ACCELERATED TARNISHING OF SOME CHALCOPYRITE AND TENNANTITE SPECIMENS

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ABSTRACT

Chalcopyrite in contact with silver minerals, especially native silver, undergoes rapid tarnishing that appears to be caused by the surface diffusion of silver onto the chalcopyrite, followed by its reaction to form an Ag_2S film. Some tennantites undergo rapid tarnishing caused by the surface reaction of the mineral (by oxidation of As or Sb?) to form silver-bearing Cu_2S or $Cu_{1.8}S$. The copper sulfide film covers the tennantite and diffuses extensively onto adjacent phases.

Keywords: chalcopyrite, tarnishing, silver activation, silver-bearing copper sulfide, tennantite, Ag_2S film, sulfide migration.

SOMMAIRE

La chalcopyrite en contact avec les minéraux d'argent, surtout l'argent métallique, se ternit rapidement à cause de la diffusion en surface de l'argent sur la chalcopyrite et d'une réaction qui produit un film de Ag_2S. Certaines tennantites se ternissent rapidement à la suite d'une réaction qui impliquerait l'oxydation de l'arsenic et de l'antimoine et qui produit un film de Cu_2S ou $Cu_{1.8}S$ argentifère. De la tennantite, ce film gagne par diffusion les minéraux voisins.

(Traduit par la Rédaction)

Mots-clés: chalcopyrite, ternissage, activation de l'argent, sulfure de cuivre argentifère, tennantite, film de Ag_2S, migration de sulfure.

INTRODUCTION

The phenomenon of the tarnishing of sulfide minerals such as chalcopyrite or tennantite has long been recognized; a given mineral from various localities shows a wide divergence in tarnishing behavior, and even within a single polished section different grains of the same mineral may tarnish quite differently. Thorpe *et al.* (1976) first reported a possible correlation between the rapid rate of tarnishing of chalcopyrite from the Kidd Creek mine, Timmins, Ontario and its silver content. Later,

Chen & Petruk (1978) observed similar behavior for chalcopyrite from the Heath Steele mine, New Brunswick. Chalcopyrite with a low silver content (~ 0.1 wt. %) tarnished light brown, whereas material containing moderate silver concentrations (~ 0.4 wt. %) tarnished bluish brown, and silver-rich chalcopyrite (> 1.3 wt % Ag) rapidly tarnished iridescent blue or purple. In both studies cited above the mineral form of silver was not ascertained; this element might have been present either as submicroscopic mineral inclusions or as a solid solution in the chalcopyrite.

The phenomenon of tarnishing sulfide minerals appeared again during CANMET studies both on silver sources in massive-sulfide ores from northeastern New Brunswick and on mercury sources in a number of mines in the Timmins area, Ontario. Rapidly tarnishing chalcopyrite was observed in the ores from the Heath Steele mine (New Brunswick), McIntyre, Kidd Creek and Ross mines (Ontario) and the old Eldorado workings, Port Radium (Northwest Territories). A very reactive tennantite is associated with tarnishing chalcopyrite from the McIntyre mine, Timmins, Ontario. In view of the apparently widespread occurrence of rapidly tarnishing sulfide minerals and the potential importance of the tarnish films on trace-metal (Ag, Hg, *etc.*) distributions, the present study was undertaken to ascertain the nature of the tarnish products and to correlate the rate of tarnishing with silver concentration. To elucidate the tarnishing process, we examined polished sections of the ores optically, by X-ray-diffraction methods, by electron-microprobe analysis and by scanning electron microscopy at various times after polishing.

RESULTS AND DISCUSSION

Chalcopyrite

A hand specimen consisting mostly of chalcopyrite veined by native silver was obtained

TABLE 1. ELECTRON MICROPROBE ANALYSES OF THE TARNISHED CHALCOPYRITE SURFACE

Anal.	Ag	Cu	Fe	S	Total wt.%	Description
	Freshly polished surface analyzed on October 4, 1978.					
1.	0.0-0.3	34.1	30.5	34.9	99.5-99.8	intergrowth with silver minerals
2.	0.0	34.1	30.5	35.0	99.6	isolated grains in silicates
	Tarnished (since October 4, 1978) surface analyzed on November 6, 1978.					
3.	1.2-2.0	33.7-34.2	30.0-30.1	34.0-34.4	99.4-99.8	intergrowth with silver minerals
	Tarnished (since October 4, 1978) surface analyzed on April 19, 1979.					
4.	1.8-2.8	33.3-33.9	29.0-30.0	33.8-34.3	99.7-100.1	intergrowth with silver minerals
5.	34.4	19.7	21.3	23.2	98.6	extremely tarnished
6.	2.0	34.2	30.7	34.1	101.0	twin individual I
7.	3.9	32.9	30.1	33.9	100.8	twin individual II
8.	2.1	34.2	30.3	34.6	101.2	twin individual III
9.	11.7	29.3	26.5	32.2	99.7	rim of I, attached to native silver
10.	1.8	34.3	30.4	34.2	100.7	twin individual I
11.	3.8	33.3	29.8	34.1	101.0	twin individual II
12.	5.4	32.2	29.0	33.0	99.6	twin individual I
13.	2.8	33.4	30.3	33.9	100.4	twin individual II
14.	1.8	34.1	30.6	34.2	100.7	twin individual III
15.	0.0-0.2	33.7-34.9	30.3-30.7	34.2-35.3	99.7-100.8	untarnished grains in silicates
16.	2.1-4.3	32.3-34.1	29.1-30.0	33.2-34.6	99.0-100.5	tarnished grains in silicates
	Freshly repolished surface analyzed on May 8, 1979.					
17.	0.0-0.3	34.1-34.5	30.4-30.8	34.2-35.1	99.5-99.8	intergrowth with silver minerals
18.	0.0	34.2-34.5	30.4-30.5	34.5-35.0	99.1-99.6	isolated grains in silicates

Analytical conditions and standards: 20kV; chalcopyrite (CuKα, FeKα, SKα), argentopyrite (AgLα).
Modified EMPADR VII correction program (Rucklidge & Gasparrini 1969).

from the 208 stope, Eldorado mine, Port Radium, Northwest Territories. The native silver occurs as discontinuous irregular lamellae approximately 1 mm thick and intergrown with the chalcopyrite; the silver is 99.9% pure and contains only traces of Sb or Hg. The specimen contains numerous fine grained (5–100 μm) acanthite inclusions assaying 86.5% Ag, 0.7% Cu and 12.5% S. Trace amounts of other silver minerals such as mckinstryite (63.3% Ag, 22.8% Cu, 14.8% S), stromeyerite (54.2% Ag, 30.7% Cu, 14.6% S) and pearceite (70.2% Ag, 9.7% Cu, 5.0% As, 0.3% Sb, 0.4% Fe, 14.8% S) were also noted in the chalcopyrite. The specimen also contains small quantities of galena, barite, dolomite, sphalerite, gypsum and various silicates.

The chalcopyrite in the specimen tarnished rapidly in air, with cut surfaces becoming grey-black in a few days; in polished sections the chalcopyrite became brownish yellow or light brown within one or two hours. Several freshly polished chalcopyrite sections were examined within one hour of polishing (Table 1, analyses 1 and 2), and found to have already begun tarnishing. The surfaces had silver concentrations ranging from below the detection limit to 0.3 wt. %, depending on the distance from the associated silver minerals. The closer the reading was taken to the silver mineral, the greater was

the extent of chalcopyrite tarnishing and the higher the silver concentration of the film. Incidentally, since the electron microprobe "sees" several microns into the sample, the analyses of the thinner films are certainly biased by the underlying chalcopyrite. Significantly, the chalcopyrite occurring as isolated grains in silicates and not in contact with silver did not tarnish and had no detectable silver (Table 1, analysis 2).

After storage for one month in the laboratory atmosphere, the tarnished chalcopyrite surface was re-analyzed and found to contain 1.2–2.0 wt. % Ag (Table 1, analysis 3). When similar material was re-examined after five and a half months, the chalcopyrite was heavily tarnished. The tarnished grains were always in direct contact with silver minerals and gave surface silver readings of 1.8 to 2.8 wt. % (analysis 4). Some of the grains (analysis 5) were very tarnished, with Ag concentrations up to 34.4 wt. %. Again, because of the penetrating power of the electron beam, the analyses are likely prejudiced by the underlying chalcopyrite. The tarnish film was shown to be acanthite by X-ray-diffraction analysis. Both the degree of tarnishing and the surface concentration of Ag vary not only with distance from the associated silver mineral but also with the orientation of the chalcopyrite grains (analyses 7–14). Figure 1 (analysis 15)
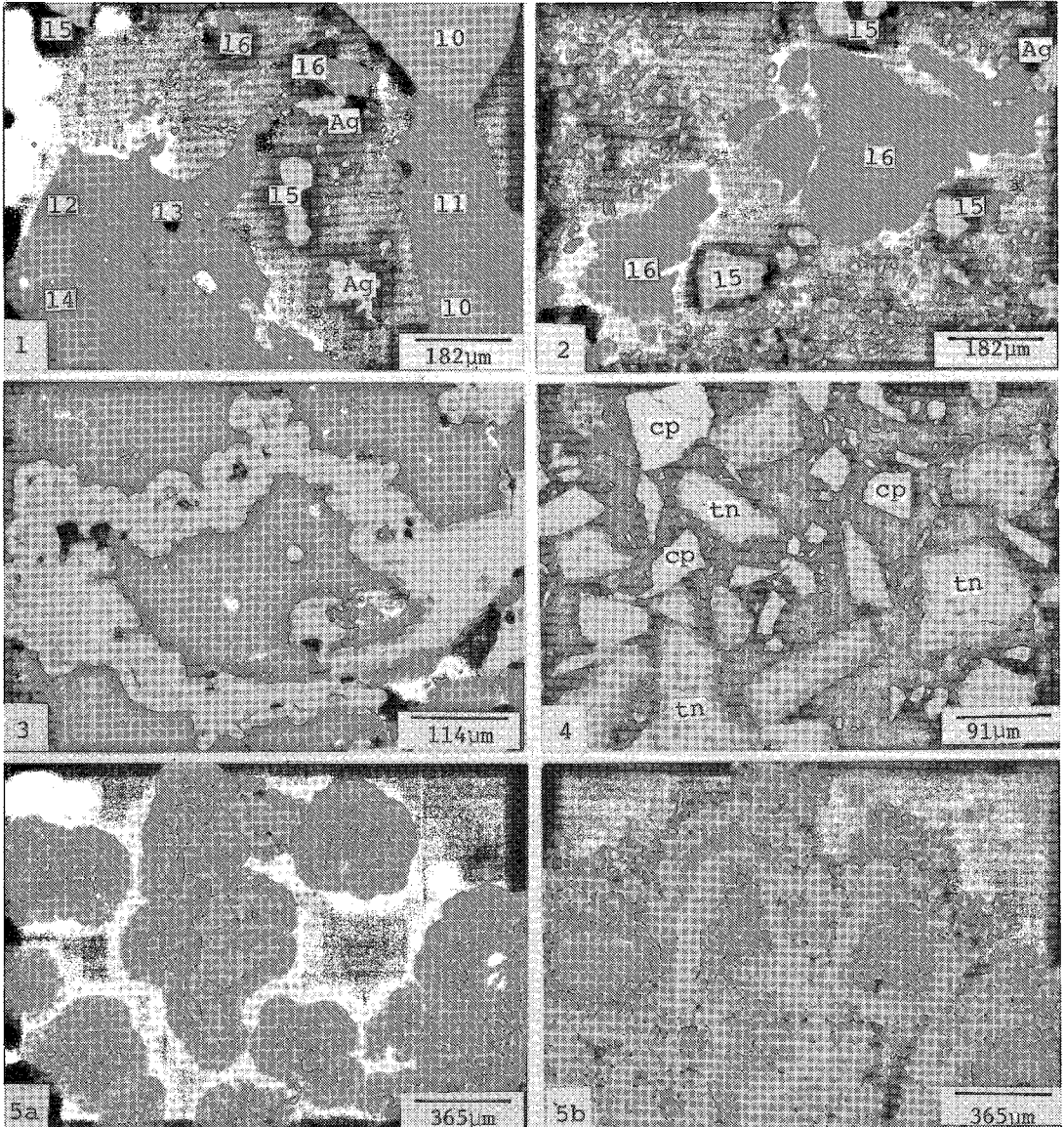
FIG. 1. Chalcopyrite showing different degrees of tarnishing due to different orientations (twinning) after four months. The chalcopyrite is intergrown with silver (not shown). Note isolated chalcopyrite grains in silicate matrix that are not tarnished. The numbers correspond to the analyses in Table 1. Ag native silver, Cp chalcopyrite.

FIG. 2. Isolated chalcopyrite grains in silicate matrix after four months. Grains attached to silver are tarnished, but liberated grains are bright. Numbers correspond to analyses given in Table 1.

FIG. 3. Tennantite in matrix of silicates (dark), showing initial stage of tarnishing. Numerous dark spots formed on the surface, and bluish-white dispersion rims developed around the tennantite grains. The isolated chalcopyrite grains (bright) have not tarnished. 1322 stope, one-week tarnishing.

FIG. 4. Crushed tennantite (tn) grains in epoxy matrix showing the initial stage of tarnishing. 3681 stope, one-week tarnishing.

FIG. 5. Tarnishing tennantite showing digenite coating and dispersion rims around the grains. Matrix minerals are silicates. 1322 stope; (5a) one-month tarnishing, (5b) same sample after six-month tarnishing.

shows a twinned chalcopyrite grain that has undergone differential tarnishing depending on the orientation. Each orientation has been more or less uniformly tarnished, but there are considerable tarnishing differences from twin to twin. Figures 1 and 2 also show isolated grains of chalcopyrite in silicate matrix, *i.e.*, not in contact with silver minerals, that have not been significantly tarnished even after the exposure period of five and a half months. By contrast, chalcopyrite grains in silicate matrix but also in contact with silver minerals were heavily tarnished (Fig. 2, analysis 16). The tarnish films are strictly a surface phenomenon; a light repolishing of the sample removed the tarnish and returned the chalcopyrite to its initial state. Analyses 17 and 18 should be compared with analyses 1 and 2, which were obtained before the tarnish period.

A tarnishing chalcopyrite specimen was also studied from the Kidd Creek mine, where the mineral is associated with native silver. The tarnished chalcopyrite surface contains 0.2–0.5 wt. % Ag, whereas the freshly repolished surface contains less than 0.05 wt. % Ag. A tarnishing chalcopyrite was found in ore from the Ross mine, where the silver sources were identified as native silver and acanthite.

It appears that the presence of silver minerals, especially native silver, can greatly accelerate the tarnishing rate of chalcopyrite. The mechanism of tarnishing seems to be surface diffusion of silver onto the chalcopyrite to form a thin layer of acanthite, Ag_2S. Silver continues to diffuse through the tarnish film and along the surface until the latter is entirely covered. The silver comes from the silver mineral and the sulfur is probably derived from the chalcopyrite. The layers are always thin and do not penetrate significantly into the chalcopyrite. Apparently there has to be a direct contact between the silver phase and the chalcopyrite, since isolated chalcopyrite grains are not significantly affected. The surface properties of the chalcopyrite are important; these are certainly influenced by crystal orientation and probably also by oxidation products or adsorbed species.

Tennantite

Tennantite specimens from the McIntyre mine (3681 stope, 1028 m level and 1322 stope, 404 m level) also underwent rapid tarnishing, but the behavior was quite different from that of chalcopyrite. The mineralogy of these samples has been reported by Dutrizac & Chen (1979). In general, the specimens consist predominantly of quartz and silicate minerals and minor amounts of tennantite as irregular masses to 6 mm; they are associated with chalcopyrite, bornite, tetrahedrite and pyrite. The tennantite usually contains inclusions of native silver, chalcopyrite, galena, pyrite and chalcocite. Native silver also occurs as veinlets or as intergrowths with bornite, gersdorffite and chalcopyrite. The compositional range of tennantite was 40.0–42.8% Cu, < 0.1–0.4% Ag, 3.8–4.9% Fe, 1.1–2.7% Zn, 12.0–14.4% As, 10.5–12.4% Sb and 26.2–27.7% S (total 99.1–101.5 wt. %) and of native silver 81.6–100.0% Ag, < 0.1–18.3% Hg and < 0.1–0.4% Au. Several polished sections were prepared and then stored in the laboratory at 21–25°C and 10–55% relative humidity.

The tennantite from the McIntyre mine tarnished rapidly in air; the tarnishing was evident in hand specimens, where the growth of black dendritic crystals onto the quartz matrix could be discerned. In polished sections, tarnishing of the tennantite started with the rapid formation of greyish to light iridescent spots on and around the tennantite grains. Next, a light grey to bluish-white coating formed on the tennantite surface and extended beyond it as a dispersion rim on the epoxy mounting medium or on the enclosing silicate matrix (Figs. 3, 4). It required three to four weeks to form the bluish-white film and the dispersion rim. The morphology of the dispersion rims varied from matted aggregates of fine crystals to coarse, well-formed dendrites (Figs. 5, 6, 7); their color varied from brown to grey to iridescent blue. After nine months of exposure to air the polished tennantite surfaces were extensively tarnished, with coarse, black dendritic crystals observed in some polished sections (Fig. 8).

A sulfide film spreading onto the adjacent phases was clearly visible under the scanning electron microscope (SEM). Figure 10 shows such a dendrite that has migrated onto the surface of the epoxy mounting medium. The film is just a few microns thick and is fairly smooth except at the leading front, where spherical and arborescent growths are evident. Figure 11 shows the leading edge at higher magnification and also illustrates the arborescent growth structure. The dendrites were analyzed by energy-dispersion methods and were found to consist of silver- (and silicon-) bearing copper sulfide; the analysis was not sufficiently accurate to distinguish between Cu_2S and $Cu_{1.8}S$. Figure 12 illustrates the nodular growth of the dendrites shown in Figure 8b. The "flow" of the copper sulfide onto the epoxy is very evident.
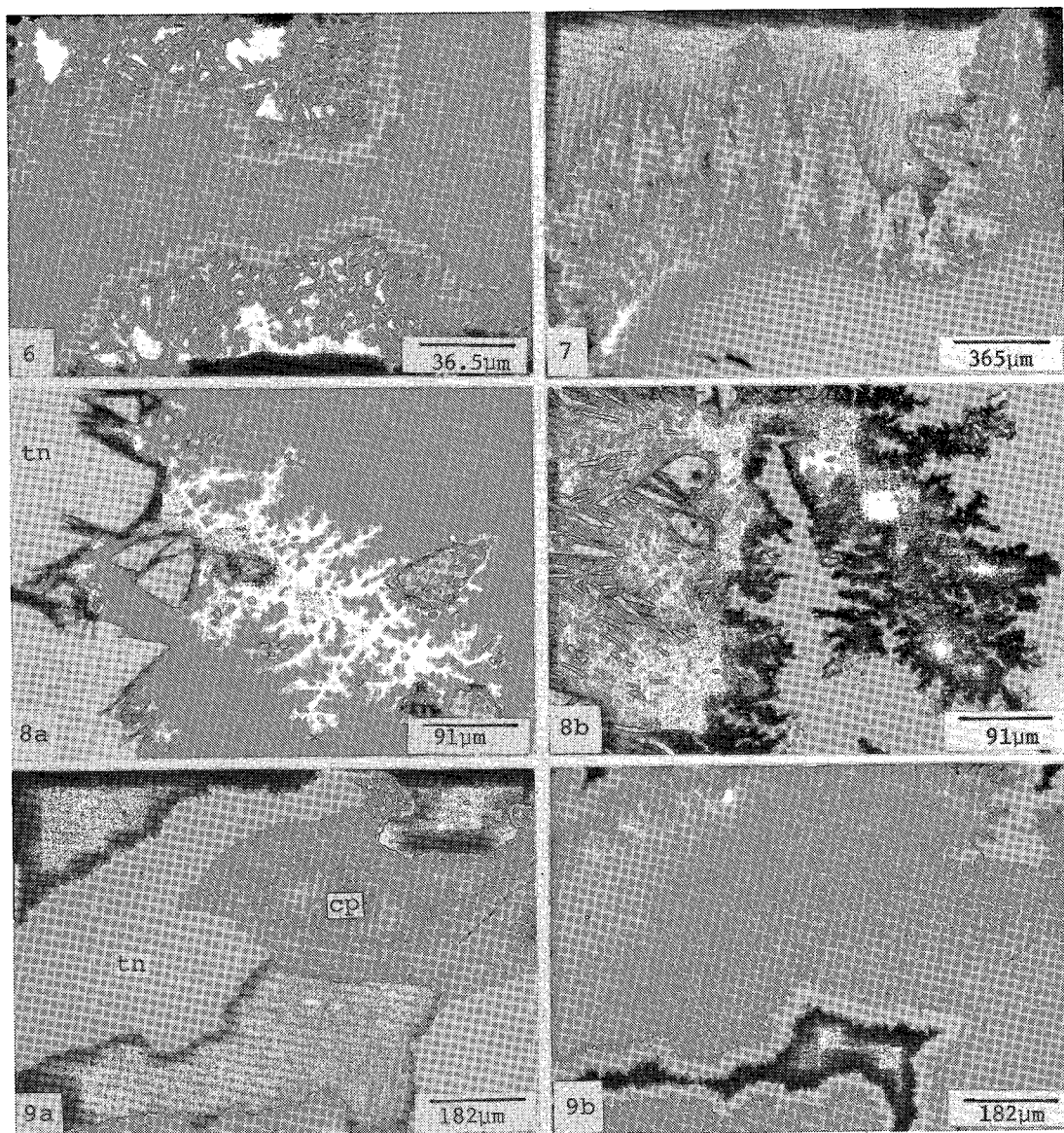
FIG. 6. Tarnishing tennantite showing bluish-white dispersion rim consisting of fine dendritic crystals. Matrix minerals are silicates. 3681 stope, one-month tarnishing.

FIG. 7. Tennantite with digenite film and sharp dendritic crystals coating the epoxy matrix. 3681 stope, three-month tarnishing.

FIG. 8. Black dendritic chalcocite (and digenite?) crystals on the surface of epoxy, growing from the dispersion rims around the tennantite grains. 1322 stope; (8a) three-month tarnishing, (8b) nine-month tarnishing.

FIG. 9. Chalcopyrite being enveloped by the tarnishing film growing from adjacent tennantite grains, in quartz matrix. (9a) half-month tarnishing, (9b) two-and-a-half-month tarnishing.

Another example of the formation of silver-bearing copper-sulfide arborescent growths at the edge of the film is illustrated in Figure 13.

Although the growth has been significant, little development of crystal faces has taken place.

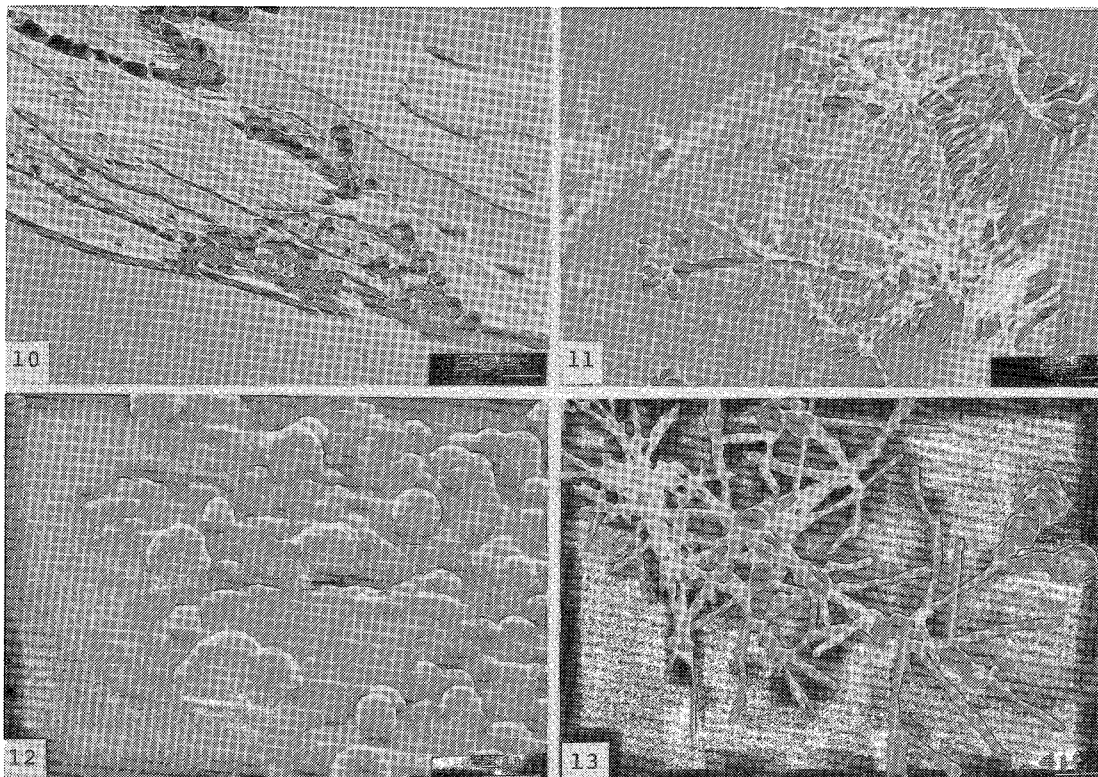The tarnish products were sufficiently thick

FIG. 10. SEM photograph of the tip of a tarnish dendrite forming from tennantite (Fig. 7) from the 3681 stope of the McIntyre mine. The film is Cu_2S; fourteen-month tarnishing.

FIG. 11. Detail of the dendrite tip shown in Figure 10, illustrating arborescent growth of Cu_2S or $Cu_{1.8}S$.

FIG. 12. SEM photograph illustrating the nodular structure of the dendrites of Figure 8b. The dendrites are Cu_2S; fourteen-month tarnishing.

FIG. 13. SEM photograph of the arborescent growth of Cu_2S or $Cu_{1.8}S$ at the leading edge of the tarnish film in the dispersion rims; fourteen-month tarnishing.

to permit their analysis by X-ray-diffraction and electron-microprobe analyses. The results are presented in Tables 2 and 3. The coarse dendritic crystals formed on the dispersion rims or on the surface of the epoxy or gangue were chalcocite (Fig. 8), whereas the dispersion rims and coatings on the tennantite were digenite or chalcocite (or both) depending on the degree of reaction (Figs. 5, 7, 9). Digenite formed only in the early stages of tarnishing and eventually was replaced by chalcocite (Table 2). Silver seems to play an important, if ill-defined, role in the tarnishing process. All the tarnish films are silver-enriched, and some of the dendritic chalcocite crystals and the dispersion rims contain up to 3.9 wt. % Ag. Table 3 presents some typical electron-microprobe data for the tarnish prod-

ucts. The results seem acceptable given that the products were not polished and are very thin. As was the case for the tarnishing chalcopyrite, the tennantite tarnishing films are strictly a surface phenomenon; light polishing removed the tarnish and restored the surface to its original state (Table 3). Although other sulfide minerals such as chalcopyrite are associated with the tennantite, the tarnish products appear to emanate from the tennantite. The films were consistently associated with tennantite and grew away from this mineral onto the other sulfides; Figure 9a illustrates this point well. The tarnish product has grown outward from the tennantite to gradually envelop the chalcopyrite grain. Also, Figures 3 and 4 show that isolated chalcopyrite grains have not been affected, whereas disper-

TABLE 2. PHASES IDENTIFIED ON TARNISHED TENNANTITE FROM McINTYRE MINE

Tarnishing Period	Products*	Description
2 months	digenite	dendritic crystals, dispersion rims and coating on tennantite; 1322 stope.
10 months	digenite	dendritic crystals, dispersion rims; 3681 stope.
	digenite + chalcocite	coating on tennantite; 1322 stope.
	chalcocite + digenite	dispersion rims and coating on tennantite; 3681 stope.
	chalcocite	dispersion rims; 3681 stope.
11 months	chalcocite	coarse dendritic crystals; 1322 stope.
	chalcocite	dendritic crystals and dispersion rims; 1322 stope.
24 months	chalcocite	dendritic crystals; 3681 stope.
	chalcocite	massive rims; 3681 stope.
	chalcocite	dendritic crystals and dispersion rims; 1322 stope.

* Identified by X-ray and electron probe or energy-dispersive
  analyzer.

TABLE 3. ELECTRON MICROPROBE ANALYSES OF TARNISHING
          TENNANTITE FROM McINTYRE MINE

	3681 stope			1322 stope			
	1.	2b.	3.	1.	2a.	2b.	3.
Ag	0.2	0.7	0.2	0.1	0.7	0.9	0.1
Cu	42.5	46.2	42.5	42.8	45.0	47.4	42.6
Fe	3.9	3.7	4.0	4.8	4.9	4.3	4.9
Zn	2.6	2.3	2.5	1.7	1.4	1.2	1.5
As	12.2	10.6	12.0	12.5	11.4	10.8	12.7
Sb	11.9	9.2	12.1	10.6	9.3	8.5	10.5
S	26.8	24.7	26.4	27.2	25.1	23.9	26.9
Total	100.1	97.4	99.7	99.7	97.9	97.0	99.2

Analytical condition and standards: 20kV; enargite (CuKα, AsKα, SKα),
chalcostibite (SbLα), ZnS(ZnKα), argentopyrite (AgLα, FeKα). Modified
EMPADR VII program.

No. 1 freshly polished tennantite surface; No. 2a tennantite with
digenite and chalcocite coating, approximately 9 months of tarnishing;
No. 2b tennantite with chalcocite coating, approximately 24 months of
tarnishing; No. 3 freshly repolished tennantite surface.

sion rims are noted on the isolated tennantite grains.

The mechanism by which tennantite undergoes rapid tarnishing is obviously complex and seems different from that of chalcopyrite. For chalcopyrite the film appears to be produced by the rapid surface diffusion of silver and its subsequent reaction with sulfide to precipitate an Ag_2S film. Since native silver is the preferred silver source for rapid tarnishing, the codiffusion of sulfide with silver is not necessary; this is consistent with the lack of dendritic structure for such tarnish products. For tennantite, however, metal sulfide diffusion is indicated. For example, only by the diffusion of Cu_xS could the observed structures on epoxy or gangue minerals be explained; the dendritic structures are also consistent with the diffusion of Cu_xS. The copper sulfide product arises from the partial decomposition of the tennantite: $Cu_{12}(As,Sb)_4S_{13} \rightarrow xCu_2S + Cu_{12-2x}(As,Sb)_4S_{13-x}$.

Because the volume of tarnish product is small, the remaining tennantite phase differs only slightly from the original material. As the copper sulfide phase forms, it gradually covers the surface of the tennantite and then begins to diffuse away from the tennantite into regions of low Cu_xS activity. The rapid surface-diffusion rates may be enhanced by the presence of silver in the Cu_xS. The initial liberation of Cu_xS from

the tennantite and its diffusivity depend both on the composition of the mineral and on the atmosphere present. The tarnishing rate increases with increasing moisture content either on the surface of the specimens or in the air. The relative humidity in winter was low (10–40%), and the tarnishing rate was also relatively low. The rate of tarnishing was extremely fast if the samples were stored near the moist exhaust of an air conditioner, but was minimal if the samples were kept in an evacuated desiccator. This suggests that the reaction that frees the Cu_2S may involve an oxidation stage, possibly of the arsenic or antimony. The initial composition of the tennantite is also important in determining its tarnishing behavior. For example, tennantites and tetrahedrites from the Ross mine (Timmins), the Caribou mine (New Brunswick), Cavic (Roumania), Kremmling (Colorado), Conception del Oro (Mexico) and Dividend (Utah) did not tarnish under the same conditions. Hence, rapidly tarnishing tennantites are much more composition-dependent than tarnishing chalcopyrites. A similar situation may exist for other sulfide minerals as well. For example, a silver-bearing bornite from New Imperial mines, War Eagle, Yukon underwent rapid tarnishing and migration of the Cu_2S tarnish film onto adjacent minerals, but most bornites do not show this behavior.

CONCLUSIONS

Chalcopyrite in contact with silver minerals, especially native silver, undergoes rapid tarnishing that may be caused by the surface diffusion of silver onto the chalcopyrite, followed by its reaction with sulfide from the $CuFeS_2$. The tarnishing behavior is widespread for chalcopyrites in contact with silver minerals. Tennantite can undergo rapid tarnishing *via* the formation of a silver-bearing Cu_2S or $Cu_{1.8}S$ film that forms initially on the tennantite but that sub-sequently diffuses onto the adjacent mounting medium, silicate gangue or sulfide minerals. The formation of the tarnish film is likely caused by a selective reaction (oxidation?) of the surface that is dependent on both the initial tennantite composition and the moisture content of the atmosphere. Silver is believed to play a role in the reaction process and in the mobility of the tarnish film. Not all tennantites exhibit rapid tarnishing properties.

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