12. Supergene Ore and Gangue Characteristics

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Volcanogenic Massive Sulfide Occurrence Model

Scientific Investigations Report 2010–5070–C

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
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U.S. Geological Survey, Reston, Virginia: 2012

Suggested citation:
Koski, R.A., 2012, Supergene ore and gangue characteristics in volcanogenic massive sulfide occurrence model: U.S. Geological Survey Scientific Investigations Report 2010–5070 –C, chap. 12, 6 p.

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Mineralogy and Mineral Assemblages

In the traditional view, supergene ore and gangue minerals are the products of reactions between hypogene sulfide minerals and descending, acidic meteoric waters; these processes take place at or near the ground surface in subaerial environments (Guilbert and Park, 1986). In VMS deposits, copper and other metals are mobilized from primary massive sulfide ore and reprecipitated at depth. This precipitation of Cu sulfides with high Cu/S ratios can produce an economically significant copper enrichment at the reactive redox boundary between massive sulfide protore and downward penetrating fluids. The supergene enrichment “blanket” is overlain by an intensely altered and leached Fe oxide-rich gossan (the remains of the original massive sulfide) that extends upward to the paleosurface.

Studies of hydrothermal sulfide mounds and chimneys on oceanic spreading axes reveal a second type of gossan formation: oxidation of sulfide minerals by interaction with oxygen-rich ambient seawater. This process, sometimes referred to as “seafloor weathering,” is accompanied by formation of secondary, low-temperature Cu sulfide minerals as well as the Cu chloride mineral atacamite at the TAG site, Mid-Atlantic Ridge (Hannington and others, 1988; Hannington, 1993). Based on observations at TAG, bedded ocher overlying massive sulfide at Skouriotissa, Cyprus, has been reinterpreted as a submarine gossan (Herzig and others, 1991). Submarine and subaerial weathering processes are described in greater detail in “Weathering Processes,” Chapter 13, this volume.

The mineral assemblages of supergene enrichment zones and their related gossans for a selected group of VMS deposits are presented in table 12–1; a list of secondary minerals and their chemical formulas are presented in table 12–2. The supergene sulfide mineral assemblages in ancient deposits are dominated by a small group of Cu-rich minerals: chalcocite, bornite, covellite, digenite, and enargite. In the supergene blanket, these sulfides may be intergrown with varying amounts of relict hypogene sulfides such as pyrite, chalcopyrite, and sphalerite. Studies of analogous seafloor massive sulfides reveal that in situ seafloor weathering has produced a comparable suite of secondary sulfide minerals (TAG deposit in table 12–1) (Hannington and others, 1988).

In deposits where the zone of weathering is well developed and preserved, the gossan may contain identifiable mineral subzones dominated by sulfates, carbonates, phosphates, or oxides (table 12–1) (Scott and others, 2001). The chemical compositions of oxidized minerals in gossans reflect, to some extent, the antecedent sulfide mineralogy (Boyle, 1996). For example, high Pb contents (Pb tends to be less mobile in these environments) and secondary Pb carbonate and sulfate minerals (cerussite, smithsonite, anglesite) occur in gossanous zones overlying VMS mineralization containing significant amounts of galena (Scott and others, 2001). In deposits of the Bathurst mining camp and the Iberian Pyrite Belt, complex sulfates or sulfate-arsenate minerals such as plumbojarosite and beudantite also act as significant sinks for Pb in the oxidization zone (Boyle, 2003; Nieto and others, 2003).

The residual concentration of precious metals in gossans, in the form of native gold, electrum, and a variety of silver minerals, can be economically important in VMS deposits (Boyle, 1996). At the Canatuan (Philippines) VMS deposit, for example, Sherlock and Barrett (2004) estimate a 45 percent increase in gold content, as electrum, in gossan weathered from pyritic massive sulfides. Likewise, the concentration of native gold in gossan overlying the Flambeau (Wisconsin) VMS deposit corresponds to a sixfold Au enrichment relative to massive sulfide protore (Ross, 1997). Boyle (1996) lists Au and Ag enrichments in gossans of four Canadian VMS deposits as follows: Murray Brook (2.5, 1.2), Caribou (4.0, 2.4), Heath Steele (3.5, 2.5), and Windy Craggy (8.5, 3.4). Studies of modern seafloor mineralization also reveal enrichment of gold in oxidized zones of massive sulfide deposits (for example, TAG: Hannington and others, 1988; Escanaba Trough: Törmänen and Koski, 2005).

Paragenesis and Zoning Patterns

The development of a supergene enrichment zone along with its overlying gossan in VMS deposits produces a distinctive paragenetic sequence. For illustrative purposes, a diagram compiled by Boyle (2003), based on supergene mineralization at numerous deposits in the Bathurst mining camp, captures some of the complexity of supergene mineral successions (fig. 12–1). During early stages of alteration, the less resistant minerals chalcopyrite, sphalerite, and tetrahedrite (if present)

Table 12–1. Mineral assemblages of supergene environments in selected volcanogenic massive sulfide (VMS) deposits. Minerals in italics are present in minor or trace amounts.

New South Wales, Australia[1]	Flambeau VMS deposit, Wisconsin[2]	Bathurst deposits, Canada[3]	Bisha mine, Eritrea[4]	TAG site, Mid-Atlantic Ridge[5]
Gossan: goethite, hematite	**Chert gossan:** quartz (chert), hematite, goethite, jarosite, native *copper, native gold*	**Massive sulfide gossan:** goethite, amorphous silica, jarosite, plumbojarosite, argentojarosite, beudantite, scorodite, *bindheimite*	**Hematite-goethite-quartz oxide zone (gossan)**: hematite, goethite, quartz, chalcedony, *native gold, pyrargyrite*	**Oxidized sulfides**: amorphous Fe oxyhydroxide, goethite, jarosite, amorphous silica, atacamite, *native copper*
Phosphate zone: pyromorphite	**Argillic gossan:** quartz, hematite, goethite, chlorite, montmorillonite, *alunite-jarosite*		**Kaolinite-quartz-sulfate zone:** kaolinite, illite, gypsum, alunite, quartz, *beudantite, anglesite, cerrusite, siderite, chlorargyrite, native gold*	
Carbonate zone: cerussite, smithsonite	**Ankerite gossan:** ankerite, hematite, *native gold*			
Sulfate zone: anglesite, alunite, plumbojarosite, *malachite, azurite, barite, stolzite, scorodite*	**Oxide zone:** cuprite, goethite, malachite, azurite, *native silver*			
Supergene sulfide zone				
chalcocite, enargite	chalcocite, bornite, chalcopyrite	covellite, chalcocite, digenite, *acanthite, anglesite*	chalcocite, digenite, covellite, bornite, *enargite*	digenite, covellite, borite, *native gold, native copper*
Primary massive sulfide				
pyrite, sphalerite, galena, chalcopyrite, *arsenopyrite, tetrahedrite-tennantite*	pyrite, chalcopyrite, sphalerite, *galena, pyrrhotite*	pyrite, sphalerite, galena, chalcopyrite, *arsenopyrite*	pyrite, sphalerite, chalcopyrite, galena, pyrrhotite, *arsenopyrite, tetrahedrite, tennantite*	marcasite, pyrite, sphalerite, chalcopyrite, *bornite*

[1] Scott and others (2001)

[2] May and Dinkowitz (1996)

[3] Boyle (2003)

[4] Barrie and others (2007)

[5] Hannington and others (1988); Hannington (1993)

are replaced by chalcocite, digenite, covellite, and other Cu-rich sulfides. Acanthite may form in the supergene zone as silver is released from tetrahedrite. As oxidizing conditions extend to greater depths, covellite and digenite are ultimately replaced by chalcocite (Boyle, 2003).

With encroachment of the oxidation front, supergene sulfides as well as pyrite and other remaining primary sulfides become unstable. The susceptibility of pyrrhotite to oxidation implies a rapid breakdown of pyrrhotite-rich ores. Dissolution of galena and arsenopyrite, if present, promotes the precipitation of a variety of Pb- and As-bearing metal sulfate and carbonate minerals (fig. 12–1; table 12–1). Gold mineralization resulting from dissolution of Au-bearing arsenopyrite and pyrite grains can also be included in the supergene paragenesis (fig. 12–1). Coincident with mineral changes in the supergene enrichment zone, primary carbonate minerals are dissolved and alumino-silicate minerals are replaced by clays and amorphous silica in the gossan. The mature stage of gossan development is represented by an assemblage of Fe oxides, quartz (or amorphous silica), clay minerals, sulfates, and carbonates overlying the supergene enrichment blanket.

Zonation of supergene minerals is most prominently developed in a vertical sense with respect to the weathered paleosurface. A basic weathering profile for VMS deposits contains four zones from the original ground surface downward: (1) a leached capping dominated by Fe oxides, clay minerals, and quartz, (2) an oxidized zone dominated by secondary sulfates, (3) the supergene enrichment zone with abundant chalcocite and other Cu-rich sulfides, and (4) the top of the underlying massive sulfide protore. More complex zonation patterns are evident in mature supergene profiles developed on VMS deposits, especially deposits rich in Zn, Pb, and As (table 12–1). The thicknesses of individual zones are highly variable and increase toward margins of massive sulfide bodies and along structural features crosscutting protore.

Table 12–2. Mineralogy of supergene sulfide zones and gossans.

[Sources: Hannington and others (1988); May and Dinkowitz (1996); Scott and others (2001); Boyle (2003); Sherlock and Barrett (2004); Barrie and others (2007). Mineral formulas are from Frye (1981)]

Mineral	Formula
Supergene	
chalcocite	Cu_2S
bornite	Cu_5FeS_4
digenite	Cu_9S_5
covellite	CuS
enargite	Cu_3AsS_4
chalcopyrite	$CuFeS_2$
acanthite	Ag_2S
Gossan	
goethite	$FeO(OH)$
hematite	Fe_2O_3
amorphous Fe oxyhydroxide	
amorphous silica	$SiO_2 \bullet nH2O$
quartz	SiO_2
kaolinite	$Al_2Si_2O_5(OH)_4$
chlorite	
montmorillonite	
gypsum	$CaSO_4 \bullet 2H_2O$
jarosite	$KFe_3(SO_4)_2(OH)_6$
plumbojarosite	$PbFe_6(SO_4)_4(OH)_{12}$
argentojarosite	$AgFe_3(SO_4)_2(OH)_6$
alunite	$KAl_3(OH)_6(SO_4)_2$
beudantite	$PbFe_3(AsO_4)(SO_4)(OH)_6$
corkite	$PbFe_3(PO_4)(SO_4)(OH)_6$
hinsdalite	$(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6$
plumbogummite	$PbAl_3(PO_4)(PO_3OH)(OH)_6$
anglesite	$PbSO_4$
barite	$BaSO_4$
pyromorphite	$Pb_5Cl(PO_4)$
siderite	$FeCO_3$
cerussite	$PbCO_3$
smithsonite	$ZnCO_3$
ankerite	$CaFeMg(CO_3)_2$
malachite	$Cu_2CO_3(OH)_2$
azurite	$Cu_3(CO_3)_2(OH)_2$
scorodite	$FeAsO_4 \bullet 2H_2O$
bindheimite	$Pb_2Sb_2O_6(O,OH)$
cinnabar	HgS
cuprite	Cu_2O
stolzite	$PbWO_4$
native silver	Ag
acanthite/argentite	Ag_2S
chlorargyrite	$AgCl$
iodargyrite	AgI
native gold	Au
electrum	(Au,Ag)
native copper	Cu
atacamite	$Cu_2Cl(OH)_3$

Textures, Structures, and Grain Size

A variety of textures related to replacement and dissolution reactions are prominent characteristics of the weathering and supergene mineralization zones. Overgrowths and replacement rims of bornite, covellite, or chalcocite on chalcopyrite are frequently observed indicators of incipient supergene alteration. Chalcocite typically occurs as soft sooty coatings on other minerals. More advanced alteration of primary sulfides results in partial to complete pseudomorphous replacement textures, first involving Cu sulfides, then various combinations of secondary sulfide, sulfate, and carbonate minerals, and ultimately Fe oxides and oxyhydroxides. Secondary pyrite and galena with colloform, botryoidal, skeletal, and framboidal textures have been identified in the partly leached gossans of several Uralian deposits (Belogub and others, 2008). A major textural change during supergene processes is the development of secondary porosity. Porous and spongy textures are typical

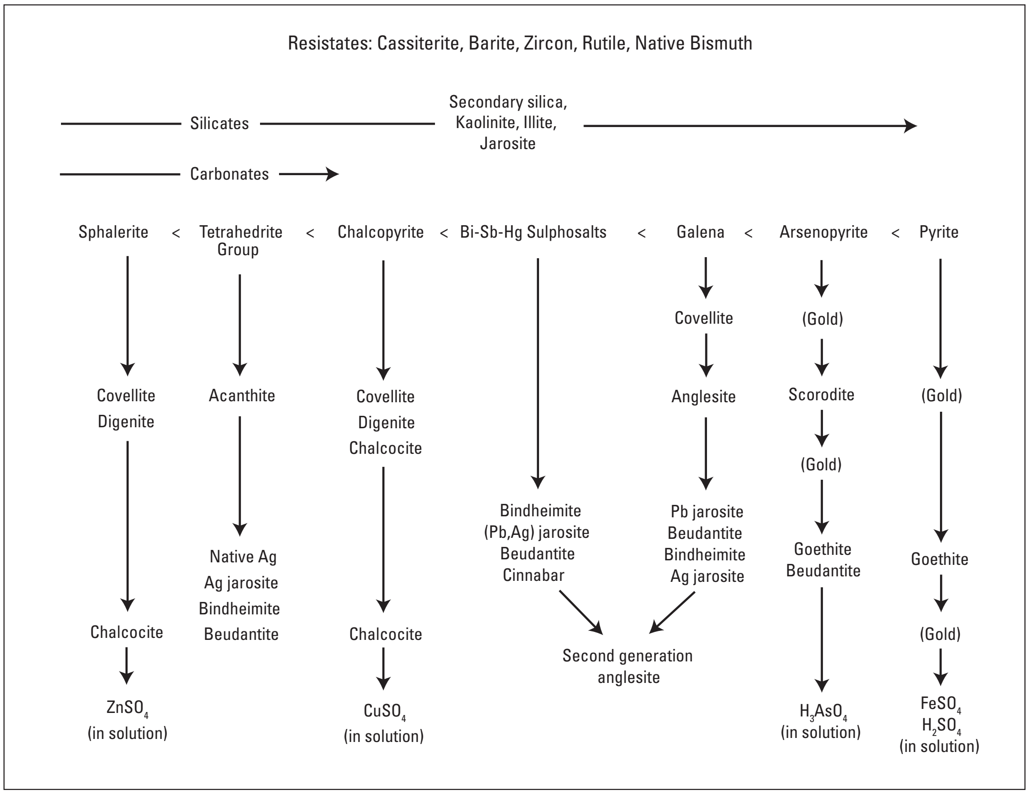

Figure 12–1. Sequence of supergene mineralization summarized from volcanogenic massive sulfide deposits in the Bathurst mining camp (after Boyle, 2003). The stabilities of sulfide minerals under oxidizing conditions increase from left to right. Thus, primary sulfides to the left (especially chalcopyrite) are readily altered and replaced by secondary copper sulfides in the enrichment zone. Oxidation of sulfosalt minerals and galena favors deposition of acanthite in the enrichment blanket and secondary lead minerals in the oxide zone. The precipitation of gold during oxidation of arsenopyrite and pyrite is also indicated. Following dissolution of sulfide and carbonate minerals, the leached gossan is represented by secondary silicates, iron oxides, and oxidation-resistant minerals such as cassiterite and barite. [Ag, silver; Bi, bismuth; Hg, mercury; Pb, lead; Sb, antimony]

of the supergene enrichment zone as well as in gossanous material, especially the cellular boxworks resulting from dissolution of pyrite. Iron oxyhydroxides and other secondary minerals typically appear as colloform and botryoidal infillings within void spaces or laminar overgrowths on resistate minerals such as quartz or cassiterite. The occurrences of beudantite in gossans of the Bathurst mining camp illustrate a variety of supergene textures: microcrystalline coatings, massive spongy interstitial material, vermiform layers lining voids, cubic crystal masses, and colloform masses (Boyle, 2003).

Fragmental zones are a common structural feature of VMS gossans. They appear to represent solution collapse breccias that form after extensive dissolution of primary sulfide and carbonate minerals (Sherlock and Barrett, 2004). Poorly consolidated layers of quartz and pyrite sand in gossans overlying supergene enrichment zones are another distinctive feature of VMS deposits in Canada, the United States, and the southern Urals (Boyle, 1994; May and Dinkowitz, 1996; Belogub and others, 2008). These sands may result from leaching of sulfide-bearing gossan during advective flow of modern groundwaters (Boyle, 1994).

Pseudomorphic replacement and void infilling mineralization result in grain size variations that are equivalent to or of a finer grain than that of sulfide minerals in the protore. The following occurrences of beudantite in gossans of the Bathurst mining camp are representative of the fine-grained nature of secondary minerals: microcrystalline coatings, massive spongy interstitial material, vermiform layers lining voids, cubic crystal masses, and colloform masses (Boyle, 2003).

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