text{Zn})\text{SO}_4 \cdot \text{H}_2\text{O}$
Posnjakite	$\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$
Pseudomalachite (see libethenite)	$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$
Scorodite (see chenevixite)	$\text{Fe}^{+++}\text{AsO}_4 \cdot 2\text{H}_2\text{O}$
Turquoise	$\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$
Voltaite	$\text{K}_2\text{Fe}_8\text{Al}(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$
Wroewolfeite (Langite)	$\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$

Copper oxide minerals form (1) through direct precipitation as supergene solutions reach saturation with a specific mineral component(s), or (2) via replacement of sulfides, oxides, or silicate minerals. In most environments, oxidation of hypogene sulfides with high S/metal (S/Me) mole ratios, such as pyrite, marcasite, and pyrrhotite, results in at least incipient destruction of the original sulfide and the resultant dissolution of iron as  $\text{Fe}^{+++}$  and sulfur as  $\text{SO}_4^-$ . However, oxidation of sulfide-bearing rocks with low total pyrite content and of minerals with S/Me ratios of approximately unity, such as chalcocite, idaite ( $\text{Cu}_3\text{FeS}_4$ ), pentlandite, enargite, and arsenopyrite, usually results in the formation of combined Fe and metal oxides having geochemically limited mobilities because there is insufficient acidity generated during weathering to ensure complete removal of the original mineral components. For this reason, chalcocite

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## SUPERGENE OXIDATION OF COPPER SULFIDE DEPOSITS, CONT.

oxidation generally leads to the development of local hematite ± goethite halos adjacent to the replaced mineral grain, accompanied by copper oxides that are stable in the near-neutral to moderately low pH range.

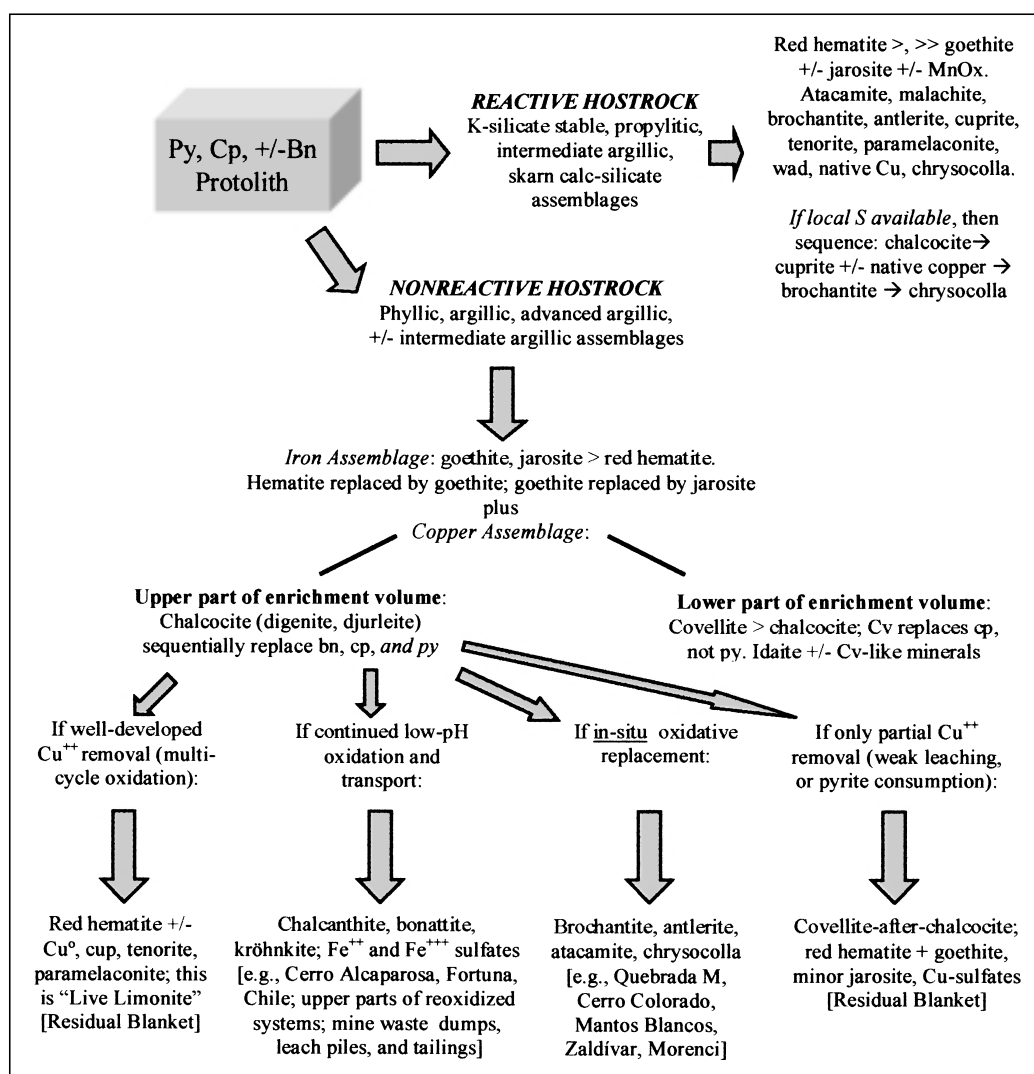
Figure 4 shows reaction paths for copper oxide minerals formed within (1) reactive host rock and (2) relatively non-reactive host rock, starting with a protolith containing pyrite, chalcocopyrite, and minor bornite. The geochemical reactivity of host rocks is significant (Marozas, 1982; Pinson, 1992) because the quantity of silicate minerals available for acid neutralization directly influences the local leaching and oxide zone geochemical environment. Although the abundance of reactive minerals is important in determining how a rock mass will react to acidic solutions, reaction kinetics may inhibit the ability of a reactive protolith to neutralize acid, sulfate-bearing solutions. The relatively slow reaction of most silicates with acidic solutions generated via pyritic sulfide oxidation is especially notable in mine environmental remediation studies in which reactive silicates comprise part of the acid-buffering component of a mine waste (Walder and Chávez, 1995).

The mineralogy of the host rock plays a very significant geochemical role in the development of the gangue and ore mineral assemblages occurring in the copper oxide zone. This is because host-rock silicates and oxides, comprising the volumetrically dominant minerals in the weathering environment, offer exchangeable cations and thus are capable of consuming hydrogen ions via hydrolysis. The greater the quantity of reactive silicates and oxides such as feldspars, mafic minerals, and carbonates, the greater the ability of a wall rock to neutralize acid, sulfate-bearing solutions. This buffering capacity is limited in rock that has already been subjected to phyllic, argillic, and advanced argillic alteration, because phyllosilicates and clays characteristic of these assemblages have only limited capacity to exchange cations for H<sup>+</sup>.

In Figure 4, arrows show the sequential development of copper oxide and associated sulfides, with paths determined by protolith sulfide ratios and the completeness of weathering reactions. The paths lead to oxide assemblages that are

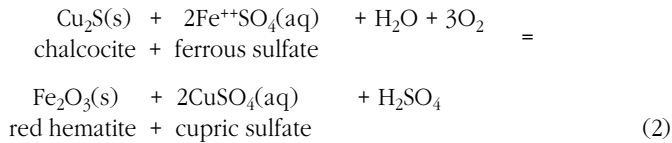
mineralogically distinct because the geochemical conditions that form the various assemblages are dictated by specific combinations of sulfide and host-rock mineralogy, structural setting of the weathering rock mass, and lithologic variations.

These geochemical conditions produce the mappable mineral assemblages characteristic of the oxide zone. Interpretation of the environment of formation of the mineral assemblages is an important part of the economic evaluation of copper oxide (and sulfide) prospects. For example, chalcocite oxidation and leaching produces an assemblage of Fe oxides referred to as “live limonites”; this term really refers to “red hematite-dominant” Fe oxide assemblages, generated as a result of copper removal by supergene solutions derived from residual acid production. Thus, the generation of red hematite during oxidation of supergene sulfides having very minor iron may be explained by the oxidation of chalcocite in low-pyrite or high-pyrite environments, as in the following reactions.

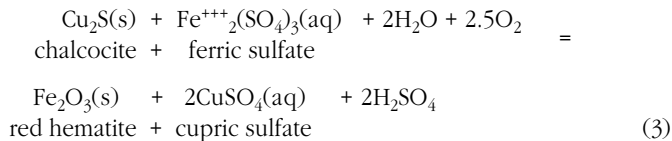


**Figure 4:** Paragenesis of copper oxides starting with a pyrite-dominant protolith. Copper oxide assemblages are a function of successive oxidation-mobilization-accumulation cycles, with paths shown for geochemically reactive and nonreactive host rocks. Lower tier shows mineral assemblages resulting from various oxidation scenarios, beginning with a supergene sulfide assemblage. The oxidation of sulfidic mine wastes mimics that shown here for natural systems, with corresponding applications for environmental remediation of abandoned minesites.

A low total residual pyrite environment results in the formation of substantial ferrous sulfate, which participates in oxidation reactions as follows:



If residual pyrite content of an oxidizing protore is relatively high, this results in generation of ferric sulfate, which participates in oxidation reactions as follows:



In each environment, copper is liberated and hematite takes the place of the now oxidized and dissolved copper sulfide. At least traces of copper remain associated with the newly generated red hematite. This copper may occur as “geochemical copper” adsorbed onto the surface of iron oxides or as minute grains of distinct copper minerals admixed with the red hematite. The association of abundant hematitic Fe oxides with trace copper is common in leached environments, which otherwise show no obvious copper oxide occurrence. These oxides are termed “almagre” or “sangre de toro” in Central and South America, and may contain economically important quantities of copper. In some cases, the copper may occur as cuprite or native metal, rendering copper recovery difficult (e.g., portions of the Ray, Arizona, oxide zone). In cases where pyrite was present in stoichiometric excess (usually greater than 5–7 vol % pyrite), its oxidation may produce enough acid to remove essentially all iron and copper, such that supergene iron oxide abundance and copper content may each be minor.

With the descent of metal-bearing, acid sulfate-rich fluids, hypogene sulfides may be replaced initially by chalcocite, djurleite ( $\text{Cu}_{1.96}\text{S}$ ) or digenite ( $\text{Cu}_{1.8}\text{S}$ ), with subsequent replacement of these sulfides by copper oxides as availability of reduced sulfur diminishes as sulfides are consumed. Covellite develops in environments that lack abundant dissolved  $\text{Cu}^{++}$ , usually by in situ oxidation and replacement of chalcopyrite or bornite, rarely pyrite. Hence, the paragenesis of sulfide replacement may involve several copper sulfides prior to ultimate copper oxide development. Replacement of sulfide assemblages having low S/Me ratios or high copper contents (covellite, chalcocite, digenite, bornite) may result in the direct precipitation of copper oxides—e.g., at Radomiro Tomic (Arcuri and Brimhall, 1998); Quebrada “M” in the El Salvador district, Chile, and Morenci, Arizona—because the local geochemical environment is moderately low to near-neutral pH, which is favorable for copper oxides that are stable in the range of pH 4 to 9 (Fig. 3; see also Anderson, 1982).

## COPPER OXIDE PARAGENESIS AND ZONING

The paragenetic sequence of copper oxide minerals observed from many oxidized copper-bearing orebodies reveals that a specific series of progressive mineralogic changes takes place during supergene oxidation, transport, and precipitation. This section

discusses copper mineral paragenesis and spatial zoning in the context of mineralogic associations, protolith compositions, and host-rock alteration assemblages.

Copper deposits in which pyrite is a volumetrically significant component are characterized by copper oxide assemblages reflecting low pH environments. Pyrite rarely shows direct replacement by copper oxides because the microenvironment developed by pyrite oxidation is usually so acidic that only copper sulfates and an attendant series of iron sulfates, such as jarosite, coquimbite, copiapite, melanterite, and voltaite, are stable. For example, if pyrite contents are such that the neutralizing capacity of host rock is exceeded and pH of <2 solutions are generated, the copper sulfate minerals bonattite, chalcantite, kröhnkite and wroewulfite are stable (Table 3). These minerals form in the uppermost parts of the oxidation system, topographically above near-neutral pH-stable sulfates such as brochantite, posnjakite, and antlerite. Evidence of such low pH conditions and the mineralogy produced in the oxide zone is present at Chuquicamata (Jarrell, 1944), Fortuna de Cobre (R. Nordin and R. Chavarría, pers. comm., 1999), Lomas Bayas, and Cerro Alcaparosa, Chile. A similar environment is generated during the post-mining oxidation of pyritic sulfide ore deposits and mine wastes.

If sufficient copper is available in an oxidized solution, and if reduced sulfur is present, the minerals chalcocite, djurleite, and digenite replace pyrite. Covellite, idaite, and covellite-like sulfides replace chalcopyrite and bornite, and rarely, pyrite. Chalcocite and digenite are the most common replacement products in the upper portions of a sulfide enrichment zone, with covellite at greater depths (Flores, 1985); djurleite is the most abundant supergene copper sulfide in some ore deposits, e.g., Michilla (Soto and Dreyer, 1985) and San Bartolo (Flint, 1986), Chile. However, successive replacement of chalcocite and digenite is common when the composition of an oxidized supergene solution changes as pyrite is consumed in the source region(s). Hence, moderate pH stable oxide minerals are favored, resulting in copper sulfide replacement by geochemically appropriate copper oxides.

Copper oxide mineral associations generally are consistent because oxidizing sulfide systems experience a consistent series of chemical reactions that permit only the development of characteristic mineral paragenetic relationships. Brochantite replaces chalcocite in weathering systems in which moderately low to near-neutral pH values are maintained, such as in portions of the orebodies at Quebrada “M”, Cerro Colorado, and Quebrada Blanca, Chile, and Morenci, Arizona. If chloride activity is high in a near-neutral pH weathering environment (Rose, 1976), the copper hydroxychloride atacamite [ $\text{Cu}_2\text{Cl}(\text{OH})_3$ ] replaces chalcocite (Mantos Blancos, Michilla, Santo Domingo, and Buena Esperanza, Chile; Florence Junction, Arizona). Antlerite replaces chalcocite in environments having lower pH than characterizes brochantite (Anderson, 1982); e.g., La Escondida and Chuquicamata, Chile. Ore petrography studies (Chávez, 1983; Arcuri and Brimhall, 1998) suggest that most of the brochantite-antlerite-atacamite formed through chalcocite replacement represents in situ oxidative replacement of chalcocite rather than copper addition as a sulfate or chloride. Indeed, these green copper oxides contain less copper than chalcocite, so destruction of chalcocite via simple replacement usually represents copper loss (leaching) rather than enhancement. In some systems, these copper sulfates replace cuprite (for example, at Collahuasi and El Abra, Chile),

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## SUPERGENE OXIDATION OF COPPER SULFIDE DEPOSITS, CONT.

representing an in situ replacement assemblage with little or no significant copper addition or transport.

In systems characterized by near-neutral or slightly alkaline pH environments, cuprite replaces chalcocite (e.g., Cerro Colorado, Copucha (Sierra Gorda), and El Abra, Chile; locally at Ray, Arizona, and Santa Rita, New Mexico). Cuprite represents an intermediate replacement product in many oxide zones, and is almost always replaced by other copper oxide minerals. Native copper usually occurs with cuprite—El Abra, Chile; Santa Rita, New Mexico; Ray, Arizona; Piedras Verdes, Mexico (Dreier and Braun, 1995); San Jorge, Argentina (Williams et al., 1999)—but rarely directly replaces chalcocite. Native copper occurs generally at greater depth than cuprite (Anderson, 1982).

Malachite and azurite are common constituents of copper oxide zones in which carbonate is available from sedimentary sources (notably in oxidized skarn systems, e.g., Christmas, Koski and Cook, 1982; Morenci, Arizona, and Cananea, Mexico, Velasco, 1966), atmospheric sources, and/or indigenous bacteria cells (Enders, 2000). Carbonates, along with the mineraloid chrysocolla, generally comprise paragenetically late minerals, replacing earlier oxides and sulfides and occurring as transported constituents occupying otherwise “clean” fractures, including fractures showing no evidence of prior mineralization (e.g., southern Perú coastal batholith).

In geochemically mature copper oxide systems developed under near-neutral to alkaline pH conditions, malachite and chrysocolla are typically the most important copper minerals, with tenorite, paramelaconite, and neotocite are volumetrically minor. This is probably because carbonates and silicates are most stable in a well-developed oxidation environment in which sources of low pH solutions have been consumed, and because indigenous and atmospheric sources of silica and carbonate, respectively, are readily available. Incipient and generally subeconomic fracture-controlled copper carbonates and chrysocolla occur paragenetically late in oxidized copper deposits at Cerro Colorado and Cerro Chorchá, Panamá; along the southern Perú coastal batholith and in adjacent northern Chile, and in late-stage oxidation assemblages in the southwest United States. Exotic copper deposits (Newberg, 1967; Angúita, 1997; Mote and Brimhall, 1997; Münchmeyer, 1997) are almost exclusively chrysocolla dominant, with minor atacamite, copper wad, tenorite, and/or Fe-Mn-Cu oxides (including neotocite).

Tenorite and paramelaconite, the black copper oxides, occur in the upper zones of copper systems in which high host-rock reactivity and low pyrite content produce alkaline to neutral pH environments. If carbonate is available to buffer low pH solutions produced through sulfide oxidation, tenorite and paramelaconite may occur in local environments characterizing oxidized pyritic sulfide systems, especially skarns (e.g., Morenci, Arizona). At El Abra, Chile, tenorite and paramelaconite comprise the constituent minerals in neotocite; along with chrysocolla, neotocite occurs in surface outcrops and at shallow depths of the El Abra oxide orebody within reactive host rock comprising biotite-stable diorite porphyry. The tenorite and paramelaconite association grades with increasing depth to the assemblage cuprite ± native copper (A. Moraga, pers. comm., 1999); this assemblage is replaced by and grades with depth to brochantite. This change with depth is consistent with a gradual change in copper oxidation state, decreasing with increasing

distance from the former erosional surface. The observed paragenesis, in which black copper oxides replace the assemblage cuprite + native copper ± brochantite, supports the argument that the occurrence of tenorite ± paramelaconite ± neotocite indicates the most oxidized zones of a weathering, low total sulfide protolith.

The paragenetic paths shown in Figures 3 and 4 summarize the observations above. Oxidation products for arsenic-bearing ores, common components of hydrothermal ore deposits, are summarized in Figure 3. Arsenopyrite, when oxidized in an environment containing pyrite, yields the iron arsenate scorodite characteristic of the upper portions of an oxide zone. Similarly, enargite oxidation in the presence of pyrite produces scorodite (Summitville, Colorado; La Candelaria breccia at Morenci, Arizona; La Grande, Collahuasi district, Chile). In a low pyrite environment, enargite is replaced by a series of apple green to pastel blue copper arsenates such as chenevixite, ceruleite, and lavendulan (e.g., in the weathered epithermal Cu-Au-As systems at El Guanaco and La Grande, Chile, and in the oxide zone at Chuquicamata, Chile).

## EXAMPLES OF COPPER OXIDE DEPOSITS

The following examples of settings in which copper oxides of economic importance have developed demonstrate that both the mineralogy and amount of copper oxides vary significantly.

### Systems Displaying Limited Copper Mobility

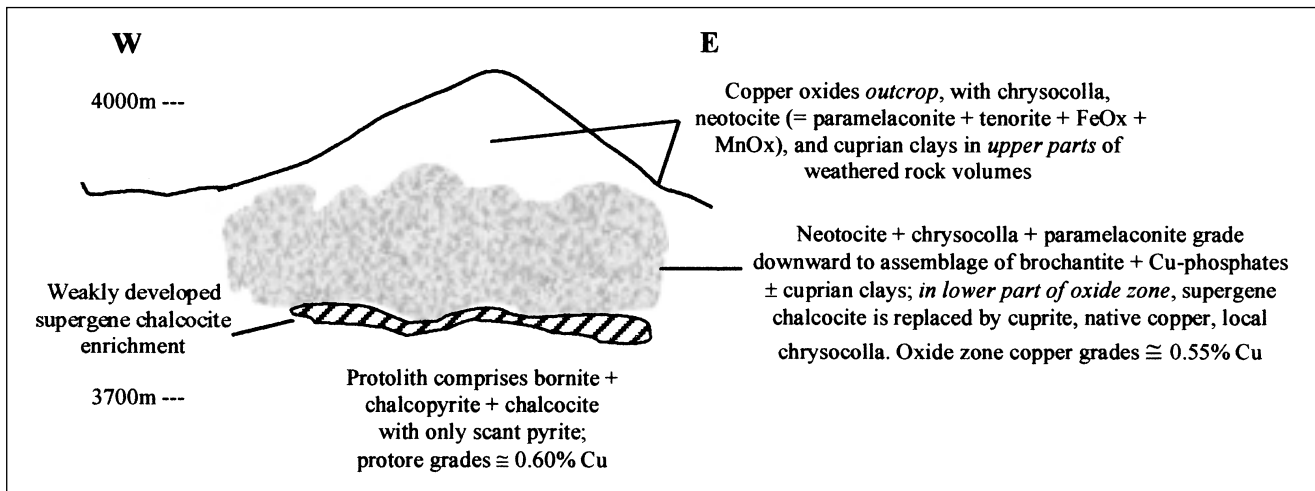
*El Abra.* The El Abra porphyry copper deposit of northern Chile is an example of supergene oxidation generated within a reactive host-rock environment (Fig. 5). This world-class ore deposit comprises a well-developed, fracture-controlled copper oxide orebody derived from essentially in situ oxidation of a low-pyrite, chalcopyrite + bornite + chalcocite protolith assemblage hosted by dioritic intrusions. Host-rock alteration consists of ubiquitous biotite with subordinate K feldspar replacement and veining. Incipient white phyllosilicate overprint of the K silicate assemblage occurs locally and distal to the K silicate assemblages.

Copper oxides at El Abra comprise assemblages characteristic of moderate-pH weathering environments because insufficient pyrite was available for production of low-pH supergene solutions. The oxide orebody outcrops, with surface and near-surface oxides comprising chrysocolla, paramelaconite ( $\text{Cu}_4\text{O}_3$ , similar in occurrence to tenorite,  $\text{CuO}$ ), and neotocite, shown by X-ray diffraction studies to be a physical mixture of Fe and Cu oxides, notably tenorite. This assemblage gives way at depth to brochantite and copper phosphates, such as pseudomalachite. Suprajacent to and within the weakly developed chalcocite enrichment volume and in the upper portions of the hypogene sulfide zone, cuprite, native copper, brochantite, and chrysocolla are developed. This latter assemblage displays a typical paragenetic sequence in which chalcocite is replaced by the sequence:

Chalcocite → cuprite ± native copper → brochantite → chrysocolla

Because copper grades in the oxide zone are essentially the same as those in the hypogene protolith, it is interpreted that the El Abra copper oxide-copper sulfide orebody represents in situ oxidation of the hypogene sulfide assemblage, with copper transport limited to perhaps several tens of meters. The development of copper oxides from oxidation of a low-pyrite, reactive protolith containing low S/Me ratio minerals at El Abra is similar to that observed at Radomiro Tomic (Acuri and Brimhall, 1998, 1999), and other



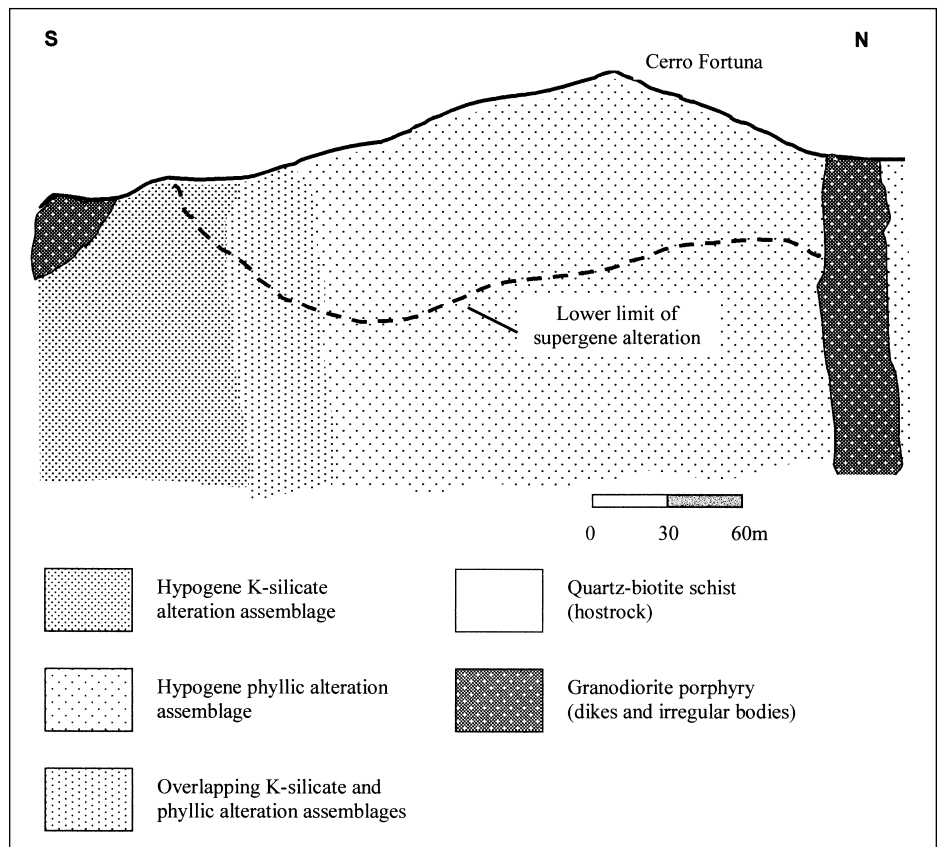


**Figure 5:** Generalized vertical cross section through the El Abra porphyry system, II Region, northern Chile. In situ development of copper oxides from a low pyrite, K silicate stable, (bn + cp + cc)-bearing protolith engendered near-neutral pH stable minerals and no significant copper grade enhancement in the oxide zone. The copper oxide zone consists of up to approximately 200 m of mineralized host rock, beginning at the present topographic surface. Upper and lower portions of the El Abra oxide zone may be defined on the basis of dominant copper mineralogy, as shown; the lower oxide zone displays a gradational contact with underlying and erratically-developed chalcocite enrichment. Simplified from Hawley, Moraga, and Molina (pers. comm., 1999)

northern Chile ore deposits hosted by intermediate volcanic rocks, such as the atacamite-chrysocolla assemblages at Mantos Blancos (Chávez, 1983) and Michilla (Soto and Dreyer, 1985). An exotic copper oxide resource (Ichuno) exists adjacent to the principal copper oxide orebody at El Abra. This occurrence may be explained by an eroded copper source rock, possibly a phyllic alteration assemblage, formerly located suprajacent to the present potassic core of the El Abra porphyry system (A. Moraga and A. Molina, pers. comm., 1999).

**Piedras Verdes.** Dreier and Braun (1995) describe the occurrence of incipient copper oxide development from the Piedras Verdes porphyry copper deposit, Sonora, Mexico (Fig. 6). This occurrence comprises a low-grade, low total sulfide protolith hosted by an alteration assemblage of biotite + K feldspar + quartz + tourmaline, with adjacent pyritic protolith hosted by a phyllic alteration assemblage. Protolith copper concentrations are on the order of 1,500 ppm, as chalcopyrite.

Piedras Verdes represents an excellent example of the control of copper oxide development by alteration mineralogy. Where reactive K silicate assemblages exist, weathering has resulted in the in situ development of a hematitic-goethitic oxide assemblage of nearer-surface chrysocolla, neotocite, and tenorite, changing with depth to cuprite + native copper. Copper-oxide-zone copper grades at Piedras Verdes are



**Figure 6:** Vertical south-north cross section through a portion of the Piedras Verdes porphyry copper deposit, Sonora, México, simplified from figure 4 of Dreier and Braun (1995). Upper diagram shows general alteration mineral assemblage distribution, with host rock consisting of quartz-biotite schist and minor granodiorite porphyry. Dashed line shows base of significant supergene-derived host-rock alteration, thickening in the portion of the deposit characterized by phyllic alteration and developed only to a limited extent in K silicate stable assemblages. Lower diagram depicts copper oxide and sulfide zones. Piedras Verdes copper oxides are well developed within the K silicate stable alteration assemblages but show only incipient occurrence in the phyllic zone. Copper sulfides, dominated by chalcocite, are found subjacent to phyllic assemblages but are weakly developed in the K silicate stable assemblages. Protore sulfides consist of pyrite ± chalcopyrite ± molybdenite.

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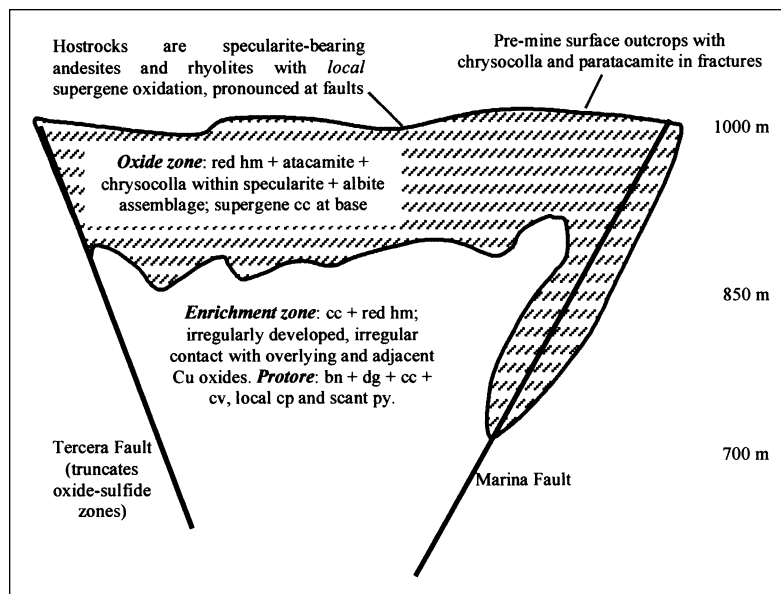
## SUPERGENE OXIDATION OF COPPER SULFIDE DEPOSITS, CONT.

essentially equal to those of the hypogene sulfides from which they were derived, indicating that no significant copper transport has taken place (Dreier and Braun, 1995). This spatial distribution of copper oxides and similarity in hypogene-supergene copper oxide grades mimics that observed in portions of the copper oxide zone at San Jorge, Argentina (Williams et al., 1999), and at El Abra, and is interpreted to indicate restricted copper mobility within a weakly mineralized, reactive protolith. The copper oxide minerals observed also indicate a near-neutral pH environment of formation (Anderson, 1982). Notably, where there is phyllic alteration with high pyrite content, weathering-generated oxidation is deeper and better developed, resulting in the formation of a moderately developed chalcocite resource. Dreier and Braun (1995) report that oxidation of the chalcocite enrichment blanket yielded an in situ assemblage of chrysocolla, neotocite, tenorite, and malachite.

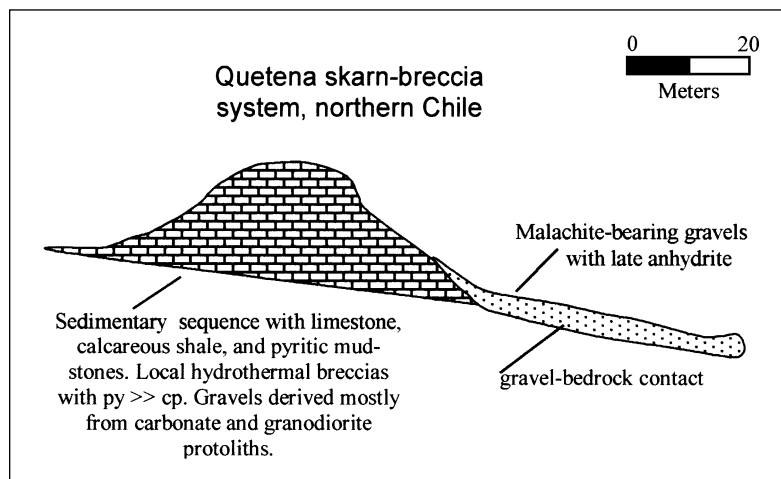
**Mantos Blancos.** The Mantos Blancos district of Antofagasta province, northern Chile (Chávez, 1983, 1984), hosts a generally low-pyrite, andesite- to rhyolite-hosted series of bornite + digenite + chalcopyrite ± covellite ± specularite orebodies. Figure 7 shows a portion of the Nora orebody, and the general occurrence of copper oxides comprising paratacamite (mapped locally as atacamite) and chrysocolla. Host-rock alteration comprises well-developed albitization with subordinate but geochemically important chloritization, specular hematite development, and local replacement by carbonates. Because albitic feldspar and chlorite were available for hydrolysis, and because only limited amounts of pyrite were available for acid generation, the oxide assemblage at Mantos Blancos is characteristic of a near-neutral pH environment, and the copper oxides are thought to represent only local (tens of meters) metal mobility.

The occurrence of specularite relics within some oxide volumes indicates that acidic solutions capable of transporting cupric ion did not react on a wholesale basis with Mantos Blancos host rocks because specularite would have been destroyed during such interaction. The near-surface occurrence of chrysocolla and subjacent atacamite at Mantos Blancos suggests high chloride activity relative to that of available sulfate; this is similar to the mineral zoning and paragenesis described by Arcuri and Brimhall (1998, 1999) for the Radomiro Tomic deposit immediately north of Chuquicamata.

**Quetena.** Figure 8 shows the Quetena skarn-breccia system, northern Chile, in which exotic malachite and atacamite are developed in carbonate clast conglomerates derived from erosion of silty limestones. The protolith mineral assemblage at Quetena consists of pyrite-dominant sulfides in marble skarn and hornfels derived from intercalated limestones and mudstones, with locally developed white phyllosilicate replacement of siliciclastic components within the limestones. Malachite and atacamite occur as millimeter-scale coatings on carbonate clasts; these minerals form interlayered rinds, indicating that conditions favoring carbonate and chloride



**Figure 7:** Schematic east-west cross section through the Mantos Blancos Cu-Ag system, II Region, northern Chile. Host andesites and rhyolites have been albitized and variably chloritized, so rocks have substantial capacity for acid-neutralizing hydrolysis reactions. Such reactions buffer low pH solutions generated via weathering-related destruction of protolith sulfides and determine the resulting atacamite + chrysocolla oxide mineral assemblage. Copper transport distances were very restricted in this environment, probably limited to several tens of meters and generally along through-going fractures. Scant but widespread native copper and silver occur within the copper oxide zone and generally below atacamite-chrysocolla.



**Figure 8:** Generalized vertical cross section through the Quetena skarn-breccia system southwest of Chuquicamata, Chile. Holocene gravels derived from carbonates and calcareous clastic sedimentary rocks conducted acid copper-bearing solutions near or at gravel-bedrock contact, forming incipiently developed malachite + atacamite + anhydrite as clast coatings. Although supergene solution pH was likely very low during initial oxidation of pyrite-bearing protolith, transport distances for copper were restricted by the highly reactive paleochannel gravels; maximum transport distances at Quetena are on the order of 200 m.

precipitation alternated, despite the obvious carbonate source within the local wall rock and gravels. This is probably because source-rock carbonates, although serving as pH buffers, had elevated local sulfide contents of 4 to 5 vol percent pyrite. Under such conditions, acidic solutions were generated during weathering and were capable of liberating and transporting copper from protolith chalcopyrite into

the alluvial gravels developed on hill slopes adjacent to the eroding skarn-breccia system. Paragenetically latest anhydrite occurs as millimeter-scale patinas covering copper oxides, probably the result of gypsum dehydration. The maximum copper transport distance at Quetena is on the order of 200 m.

### Systems with Evidence for Enhanced Copper Mobility

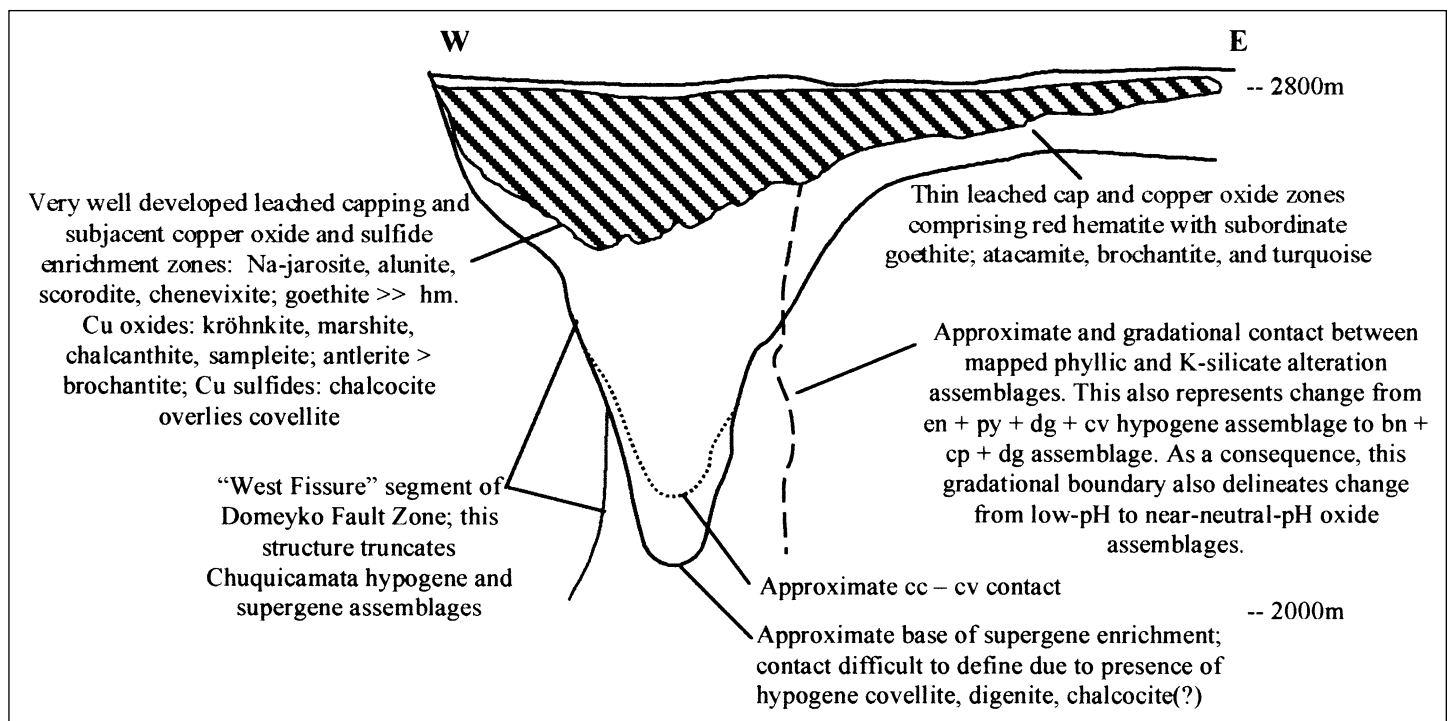
One of the best-developed leached capping–copper oxide zone–copper sulfide enrichment zone sequences is shown by the giant Chuquicamata porphyry system, northern Chile (Little, 1926; G. Ossandón et al., unpub. data). Jarrell (1944) described the occurrence of copper oxides in the near-surface environment, suggesting that in-place oxidation of supergene sulfides produced the thick and well-developed copper oxide zones in the original Chuquicamata orebody. Because the Chuquicamata orebody comprises two mineralogically distinct ore types, supergene oxidation and consequent development of copper oxide mineral assemblages are also spatially and mineralogically distinct. Figure 9 is a schematic west-east vertical cross section through the Chuquicamata mine area, showing the general distribution of oxide minerals in the upper parts of the orebody.

Detailed mapping (J. Rojas de la Rivera, pers. comm., 1999) shows that two general alteration zones can be defined, comprising K silicates (with chalcopyrite + bornite + digenite) and phyllic with incipient advanced argillic alteration (with pyrite + enargite + covellite). These alteration assemblages appear to have developed within a single intrusive rock unit. The Domeyko fault zone (“West Fissure” in Figure 9), has faulted the Chuquicamata orebody along its western margin, forming an abrupt contact against the phyllic alteration assemblage.

Within the K silicate assemblage, weathering has produced only limited oxidation, with an assemblage of hematite > goethite, atacamite, and local turquoise-chalcosiderite typical of near-neutral pH conditions. However, the depth of enrichment is greatly enhanced in the phyllic alteration assemblage, with oxidation on the order of nearly 1 km deep, resulting in a well-developed low pH, stable assemblage of natrojarosite, goethite, chalcantite, kröhnkite, and antlerite. Below this deeply oxidized rock column is a well-developed supergene chalcocite ± covellite enrichment zone that displays an apparently gradual and poorly defined contact with hypogene pyrite + enargite + covellite ± tennantite.

Because the host-rock phyllic alteration assemblage has only minor capacity to neutralize acidity, solutions generated from the oxidation of protolith with very high pyrite content produced a very low pH, stable copper and iron oxide assemblage, dominated by sulfates. These solutions were also able to transport copper away from the near-surface environment until they reacted with reduced sulfur, producing the exceptionally well developed chalcocite ± covellite enrichment volume at Chuquicamata. Lateral transport of copper at the southern margin of the Chuquicamata orebody produced the economically important Mina Sur (Exótica) exotic copper deposit (Angüita, 1997; Münchmeyer, 1997), which is a paleodrainage system containing copper transported at least 6 km away from the Chuquicamata mine area. This scale of copper transport is similar to that noted in the mineralized gravels of the Huiniquintipa Este sector of the Collahuasi district north of Chuquicamata and the Damiana copper resource within the El Salvador district, Chile (Mote and Brimhall, 1997).

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**Figure 9:** Simplified east-west vertical profile of the Chuquicamata, Chile ore deposit, modified slightly from José Rojas (pers. comm., 1999). As with the Piedras Verdes system, alteration mineral assemblages control copper and iron oxide distribution and zoning. Protolith at Chuquicamata appears to have been a single, large-scale intrusive unit of intermediate composition (Ossandón et al., unpub. data), so copper and iron oxide distributions are a function of fracture density and alteration mineralogy, including sulfide types and abundance, rather than protolith composition. Although the contact between supergene and hypogene mineral assemblages is difficult to define, the vertical column of preserved leaching-oxidation-enrichment at Chuquicamata approaches 1 km.

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**SUPERGENE OXIDATION OF  
COPPER SULFIDE DEPOSITS, CONT.**

**EXPLORATION IMPLICATIONS**

Copper oxide zones are the product of sulfide destruction produced by weathering under oxidizing conditions. Supergene sulfides produced by the same process are not preserved unless development of an oxide profile is limited by water table ascent or the onset of an arid climate (Alpers and Brimhall, 1989), lack of acid-generating sulfides in a source region, and/or presence of reactive silicates and oxides. Current exploration for copper ore deposits favors oxide targets because the leaching technologies developed for metal recovery permit mining of relatively low grade materials. Consequently, knowledge of the mineral zoning and mineralogic composition of copper oxide deposits is important in exploration and economic evaluation of these systems.

Copper oxide occurrences display consistent vertical and lateral zoning patterns that mimic the hand specimen-scale paragenesis shown by individual copper oxide minerals. Weathering-derived copper mineral distribution is characterized by a supergene geochemical stratigraphy comprising copper oxides, iron ± manganese oxides, and copper sulfides. This stratigraphy begins at the surface with a leached rock volume typified by the occurrence of iron oxides and residual copper and manganese minerals. Depending on the distribution of fractures in the host-rock mass, leached zones may occur within and below both copper oxide and copper sulfide horizons. Indigenous copper oxide zones, generated via in situ oxidation of a sulfide-bearing rock, are usually developed so that the most reduced copper oxides (native copper and cuprite) are formed in the lower portions of the oxide column, suprajacent to and replacing supergene copper sulfides.

As oxidation continues, hydroxy-sulfates are developed at the expense of native copper and cuprite, so brochantite, antlerite, and related sulfates comprise minerals in the topographic middle of an oxide column. As oxidation matures and acid-generating minerals are consumed, supergene solution pH becomes more moderate, and the upper parts of the geochemical stratigraphy develop chlorides, silicates, and phosphates. Contacts between mineral sub-zones within the copper oxide zone are gradational, and may be erratic if tectonic and/or structural settings allow the phreatic zone and capillary fringe to vary vertically and/or laterally. Very soluble iron and copper sulfates develop throughout the oxide zone column if oxidizing pyritic sulfides continue to supply acidic solutions.

This bottom-to-top copper oxide zoning is mappable vertically, and in exotic systems, laterally (Angúita, 1997; Münchmeyer, 1997). Interpretation of the distribution and mineralogy of copper oxides encountered in surface outcrops and in drill hole intervals permits development of a model for the geochemical environment(s) responsible for metals oxidation, transport, and precipitation within a sampled oxidation profile. Copper oxide prospects may then be evaluated for their potential for the occurrence of a target ore mineral assemblage. For example, in exploration for large-tonnage, low-grade deposits, green copper oxides are a more metallurgically favorable target than a cuprite-native copper mineral assemblage. Exploration for brochantite-antlerite-chrysocolla would target the middle of a well-developed copper oxide zone or the upper portions of a weathering profile showing only incipient development.

The lateral mineral zoning at the margins of a weathered sulfide ore deposit, including exotic mineral occurrences, can be used to assess the geochemical maturity of the oxidation environment and the direction(s) from which supergene solutions deposited copper minerals. Integration of geochronologic results with studies of landform development, geomorphology, and the distribution of copper oxides and sulfides (e.g., Clark, 1967; Sillitoe and McKee, 1996) provides complementary information useful in assessing the geologic history of an exploration target, and the consequent economic potential of copper oxide ore deposit occurrence. Metallurgical studies will dictate which portions of a copper oxide assemblage, if any, are economically extractable if host-rock reactivity is recognized to be high. At the termination of mining, understanding copper oxide mineral genesis is useful in directing efforts at mine remediation and ultimate recovery of copper from mine wastes.


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