

MINERALOGICAL PROFILE OF SUPERGENE SULFIDE ORE IN THE WESTERN COPPER AREA, MORENCI MINE, ARIZONA

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ABSTRACT

The intergrowths and compositions of supergene copper sulfide minerals from drill hole MOR-4511 in the Western Copper area of the Morenci mine, Greenlee County, Arizona, have been examined by reflected light microscopy and electron probe microanalysis (EPMA) to better understand the formation of supergene sulfides with implications for hydrometallurgical processing. The supergene copper sulfides occur in three main textures: partial to complete replacement of chalcopyrite, partial replacement of pyrite, and partial to complete replacement of one another. Compositions of copper sulfides vary widely, but (Cu+Fe):S ratios of 1.80 ± 0.05 , 1.92 ± 0.03 , and 1.10 ± 0.10 are dominant. No stoichiometric Cu_2S was found. At shallower depths in the supergene blanket and near/within faults, high (Cu+Fe):S phases (with ratios of 1.80 ± 0.05 and 1.92 ± 0.03) replacing primary chalcopyrite and pyrite or lower (Cu+Fe):S supergene sulfides are dominant, and near the base of the blanket low (Cu+Fe):S phases (with ratios of 1.10 ± 0.10) replacing primary chalcopyrite or higher (Cu+Fe):S supergene sulfides gradually become more dominant. This indicates high concentration of Fe^{3+} , Fe^{2+} , and Cu^{2+} , necessary to form high (Cu+Fe):S phases, at shallower depths and near sources of unreacted fluid, such as faults. Formation of low (Cu+Fe):S phases directly from chalcopyrite or from high (Cu+Fe):S phases could be controlled by decreased concentrations of iron species and Cu^{2+} due to reaction with primary chalcopyrite and pyrite as fluids descend or migrate away from faults, reduced access to supergene fluids, and/or lower pyrite-chalcopyrite ratios. The compositional patterns of supergene copper sulfide minerals observed at Morenci are similar to those observed in other supergene enrichment blankets of porphyry copper systems worldwide and are even more similar to compositions seen in leaching experiments of synthetic copper and copper-iron sulfides.

Keywords: chalcocite, copper sulfides, supergene enrichment, porphyry copper, electron microprobe analysis, Morenci, Arizona.

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INTRODUCTION

Porphyry copper deposits contain some of the largest endowments of copper on Earth. They are characterized by large tonnages of relatively low-grade Cu-bearing minerals in vein stockworks and disseminations within hydrothermally altered rock (e.g., Seedorff *et al.* 2005). Supergene processes acting initially on primary low-grade ore in exhumed porphyry systems produce diverse sulfide, oxide, and oxy-salt copper phases to form supergene enrichments. It is common for subsequent supergene cycles to leach and enrich the prior-formed supergene deposits to produce masses of rock with chalcocite and oxide copper having significantly higher grade than the primary ore (Anderson 1982, Titley & Marozas 1995, Chavez 2000, Sillitoe 2005). Processing of supergene sulfide “chalcocite” ores is typically carried out *via* concentration or leaching whereby the copper oxides, such as chrysocolla, are recovered by solvent-extraction-electrowinning (SX-EW) methods.

Mineralogical characterization of supergene processes in copper deposits is exceedingly important for mineral processing methods and recovery determinations. Supergene sulfide deposits often contain a mixture of minerals in the Cu–S system (Table 1). The Cu-sulfide minerals typically occur in varying amounts with hypogene sulfides consisting principally of pyrite, chalcopyrite, bornite, and molybdenite, which each react differently in processing methods using sulfuric acid-ferric sulfate leach solutions. Leaching studies of chalcopyrite (e.g., Córdoba *et al.* 2008) and other copper bearing minerals using acidic Fe^{3+} solutions determined relative recovery amounts specific to individual minerals that have broad application to processes used in modern heap-leach operations (Sullivan 1933, Goble 1981, Whiteside & Goble 1986).

However, there are comparatively few detailed mineralogical studies of natural supergene copper sulfides. Sillitoe & Clark (1969) studied the supergene copper and copper-iron sulfides in the Copiapó mining district, Chile, and Goble & Smith (1973) conducted an electron microprobe study on copper sulfides in red bed copper deposits of Alberta. Reich *et al.* (2010) used electron microprobe, secondary ion mass spectrometry, and transmission electron microscopy to investigate trace element chemistry of supergene digenite in Chilean copper deposits. Reich & Vasconcelos (2015) provided a summary of supergene processes and mineralogy in copper deposits, and Zammit *et al.* (2015) described the roles of microbial action in supergene processes that lead to the formation of enrichment blankets. Mineralogical

TABLE 1. MINERALS IN THE SYSTEM Cu–S

Name	Formula	Cu:S
Chalcocite	Cu_2S	2
Djurleite	$\text{Cu}_{31}\text{S}_{16}$	1.9375
Digenite*	Cu_9S_5	1.8
Roxbyite	Cu_9S_5	1.8
Anilite	Cu_7S_4	1.75
Geerite	Cu_8S_5	1.6
Spionkopite	$\text{Cu}_{39}\text{S}_{28}$	1.39
Yarrowite	Cu_9S_8	1.125
Covellite	CuS	1
Villamaninite	CuS_2	0.5

Note: * Digenite is stable only in the system Cu–Fe–S. Bold entries have known crystal structures. Data for villamaninite are from Bayliss (1989), all other data are from Anthony *et al.* (1990).

descriptions of supergene copper sulfides in the southwestern United States generally consist of varying proportions of chalcocite and covellite that replaced chalcopyrite and pyrite. One example is the porphyry copper-molybdenum deposit at Morenci, Arizona, where a general overview of supergene copper sulfide mineralogy was provided by Enders (2000), but a detailed mineralogical study of supergene enrichment is lacking.

The Morenci mine in Greenlee County, Arizona (Fig. 1), produces copper from supergene and hypogene deposits. Historically, the highest-grade ores at Morenci were oxide copper deposits within skarn and massive chalcocite from enriched veins and stockworks in monzonitic stocks. With the depletion of these high-grade ores, mining progressed to open-pit methods to recover copper from the immense tonnages of relatively lower-grade chalcocite using concentrators. The implementation of SX-EW technology in the late 1980s at Morenci provided for the recovery of copper from oxide copper and low-grade chalcocite that is not of sufficient grade for concentrating. Morenci currently recovers copper from concentrating, heap leaching of chalcocite, and run-of-mine leaching of oxide copper and chalcocite. The reserves at Morenci total 12.1 billion pounds of recoverable copper from 664 metric tonnes of mill ore grading 0.42% Cu, 356 million metric tonnes of heap leach averaging 0.51% Cu, and 2243 million metric tonnes of run-of-mine leach with an average grade of 0.18% Cu (Freeport McMoRan 2016 Form 10-K Report).

This study was undertaken to aid ore processing at Morenci and to better understand the mineralogy of

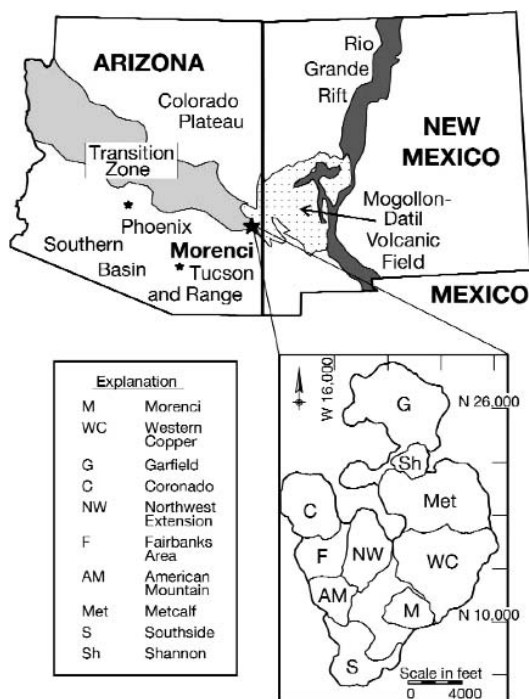


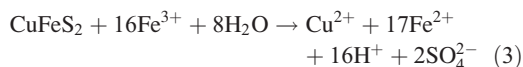
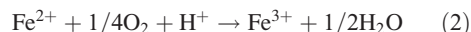
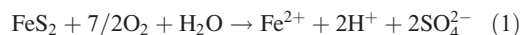
FIG. 1. Location map, from Enders *et al.* (2006). Western Copper (WC) is at the middle right in the lower right hand inset.

supergene sulfide minerals and the natural processes governing the formation of supergene copper sulfides. The results from this study also provide mineralogical characteristics that could be useful in leach processing and recovery determinations.

SUPERGENE PROCESSES IN PORPHYRY COPPER DEPOSITS

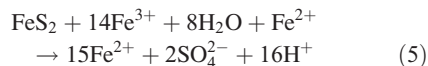
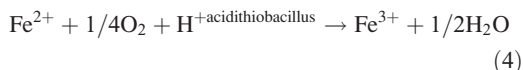
The formation of enriched sulfide ore in porphyry systems is broadly dependent upon hypogene ore mineralogy, lithology of host rocks, and character of alteration (Titley & Marozas 1995). Ideal conditions for formation of supergene sulfides are high pyrite-chalcopyrite ratios in hypogene ore hosted in felsic igneous rocks or quartz-sericite or quartz-K-feldspar sediments, alteration assemblages consisting of sericitic or quartz-K feldspar assemblages, and sufficient permeability to allow the downward migration of supergene fluids.

Water reacting with pyrite forms sulfuric acid and ferric ion [reactions (1) and (2)] under oxidizing conditions, which then react with chalcopyrite to dissolve copper by reaction (3):



Copper-rich solutions migrate downward and precipitate copper sulfide minerals by reaction with hypogene and/or other supergene sulfide minerals lower in the deposit. The simplified supergene profile (Fig. 2) consists of two zones: (1) a barren, leached zone in which hypogene sulfides were oxidized and much of the copper mobilized, leading to very low copper grades occurring with varying amounts and types of iron oxides; the first zone caps (2) a zone of enrichment in which supergene sulfides replace hypogene sulfides (Titley & Marozas 1995). Oxide copper zones that include chrysocolla, brochantite, tenorite, and native copper with hematite and/or goethite occur within or proximal to the leached zone and are the product of *in situ* oxidation of hypogene or supergene sulfide minerals that likely formed as a result of low pyrite-chalcopyrite ratios, reactive host rocks, and other factors which inhibit the leaching and transport of copper (Chavez 2000).

Additionally, bacterial action is thought to play an essential role in supergene processes. Acidithiobacillus bacteria, found by Enders *et al.* (2006) in the 5200 bench of the Metcalf area at Morenci, catalyze the normally very slow process of abiotic pyrite oxidation, resulting in a rate five orders of magnitude faster than abiotic oxidation alone [reactions (4) and (5)]:



According to Enders *et al.* (2006), this increase in reaction kinetics allows for the formation of supergene enrichment over hundreds to thousands of years, assuming purely microbial action.

GEOLOGY OF THE MORENCI DEPOSIT

Morenci is located in southeastern Arizona, approximately 175 km northeast of Tucson (Fig. 1). A laterally extensive chalcocite-enriched blanket is situated within and atop a hypogene Cu-Mo deposit associated with Early Eocene (54–56 Ma) monzonitic stocks. The monzonitic stocks were emplaced as a large composite stock with numerous and extensive

dikes within Proterozoic granitoids and Paleozoic sedimentary rocks. A notable feature of the Morenci district is the widespread sericitic stockwork veinlets developed within Eocene stocks and adjacent Proterozoic granitoids. Beneath the sericitic alteration is a zone of K-silicate veinlets containing pyrite, chalcopyrite, and molybdenite that is best developed as ore shells proximal to the Eocene stock contacts.

The Morenci district is cut by faults of variable ages and orientations. A set of northwest-trending faults controlled emplacement of Eocene dikes and major base metal veins. Displacing these are a set of north-trending and a final set of northwest-trending faults that are leached and which controlled chalcocite enrichment at depth.

A Neogene conglomerate containing discontinuous exotic copper and iron oxides was deposited in the southern part of the district and is cut by northwesterly trending faults and a major northeasterly trending break named the San Francisco fault.

WESTERN COPPER STUDY AREA

The Morenci mine is currently mining and processing supergene and hypogene ores from several open pits (Fig. 1). One of these pits is Western Copper, where mining is exploiting a large and extensive supergene enrichment blanket that overlies hypogene ore consisting of chalcopyrite, pyrite, and molybdenite veinlets that constitute a significant portion of milling ore reserves. The chalcocite blanket at Western Copper is a continuation of a district-wide enriched zone that extends about four kilometers west and seven kilometers north of Western Copper, part of which was mined historically as the Clay orebody in the Morenci pit.

The Western Copper area was identified for study because it contains a large proportion of the Morenci reserves, and a significant amount of these reserves consists of supergene chalcocite enrichment. Diamond drill hole 4511 was selected for sampling because it provides a complete interval of core through the enriched zone and it is within an area that will be mined and processed within the near- to medium-term.

Eocene monzonitic stocks and dikes comprise the lithologies in core hole 4511. From the hole collar to a depth of about 175 m is a leached zone consisting of quartz, clays, and a mixture of earthy goethite and hematite; no sulfide minerals are present. A transition zone containing partially leached chalcocite extends from 175 to 200 m, the upper limit of unoxidized sulfides. Supergene copper sulfides predominate over oxide minerals and hypogene chalcopyrite between 200 and 525 m. Copper sulfides occur as replacements of chalcopyrite in veinlets and as disseminations in

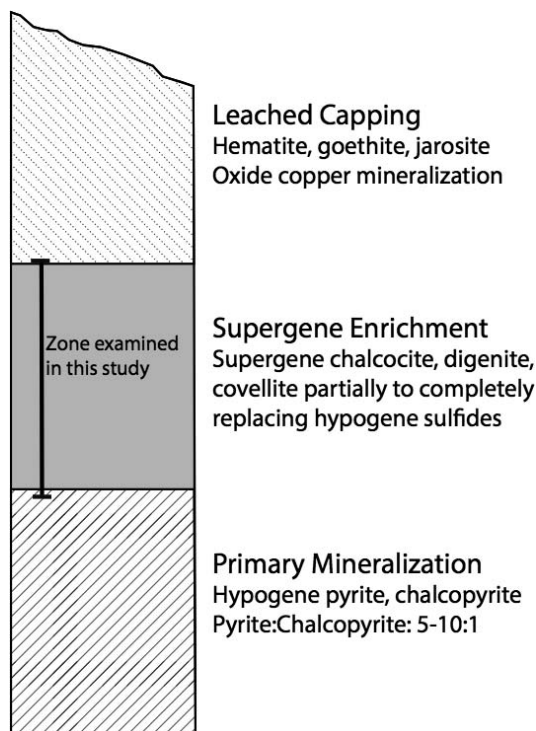


FIG. 2. Simplified geologic section illustrating a supergene profile in a porphyry copper deposit (modified from Titley & Marozas 1995). The uppermost zone is the leached cap, containing hematite, goethite, jarosite, and oxide copper minerals such as tenorite, brochantite, and cuprite. Below the leached zone is the zone of supergene sulfide enrichment where supergene chalcocite, digenite, and covellite replace hypogene pyrite and chalcopyrite. Beneath the supergene enrichment is unaltered hypogene ore dominated by pyrite and chalcopyrite. The vertical bar illustrates the location of the portion of MOR-4511 utilized in this study.

porphyry, rimming or completely replacing pyrite or chalcopyrite. Faults were logged at 200, 202, 217, 252, 306, and 376 m. Fault zones contain rounded quartz-rich grains and shattered pyrite and chalcopyrite in gray to red gouge with rounded pebbles of altered rock. All fault zones contain copper sulfides rimming and replacing chalcopyrite and pyrite. The red color of fault gouge at 200 and 202 m is caused by finely divided hematite.

MATERIALS AND EXPERIMENTAL METHODS

Sulfide-containing pieces were cut from half-split HQ core from drill hole MOR-4511, cast in epoxy, and polished for analysis. Each sample was examined and

interpreted under the ore microscope before electron microprobe analysis.

Electron microprobe analyses were performed at the Lunar and Planetary Laboratory at the University of Arizona using a Cameca SX50 electron microprobe with beam conditions of 15 kV and 40 nA. Each sample was analyzed for Cu, Fe, As, and S using a chalcopyrite standard and $K\alpha$ lines for Cu, Fe, and S and a NiAs standard and $L\alpha$ line for As. Detection limits were 0.064 wt.% Cu, 0.028 wt.% Fe, 0.038 wt.% As, and 0.018 wt.% S. Arsenic was below detection limit in every sample analyzed, and no other elements were detected in WDS scans. Each composition was normalized to one anion, using an average of five analysis points, though as few as two to as many as eight analyses were used in some cases. Compositions of all supergene sulfide phases are presented as the ratio of total metals (Cu+Fe) to one S anion, (Cu+Fe):S. Results of the electron microprobe study and normalizations are presented in Table 2.

RESULTS

Hypogene mineralogy

The hypogene mineralogy in drill hole MOR-4511 is relatively simple. Based on polished section interpretations, the main ore mineral is chalcopyrite, always accompanied by pyrite and quartz, in veinlets and alteration envelopes. Molybdenite infrequently occurs with chalcopyrite and supergene sulfide aggregates; it is not altered by supergene fluids. Some pyrite is sieve-textured, containing inclusions of chalcopyrite, bornite, sphalerite, and hematite. Wavelength-dispersive spectroscopy (WDS) analyses identified acanthite, a Cu-Bi-S phase, and an Ag-Bi-Te phase (most likely volynskite, AgBiTe_2) as blebs in pyrite. Pyrite was interpreted to have formed last in all samples examined.

Minerals in the host rock are K-feldspar, quartz, biotite, and minor sericite. Biotite occurs as both competent crystals of magmatic origin and disarranged "shreddy" aggregates of ore-stage hydrothermal alteration. Shreddy biotite occurs as overgrowths on primary biotite crystals and as massive aggregates. Chlorite infrequently occurs interlayered with non-shreddy biotite. Rutile, apatite, and zircon occur as inclusions predominantly in biotite but also within quartz and K-feldspar. Monazite occurs as inclusions in quartz and K-feldspar, rarely associated with rutile and zircon.

Supergene mineralogy

The supergene copper sulfide minerals form as shells on pyrite and chalcopyrite or as discreet grains

formed from total replacement of the primary sulfide, occurring both in veinlets and veinlet envelopes/areas of pervasive alteration caused by coalesced veinlet envelopes. Three supergene ore textures are present in the samples: copper sulfides replacing chalcopyrite, copper sulfides replacing pyrite, and copper sulfides replacing one another. Using the ore microscope, high and low (Cu+Fe):S phases could only be differentiated based on their reflective properties: high (Cu+Fe):S phases are a mottled gray or bluish gray, and low (Cu+Fe):S phases all have intense sky blue to bluish white reflection pleochroism and flame orange to black anisotropy, almost identical to covellite. Such low (Cu+Fe):S phases will be referred to as blue-remaining (*blaubleibender*) covellite phases, after their property of remaining blue after immersion in oil of refractive index 1.55, where covellite would turn reddish-violet (Goble & Smith 1973).

When both pyrite and chalcopyrite are present in the same sample, the supergene sulfides replaced chalcopyrite first and typically leave pyrite unaltered, regardless of location within the hole (Fig. 3). Hematite, goethite, and jarosite occur with supergene copper sulfides in some samples high in the hole but are for the most part lacking. Fault zones contain only high (Cu+Fe):S phases replacing chalcopyrite and/or pyrite and typically associated with hematite. Blue-remaining covellite phases form partial to complete crystallographically oriented replacements of chalcopyrite grains (Fig. 3). Blue-remaining covellite phases replace higher (Cu+Fe):S phases and are rarely replaced by higher (Cu+Fe):S phases (Fig. 4); in one instance they are replaced by stoichiometric Cu_2S (Fig. 3c, d).

Normalized compositions of copper sulfides show numerous metal-sulfur (Cu+Fe)/S ratios, but three distinct varieties are readily apparent. The most common copper sulfide variety has metal-sulfur ratios of 1.80 ± 0.05 , which is the composition of digenite. Less common are the varieties of copper sulfides with metal-sulfur ratios of 1.92 ± 0.03 and 1.10 ± 0.10 . Five samples contained grains with compositions between 1.22 and 1.74, generally in quantities subordinate to one of the three main varieties, and generally deeper in the supergene blanket. Overall, (Cu+Fe):S ratios decrease slightly down-hole, with (Cu+Fe):S ratios <1.5 predominant at depths below 1400 ft.

The most striking result was the lack of stoichiometric Cu_2S in any sample analyzed. It is unclear if the lack of stoichiometric Cu_2S is natural or, as noted by Pósfai & Buseck (1994), due to the transformation of chalcocite (Cu_2S) to djurleite ($\text{Cu}_{31}\text{S}_{16}$) when exposed to an electron beam. Electron beam conditions of 15 kV and 40 nA did not result in damage to supergene

TABLE 2. ELECTRON MICROPROBE DATA AND NORMALIZATIONS FOR EACH ANALYZED INTERVAL OF MOR-4511

Interval (ft)	612.4	656.2	664.0	676.5 (1)	676.5 (2)	714.0	727.1	753.8
Element								
Cu	78.60	78.20	77.89	78.12	69.62	76.83	76.37	77.23
Fe	0.11	1.64	1.01	0.42	0.01	1.61	1.98	0.10
S	21.68	20.91	21.75	22.03	30.89	22.25	22.11	21.95
Total	100.39	100.77	100.65	100.57	100.52	100.69	100.46	99.28
Atoms								
Cu	1.83	1.89	1.81	1.79	1.14	1.74	1.74	1.78
Fe	0.00	0.05	0.03	0.01	0.00	0.04	0.05	0.00
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Interval (ft)	771.4 (1)	771.4 (2)	803.0	829.1	859.3	888.8 (1)	888.8 (2)	971.3
Element								
Cu	69.09	77.52	79.05	77.73	74.88	78.49	71.38	78.84
Fe	1.36	0.42	0.05	0.05	0.78	0.02	0.01	0.01
S	29.41	21.91	20.66	21.27	22.72	21.10	28.83	20.40
Total	99.86	98.85	99.76	99.05	98.38	99.61	99.62	99.25
Atoms								
Cu	1.19	1.79	1.93	1.85	1.66	1.88	1.28	1.95
Fe	0.02	1.01	0.00	0.00	0.02	0.00	0.00	0.00
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Interval (ft)	1000.6	1031.5 (1)	1031.5 (2)	1054.0	1080.8	1115.5	1146	1166.9 (1)
Element								
Cu	74.73	77.19	78.93	76.67	78.49	78.76	78.89	77.58
Fe	2.84	0.29	0.02	0.79	0.12	0.03	0.02	0.02
S	22.41	21.95	20.58	21.81	20.72	20.82	20.76	21.88
Total	99.98	99.43	99.53	99.27	99.33	99.61	99.67	99.48
Atoms								
Cu	1.68	1.77	1.94	1.77	1.91	1.91	1.92	1.79
Fe	0.07	0.01	0.00	0.02	0.00	0.00	0.00	0.00
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Interval (ft)	1166.9 (2)	1184.6	1233.8 (1)	1233.8 (2)	1260.0	1350.3 (1)	1350.3 (2)	1376.9 (1)
Element								
Cu	70.07	68.14	78.12	70.36	78.32	69.27	77.11	78.91
Fe	0.02	0.11	0.24	0.06	0.05	0.02	0.06	0.21
S	29.34	31.42	21.64	29.47	22.25	30.09	22.36	21.60
Total	99.43	99.67	100.10	99.89	100.62	99.38	99.53	100.72
Atoms								
Cu	1.21	1.10	1.82	1.20	1.78	1.16	1.74	1.84
Fe	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.01
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Interval (ft)	1376.9 (2)	1436.3 (1)	1436.3 (2)	1445.1 (1)	1445.1 (2)	1514.2	1589.2	1615.3 (1)
Element								
Cu	77.78	69.76	77.10	69.42	77.68	67.34	65.23	75.18
Fe	0.12	0.00	0.01	0.17	0.05	0.66	6.39	0.83
S	20.78	29.14	21.40	30.04	21.75	31.42	28.19	23.96
Total	98.68	98.90	98.51	99.63	99.48	99.42	99.81	99.97
Atoms								
Cu	1.89	1.21	1.82	1.17	1.80	1.08	1.17	1.58
Fe	0.00	0.00	0.00	0.00	0.00	0.01	0.13	0.02
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE 2. CONTINUED.

Interval (ft)	1615.3 (2)	1615.3 (3)	1643.2	1718.7
Element				
Cu	68.59	66.34	70.45	76.93
Fe	0.06	0.02	2.13	0.76
S	31.46	33.42	26.42	22.85
Total	100.11	99.78	99.00	100.54
Atoms				
Cu	1.10	1.00	1.35	1.70
Fe	0.00	0.00	0.05	0.20
S	1.00	1.00	1.00	1.00

Intervals with more than one phase analyzed are followed by a number 1 through 3 in brackets.

sulfide phases visible in BSE or reflected light microscopy.

Iron is present in nearly all samples analyzed, from trace amounts up to 2.84 wt.%. Samples with higher (Cu+Fe):S, predominantly those >1.75 , have higher Fe content. The presence of Fe in more metal-rich phases is consistent with digenite, $\text{Cu}_{1.8}\text{S}$, which requires Fe to be stable (Morimoto & Gyobu 1971).

The compositional paragenesis of supergene copper sulfide minerals ranges from simple to complex. Many samples only show one generation of supergene sulfides, and therefore one generation of enrichment, which is compositionally homogeneous. In samples with multiple generations of enrichment (Figs. 4, 5), sulfides of the early generation generally have lower (Cu+Fe):S ratios than those of later generations, but there are exceptions to the rule (Fig. 4). For example, the early generations at 1233.8, 1379.6, and 1615.3 ft have higher metal-sulfur ratios than the later generations (Table 2).

Compositions of the supergene copper sulfide minerals also vary down-hole. Overall, sulfides above

1514.2 ft have a higher average metal-sulfur ratio than those at and below this depth (Fig. 6), corresponding to the chalcocite $\gg$ covellite + chalcopyrite noted by Enders (2000) in the upper portions of the supergene ore. The highest (Cu+Fe):S in MOR-4511 are between 971.3 and 1146.0 ft and average 1.87.

DISCUSSION

Comparison of natural and synthetic supergene sulfides

The compositions of supergene copper sulfide minerals in hole MOR-4511 are very similar to those from other copper deposits and synthetic phases seen in leach experiments. Goble & Smith (1973) reported large populations of natural copper sulfides with (Cu+Fe):S of 1.0, 1.75, 1.2, 1.3, 1.1, and 1.6; Whiteside & Goble (1986) showed that products of leaching of synthetic digenite in acidified ferric sulfate solution have large composition populations at 1.76 ± 0.06 , 1.1 ± 0.05 , and 1.31 ± 0.03 . The composition of the core from drill

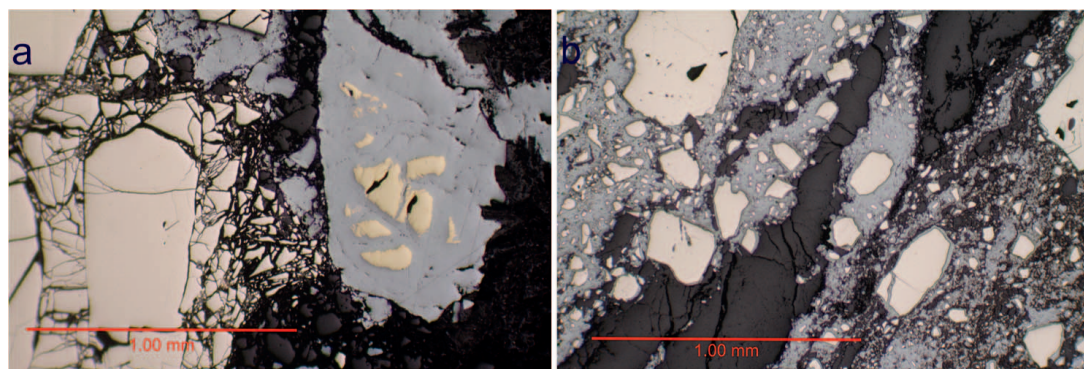


FIG. 3. Reflected light photomicrographs (plane polarized light) showing the relationship of supergene copper sulfides with pyrite and chalcopyrite in MOR-4511. (a) Chalcopyrite (brassy yellow) is mostly replaced by 1.85 (Cu+Fe):S phase (bluish gray) at 829.1 ft, while the associated pyrite (light yellow) is relatively unreplaced. (b) At 656.2 ft no chalcopyrite is present, and pyrite (light yellow) is rimmed and partially replaced by a 1.93 (Cu+Fe):S phase (gray).

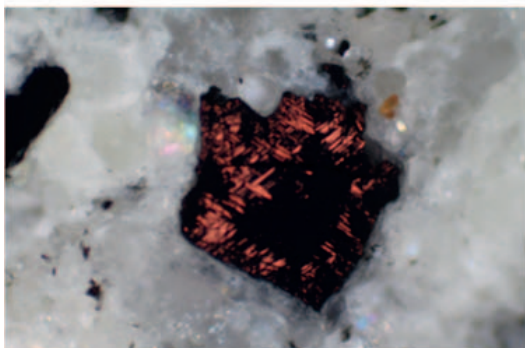
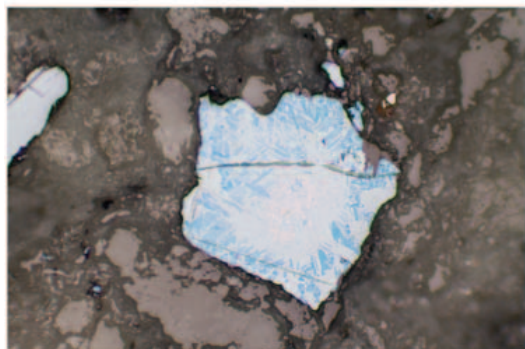
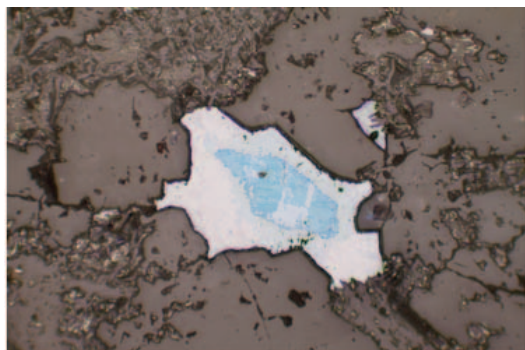
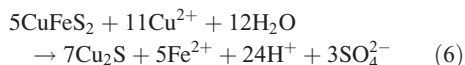


FIG. 4. Reflected light photomicrographs showing copper sulfides replacing one another. (top) Gray, porous, high (Cu+Fe):S (1.80) replacing blue to light blue, low (Cu+Fe):S (1.14) at 676.5 ft; plane polarized light. (middle) A scratched grain with a rim of blue to light blue low (Cu+Fe):S (1.21) replacing mottled bluish gray to gray 1.83 (Cu+Fe):S; plane polarized light. (bottom) Same field of view as (b), but with crossed nicols to demonstrate the extent of low (Cu+Fe):S replacement of high (Cu+Fe):S.

hole MOR-4511 overlaps with natural supergene copper sulfide and synthetic leach product populations with (Cu+Fe):S ratios of 1.80 ± 0.05 , 1.1 ± 0.10 , and 1.25 ± 0.05 .

Ore textures as evidence of supergene fluid composition

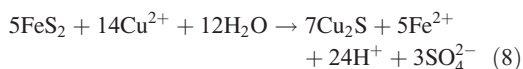
Descending fluids containing Cu^{2+} , Fe^{2+} , and Fe^{3+} from high in the supergene blanket will react with hypogene pyrite and chalcopyrite to form the ore textures seen in the core from drill hole MOR-4511. Chalcopyrite shows replacement by high and low (Cu+Fe):S phases throughout the enrichment blanket. These textures are related to the quantity of copper and iron ionic species in solution. Replacement of chalcopyrite by high or low (Cu+Fe):S phases is dependent on the concentration of Cu^{2+} according to reactions (6) and (7) (e.g., Titley & Marozas 1995):



Many examples of what appears to be high (Cu+Fe):S phases replacing chalcopyrite could also be high (Cu+Fe):S phases that replaced an earlier generation of low (Cu+Fe):S phases replacing chalcopyrite. In other samples, high (Cu+Fe):S phases unambiguously form as a direct replacement of chalcopyrite.

Formation of high (Cu+Fe):S phases directly from chalcopyrite at Morenci will be favored according to reaction (6) in areas where fluids have high Cu^{2+} and Fe^{2+} concentrations, therefore within fault zones and high in the supergene blanket, due to leaching and/or high pyrite/chalcopyrite ratio. Low (Cu+Fe):S phases will be favored according to reaction (7) when the concentrations of Cu^{2+} and Fe^{2+} are low, either because of precipitation of most Cu^{2+} and Fe^{2+} in minerals higher in the blanket, reduced access to supergene fluids, decreasing pyrite-chalcopyrite ratio of hypogene ore, or a combination of all three factors.

Pyrite has also been replaced by supergene copper sulfide minerals, but only by high (Cu+Fe):S phases and never to the extent of chalcopyrite when both are in close proximity, and there appears to be no relationship with depth. Titley & Marozas (1995) suggested that pyrite replacement by supergene chalcocite is governed by the reaction of pyrite with dissolved Cu according to reaction (8):



Lack of appreciable pyrite replacement by supergene copper sulfides when both pyrite and chalcopyrite are present in the same sample, and the lack of any pyrite replacement when only low (Cu+Fe):S phases

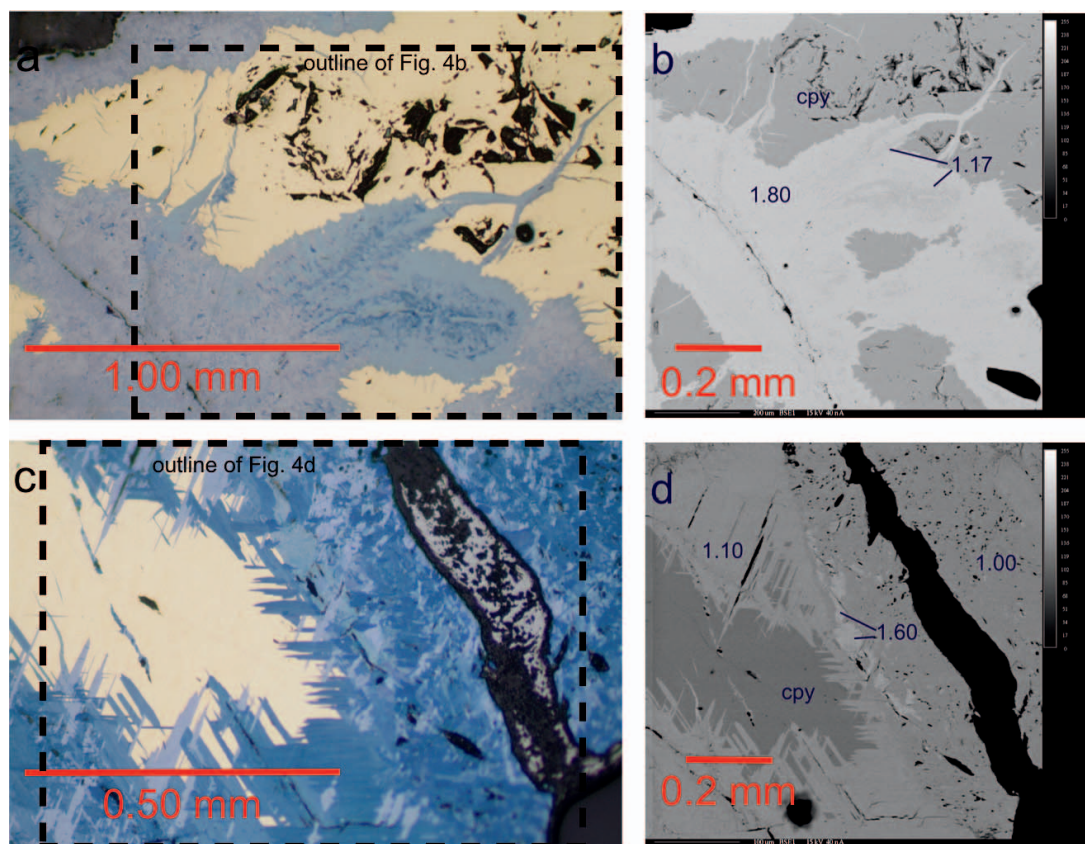


FIG. 5. Reflected light photomicrographs (plane polarized light: a, c) and BSE images (b, d) of copper sulfides replacing chalcopyrite. (a) Two generations of copper sulfides (mottled gray to bluish gray and blue) veining and replacing chalcopyrite (brassy yellow) at 1445.1 ft. Despite the mottled appearance of the higher (Cu+Fe):S phase in reflected light (gray to bluish gray), BSE imaging (b) shows the mineral to be compositionally homogeneous (brighter); metal-sulfur ratios are given on the BSE image. (c) Chalcopyrite replaced by covellite-like copper sulfides at 1615.3 ft. Here the copper sulfides appear to be one phase under reflected light, but BSE imaging (d) shows them to be three separate phases; metal-sulfur ratios are given on the BSE image. Cpy = chalcopyrite.

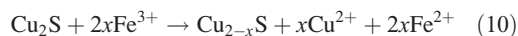
replace chalcopyrite, indicate a dependence of the replacement of pyrite by copper sulfides on the quantity of Cu^{2+} in solution. Without dissolved iron species in solution, pyrite replacement requires almost 3 moles of Cu^{2+} for each mole of pyrite, whereas chalcopyrite replacement requires only 1 mole of Cu^{2+} .

High and low (Cu+Fe):S phases replace one another throughout the core from drill hole MOR-4511. The most common replacement is high (Cu+Fe):S phases replacing low (Cu+Fe):S phases, but the reverse happens in several samples. Low (Cu+Fe):S phases only replace higher (Cu+Fe):S phases deep in the hole: at 1233.8 ft and below; in

one instance, stoichiometric CuS replaces sulfides of 1.1 and 1.6 metal-sulfur ratio (1615.3 ft). These textures are represented by the replacement of chalcocite by covellite (Walsh & Rimstidt 1986):



For phases in between chalcocite and covellite, the overall reaction becomes (Hiskey & Wadsworth 1981):



Reactions (9) and (10) moving to the right are perhaps an example of progressive leaching of Cu, under oxidizing conditions, from an older generation of enrichment as the water table is lowered. More reducing

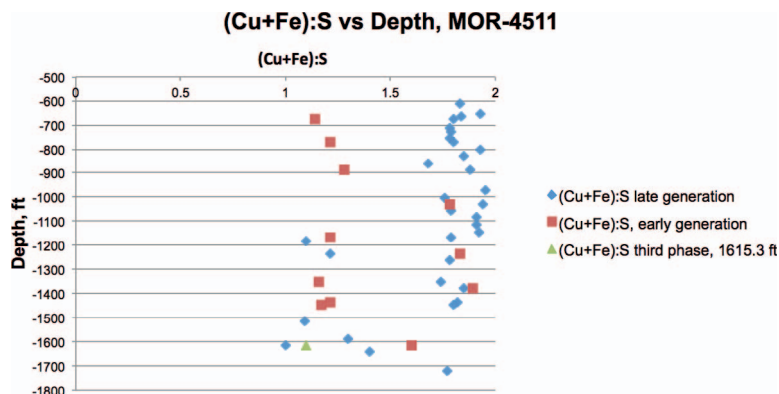


FIG. 6. Graph of supergene sulfide compositions down-hole in MOR-4511. High (Cu+Fe):S phases predominate above 1514.2 ft, and overall (Cu+Fe):S ratios are lower towards the base of the supogene blanket. Note that interval 1615.3 ft contained a minor third phase, which formed between the early and late generations of enrichment.

conditions, or higher activity of Cu^{2+} and Fe^{2+} , could move reactions (9) and (10) to the left, replacing pre-existing low (Cu+Fe):S phases from an earlier period of enrichment.

FUTURE WORK

Effect of crystal structure on formation of copper sulfides

Despite the high precision of the microprobe analyses in this study, names of minerals in the Cu–S system cannot be unambiguously applied to the studied phases because their optical properties are similar, and their structures remain unknown. Small grain size and thinness of supergene sulfide shells on pyrite or chalcopyrite hampered efforts at obtaining X-ray diffraction (XRD) data. Single-crystal XRD was attempted on some of the blue-remaining covellites, but the crystals were too small and poorly formed to obtain a reasonable diffraction pattern. Future study would call for electron-backscatter diffraction (EBSD), which can show the crystal system of small grains using an SEM. Synchrotron-based XRD or high-resolution transmission electron microscopy are perhaps better suited to characterize the crystallography of supergene sulfide phases.

Whiteside & Goble (1986) proposed that the mineralogy of the phase undergoing alteration has a direct effect on which new copper sulfide will form. Their experiments showed that a copper sulfide with a structure based on cubic close-packed (ccp) S atoms (digenite $\text{Cu}_{1.8}\text{S}$) will be leached by removal of Cu atoms only, leaving the ccp S layers intact, forming a metastable polymorph of yarrowite or spionkopite (Whiteside & Goble 1986). Our results show that

minerals within the yarrowite compositional range do indeed replace minerals within the digenite compositional range, suggesting Cu atom leaching along ccp layers.

CONCLUSIONS

The chemistry and intergrowths of supergene sulfide minerals in the Western Copper area of the Morenci mine have been examined in detail. Three main textures are present within the sulfides: partial to complete replacement of chalcopyrite, partial replacement of pyrite, and partial to complete replacement of one another. Dominant (Cu+Fe):S ratios are 1.80 ± 0.05 , 1.92 ± 0.03 , and 1.10 ± 0 . Higher (Cu+Fe):S ratios are found higher in the blanket and within and/or near fault zones. Mineral intergrowths suggest that the formation of high *versus* low (Cu+Fe):S minerals is controlled by concentrations of Cu^{2+} , Fe^{3+} , and Fe^{2+} in supergene solutions, degree of access to supergene solutions, hypogene ore grade, and/or pyrite/chalcopyrite ratio.

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