PHOTOCHEMICALLY ACCELERATED SURFACE-DIFFUSION OF SILVER ON CHALCOPYRITE, ISOCUBANITE AND PYRRHOTITE

MARIA JEPPSSON

Department of Mineralogy and Petrology, University of Lund, Sölvegatan 13, S–22362 Lund, Sweden

ABSTRACT

Tarnishing of synthetic chalcopyrite, isocubanite, and pyrrhotite in contact with jalpaite–acanthite, and of natural chalcopyrite in contact with native silver, was examined. The rate of tarnishing increased with the magnification used, illustrating a dependence on the intensity of incident light on the rate of reaction. Successive analyses using a scanning electron miroscope on a fixed spot on the surface of isocubanite and jalpaite–acanthite grains, respectively, showed a gradual increase in silver content. This increase indicates that both exposure to photons and to accelerated electrons results in an increased rate of surface diffusion of silver onto chalcopyrite, isocubanite and pyrrhotite. The rate of tarnishing is: chalcopyrite or isocubanite >> pyrrhotite >> pyrite. The rate of tarnishing or the rate of surface diffusion of silver is considered to be a function of both the surface-bonding properties of the tarnished phases and intensity of incident light.

Keywords: surface diffusion, photochemical reaction, surface-bonding properties, silver, chalcopyrite, isocubanite, pyrrhotite, pyrite.

SOMMAIRE

Ce travail porte sur le ternissement de la chalcopyrite, l'isocubanite et la pyrrhotine synthétiques en contact avec la jalpaïte–acanthite, et de la chalcopyrite naturelle en contact avec l'argent natif. Le taux de ternissement augmente selon l'agrandissement utilisé pour l'examen au microscope, ce qui démontre une dépendance sur l'intensité de la lumière incidente. Des analyses successives d'un point fixe sur la surface des cristaux d'isocubanite et de jalpaïte–acanthite au microscope électronique à balayage font preuve d'une augmentation en teneur en argent. Cette augmentation prouve que l'interaction avec des photons et des électrons accélérés provoque une augmentation du taux de la diffusion de l'argent en surface sur la chalcopyrite, l'isocubanite et la pyrrhotine. Le taux de ternissement, dans l'ordre chalcopyrite ou isocubanite >> pyrrhotine >> pyrite, ou le taux de diffusion en surface de l'argent, serait une fonction à la fois des propriétés des liaisons à la surface des minéraux ternis, et de l'intensité de la lumière incidente.

(Traduit par la Rédaction)

Mots-clés: diffusion en surface, réaction photochimique, propriétés des liaisons à la surface, argent, chalcopyrite, isocubanite, pyrrhotine, pyrite.

INTRODUCTION

A strong affinity between silver and copper has long been recognized. Fleischer (1955) suggested that chalcopyrite is a silver carrier. Amcoff (1984) suggested that correlations between copper and silver concentrations in complex sulfide ores commonly are masked by higher silver contents associated with galena. Proton- and electron-microprobe analyses of chalcopyrite from massive sulfide ores by Harris *et al.* (1984) and Cabri *et al.* (1985) showed that at least 0.3 wt.% silver can be incorporated as a solid solution in chalcopyrite.

Thorpe *et al.* (1976) indicated that tarnishing of chalcopyrite is related to its silver content, suggesting a possible correlation between the rate of tarnishing and the silver content. Chen & Petruk (1978) reported different colors of tarnished chalcopyrite, depending on its silver content. The phase relations of silver and the tarnish product were not ascertained in the studies mentioned. Chen *et al.* (1980) suggested that the degree of tarnishing of chalcopyrite and the concentration of silver vary both with the distance to the associated silver minerals and with the orientation of the chalcopyrite grains. According to Chen *et al.* (1980), the tarnish film consists of silver, which reacts with sulfur on the surface of chalcopyrite to form acanthite Ag_2S. The results of Chen *et al.* (1980) were confirmed by Remond *et al.* (1982).

In connection with work on phase relations in the system Ag–Cu–Fe–S by the present author, tarnishing could be seen in progress when the sample was illuminated in the microscope. Furthermore, the rate of tarnishing increased with an increase in magnification. The latter phenomenon implies that the rate of tarnishing is a function of the intensity of incident light. Only those parts of the syntheses that are connected with the tarnishing phenomenon are discussed.

METHODS

Chalcopyrite and isocubanite with different silver contents were synthesized using elemental S, Cu, Ag and Fe of +99.999% purity. Prior to weighing, iron was reduced in a hydrogen atmosphere at 700°C for approximately one hour. The charges were heated
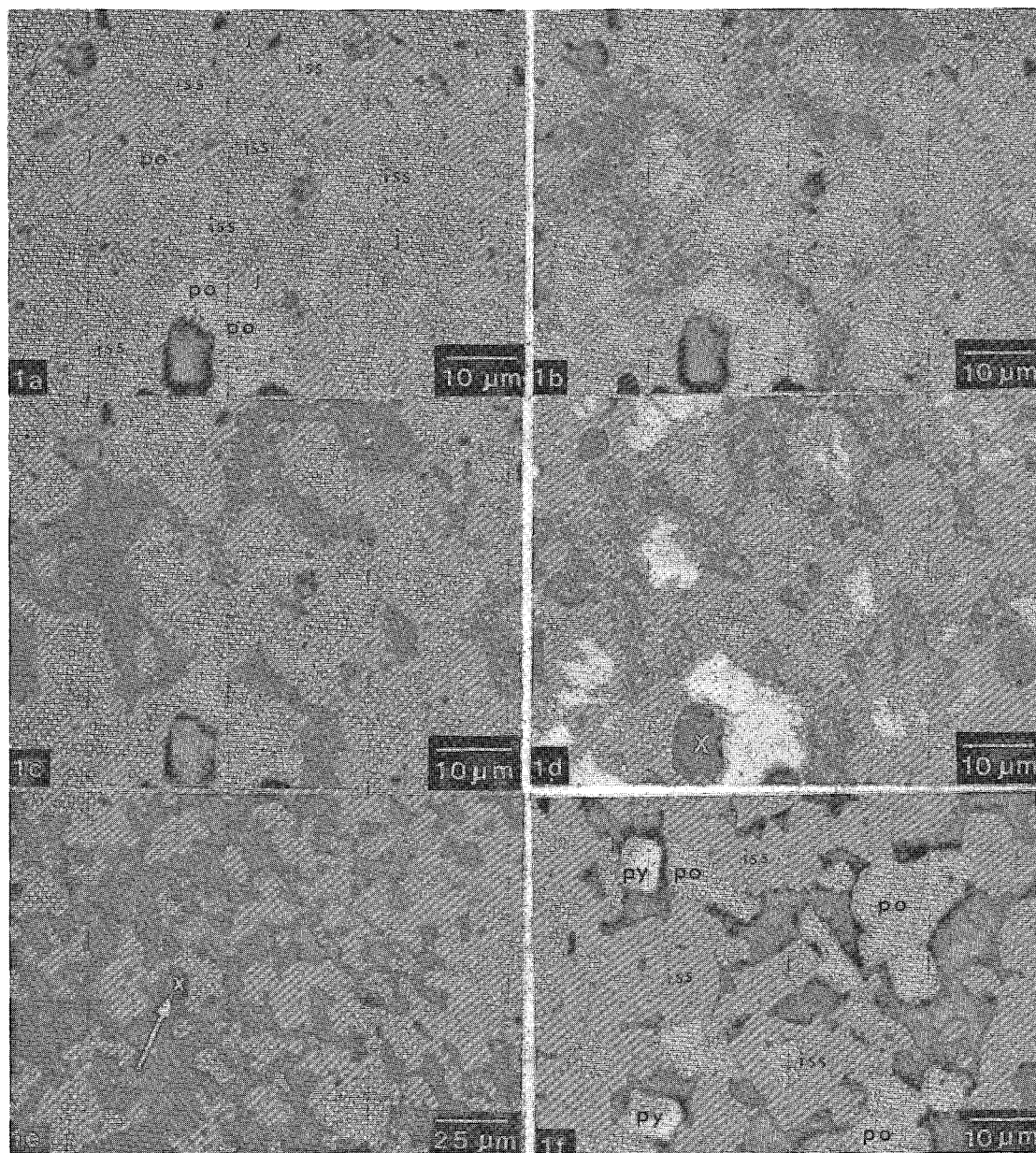
FIG. 1. Tarnished rim grown from jalpaite–acanthite onto isocubanite, with simultaneous formation of black spots in the initially light blue jalpaite–acanthite. Illumination times: (a) 1 minute, (b) 6 minutes, (c) 9 minutes, (d) 20 minutes; (e) circular area of heavily tarnished and altered jalpaite–acanthite. Tarnish formed after an illumination time of 35 minutes at a magnification of 1000×. The cross in (e) is identical with the cross in (d). (f) Photograph showing the resistance of pyrrhotite and especially pyrite to tarnishing as compared with heavily tarnished isocubanite in black jalpaite–acanthite matrix. Symbols: iss isocubanite, j jalpaite–acanthite, py pyrite, po pyrrhotite.

for one week at 500°C in evacuated and sealed glass tubes, and subsequently were homogenized, pelletized, and reheated at 500°C for an additional two weeks.

Polished sections were made from the synthetic charges and, for comparison, from metamorphosed argentiferous copper ore from Saxberget (Amcoff *et al.* 1985), and from Svärdsjö, central Sweden. A

Leitz–AMR scanning electron microscope with energy-dispersion equipment was used for analysis and photography.

To quantify the relation between the intensity of light and the rate of diffusion, the change in intensity of reflected light was measured using the exposure-time meter of a Nikon photomicroscope. Three series of measurements of the change in intensity of reflected light were performed, each starting with a different intensity of incident light. After each series, the sample was carefully repolished. Since small differences in reflecting properties of the sample after repolishing could not be avoided, the intensity of incident light was calibrated by measuring the reflecting properties of a large, carefully polished grain of natural chalcopyrite. The measurements were performed on a fixed spot of the sample, using a magnification of 1000×.

RESULTS AND DISCUSSION

Different bulk-compositions of $(Cu,Ag)FeS_2$ and $(Cu,Ag)Fe_2S_3$ with different values of the Cu/Ag ratio were prepared. The following assemblages were formed in the experiments: 1) isocubanite with lamellae of chalcopyrite + pyrite + jalpaite–acanthite $(Cu_{0.2}Ag_{1.8}S)$, and 2) isocubanite + pyrite + pyrrhotite + jalpaite–acanthite. As shown by Skinner (1966), intergrown jalpaite–acanthite at room temperature represents one phase at high temperature.

Two types of change were observed when jalpaite–acanthite in contact with chalcopyrite or isocubanite was illuminated: 1) surface diffusion immediately started from jalpaite–acanthite grains onto surrounding chalcopyrite or isocubanite grains (Fig. 1). With continuing diffusion of silver, the color of the advancing rim changed from light brown-red to light blue. 2) Simultaneously, small black spots started to form on the blue jalpaite–acanthite surface, which turned almost black after 5–10 minutes (Fig. 1). Stephens (1931) noticed that dark spots form on the surface of acanthite when exposed to light and that the reaction rate has a maximum at a wavelength of the incident light of 5200 – 5800 Å. Fischmeister (1961), in sulfidizing experiments on native silver, observed a similar texture with spots of silver sulfide forming on the surface of native silver at room temperature. The texture of the silver sulfide became coarser and attained a crystalline appearance above 91°C. Chen *et al.* (1980) observed that numerous dark spots formed on the surface of tennantite during the initial stage of tarnishing. Most strikingly, after the sample had been illuminated at a high magnification (1000×) for 35 minutes, a circular area of blue tarnished isocubanite could be seen in the present study when the magnification was changed to 400× (Fig. 1e). Also, the diffusion of silver onto the surfaces of pyrrhotite and pyrite was much slower
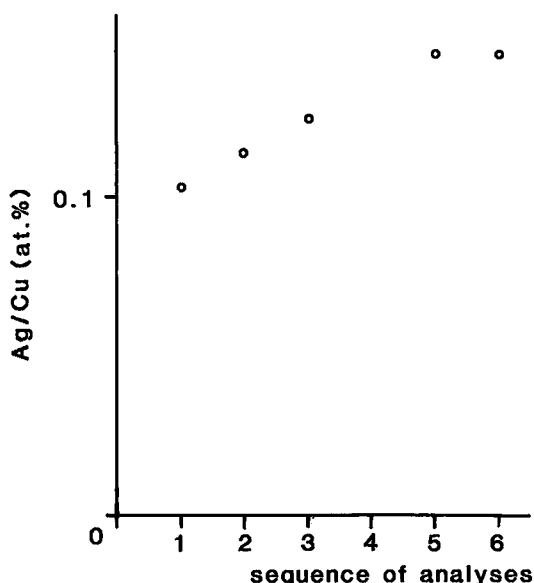

FIG. 2. Results of successive analyses on a fixed spot of untarnished isocubanite, using a counting time of 100 seconds. A successive increase in Ag/Cu ratio as a function of the increase in the relative time of electron exposure is indicated.

compared to the diffusion onto chalcopyrite or isocubanite (Fig. 1f). The tarnish film on chalcopyrite, isocubanite and pyrrhotite could easily be removed, whereas jalpaite–acanthite was considerably more difficult to repolish. Successive analyses of a fixed spot of freshly polished carbon-coated isocubanite in contact with jalpaite–acanthite showed a gradual increase in silver content (Fig. 2). The most probable explanation of this increase is that surface diffusion of silver occurred when the sample was exposed to electron bombardment.

The steep initial parts of the curves in Figure 3 show the large decrease in reflecting properties of jalpaite–acanthite with an increase in tarnishing as the color changed from light blue to black; the decrease in reflecting properties was comparatively small when chalcopyrite was tarnished. Since repolishing between the different series of measurements affected the surface energy in a rather unpredictable way, and also could have changed the relative contents of the phases, the curves in Figure 3 are somewhat tentative. In spite of this, however, it is clear that an increase in intensity of incident light results in an increase in the total change (in %). Also, Figure 3 indicates that the alteration on the surface of jalpaite–acanthite was less radical when the intensity of incident light decreased. Unfortunately, analyses of jalpaite–acanthite show suspiciously low
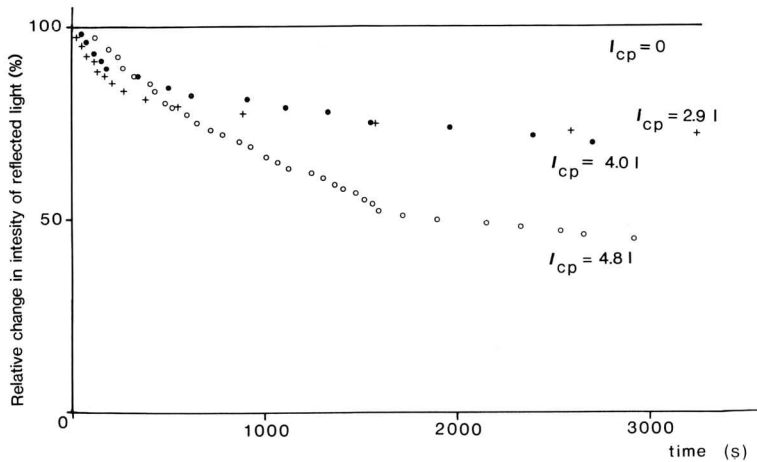
FIG. 3. Variation in the relative change (in %) with time (expressed in seconds), of measured reflected light (*i.e.,* degree of tarnishing) at different relative intensities (I) of incident light, as measured using the reflectivity of pure chalcopyrite (I_{cp}). Upper line: $I_{cp} = 0$, crosses: $I_{cp} = 2.9$ I, filled circles: $I_{cp} = 4.0$ I, open circles: $I_{cp} = 4.8$ I.
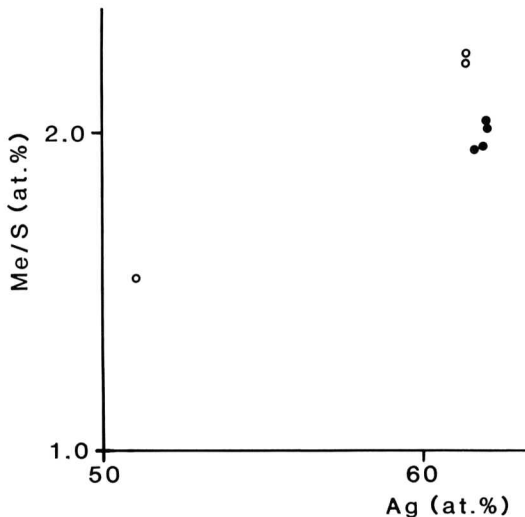

FIG. 4. Results of successive analyses on a fixed spot of tarnished (right) and untarnished (left) jalpaite–acanthite. Note the increase in silver content of initially untarnished jalpaite–acanthite as compared with similar analyses of initially tarnished jalpaite–acanthite. Filled circles: tarnished before successive analyses (1–4); open circles: untarnished before successive analyses (1–3).

metal/sulfur values (Fig. 4), and low total contents (~90 wt.%), probably as a result of surface changes during electron bombardment. However, successive analyses on the same spot of untarnished jalpaite-acanthite indicated an increase in silver from about 52 atom % to 62 atom %, where the latter value is approximately equal to the silver content of tarnished jalpaite–acanthite (Fig. 4). The rapid optical alteration and the change in composition indicate that silver or possibly acanthite formed on the surface of jalpaite–acanthite. However, since the analyses of the altered surface were affected by the underlying jalpaite–acanthite, it is not possible to determine which silver mineral was formed.

As it could not be excluded that the rate of tarnishing is thermally enhanced, the light beam was focused on the metal sensor of an electronic thermometer with a precision of 0.1°C. Although no change in temperature could be detected, this does not exclude a very small gradient because of insensitivity of the sensor. In addition, one sample was heated in air at 60°C in darkness. The resulting surface-change observed after 100 minutes is comparable with the surface change that takes place after only a few seconds of illumination using the highest magnification. Even if photochemical and thermochemical enhancements of the reaction rate simultaneously affect the present surface-process, these simple experiments clearly demonstrate the importance of the photochemical factor.

High silver contents in chalcopyrite in contact with native silver commonly are present in tarnished samples from sulfide ores in Bergslagen, central Sweden. In the complex metamorphosed sulfide ore from Saxberget, Amcoff *et al.* (1985) showed that silver is associated both with galena and with chalcopyrite. Tarnishing of the natural samples was confined to chalcopyrite and pyrrhotite in contact with
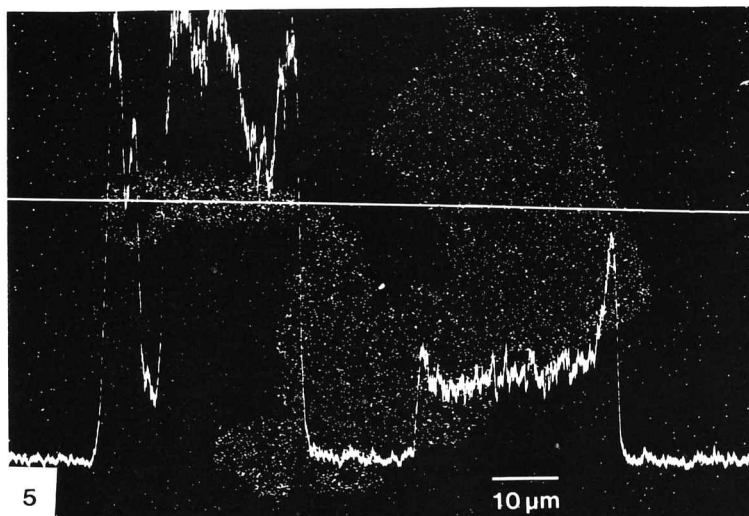
FIG. 5. Silver distribution profile across a grain of native silver (left) and chalcopyrite (right), subjected to one month of light exposure. Sample of complex ore from Saxberget, central Sweden. The discontinuity in silver content between native silver and chalcopyrite is due to a silicate grain. There is a direct contact along an interface, however, between the two former phases below the profile. The tarnishing started at this interface, which suggests surface diffusion rather than volume diffusion of silver from the bulk of the chalcopyrite grain.

silver minerals, whereas pyrite, sphalerite and galena remained unaffected for at least two months. An element profile of a sample from Saxberget, in which native silver in contact with chalcopyrite has been subjected to a few weeks of tarnishing, is shown in Figure 5. The variation of silver in the grain of native silver probably represents minor inclusions or surface irregularities. The peculiar enrichment in silver concentration at the boundary between chalcopyrite and silicate may be related to thickening of the diffusing silver-rich layer due to prior formation of grooves during polishing (Fig. 5).

Tarnishing of chalcopyrite and pyrrhotite was much slower in the natural samples. Thus, natural samples had to be illuminated in the microscope for 1 to 1.5 h before tarnishing of chalcopyrite could be detected as compared with only seconds for the synthetic sulfides. The highly reactive nature of synthetic jalpaite–acanthite at room temperature, compared with native silver, probably explains this large difference. Unfortunately, no synthetic sample with native silver in contact with chalcopyrite was available for comparison.

Storage of samples in a transparent plastic box exposed to sunlight resulted in tarnishing of the synthetic samples after a few hours, and tarnishing of the natural samples after a few days. No difference in the rate of tarnishing was observed when the samples were stored in an evacuated desiccator. Even if this suggests that neither oxygen nor air pollutants significantly affected the photochemically induced process, it cannot be excluded that galvanic cells set up through a thin film of strongly adsorbed water molecules may have been of importance. As expected, the rate of tarnishing was considerably slower when the samples were stored in darkness. However, after one month, tarnishing occurred in the form of dendrites that grew from jalpaite–acanthite onto surrounding isocubanite or chalcopyrite, whereas pyrrhotite preferably tarnished along microscratches and along grain boundaries. No dark spots formed on the surface of jalpaite–acanthite. According to Hägg (1966), the mechanism of photoreactions differs from surface reactions that take place in darkness. This difference may explain the decreased rate of tarnishing and the dendritic texture formed when the samples were stored in darkness.

The diffusion of silver from jalpaite–acanthite onto the surface of pyrrhotite aggregates is much slower than diffusion onto chalcopyrite or isocubanite grains (Fig. 1f). Most strikingly, except for the tarnishing of chalcopyrite, isocubanite and pyrrhotite, all other phases (pyrite, sphalerite, galena and silicate), as well as epoxy, remained unaffected for at least two months. This is unlike the tarnishing behavior of tennantite, wherein a partial decomposition, i.e., formation and subsequent dendritic growth of silver-bearing Cu_2S or $Cu_{1.8}S$ films on surrounding phases, is involved (Chen et al. 1980).

The large difference in the tarnishing behavior of different minerals is probably the most important observation in the present experiments. Thus, the resistance of pyrite to tarnishing may be a reflection of the stronger S – S bonds in the structure of pyrite than in that of pyrrhotite, and especially in that of chalcopyrite or isocubanite.

An explanation of the observed phenomena could be as follows: (1) highly unstable jalpaite–acanthite breaks down when electrons are excited by incident photons. (2) Liberated silver, in the form of free ions or ion complexes, reacts with neighboring sulfide phases, and acanthite is formed, as suggested by Chen *et al.* (1980). The rate of this process is largely a function of the surface properties (the availability of "reactive" sulfur) of the surrounding phases. (3) Silver rapidly diffuses over the surface of the acanthite that is formed, and continuously reacts at the acanthite "front", leading to rapid expansion of the blue areas. Thus the driving force of the observed reaction is both the intensity of incident light and the reactivity of the surrounding phases.

REFERENCES

AMCOFF, Ö. (1984): Distribution of silver in massive sulfide ores. *Mineral. Deposita* 19, 65–69.

_____, JEPPSSON, M. & SELKMAN, S. (1985): Distribution and zoning of silver and associated elements in the complex sulfide deposit at Saxberget, central Sweden. *Econ. Geol.* 80, 614–626.

CABRI, L.J., CAMPBELL, J.L., LAFLAMME, J.H.G., LEIGH, R.G., MAXWELL, J.A. & SCOTT, J.D. (1985): Proton-microprobe analysis of trace elements in sulfides from some massive sulfide deposits. *Can. Mineral.* 23, 133–148.

CHEN, T.T., DUTRIZAC, J.E., OWENS, D.R. & LAFLAMME, J.H.G. (1980): Accelerated tarnishing of some chalcopyrite and tennantite specimens. *Can. Mineral.* 18, 173-180.

_____ & PETRUK, W. (1978): Electron microprobe analyses of silver-bearing minerals in samples collected from the Heath Steele mill, New Brunswick in March 1977. *CANMET Rep.* MRP/MSL 78-23 (IR). Dep. Energy, Mines & Resources, Ottawa.

FISCHMEISTER, H.F. (1961): Growth morphology and kinetics in metal-gas reactions. *In* Reactivity of Solids (J.H. De Boer, W.G. Burgers, E.W. Gorter *et al.*, eds.). Elsevier, Amsterdam.

FLEISCHER, M. (1955): Minor elements in some sulfide minerals. *Econ. Geol., 50th Ann. Vol.,* 970-1024.

HARRIS, D.C., CABRI, L.J. & NOBILING, R. (1984): Silver-bearing chalcopyrite, a principal source of silver in the Izok Lake massive-sulfide deposit: confirmation by electron- and proton-microprobe analyses. *Can. Mineral.* 22, 493-498.

HÄGG, G. (1966): *Allmän Och Oorganisk Kemi.* Almqvist & Wiksell, Uppsala, Sweden.

REMOND, G., HOLLOWAY, P.H., HOVLAND, G.T. & OLSON, R.R. (1982): Bulk and surface silver diffusion related to tarnishing of sulfides. *Scanning Electron Microscopy* III, 995-1011.

SKINNER, B.J. (1966): The system Cu–Ag–S. *Econ. Geol.* 61, 1-26.

STEPHENS, M.M. (1931): Effect of light on polished surfaces of silver minerals. *Amer. Mineral.* 16, 532-549.

THORPE, R.I., PRINGLE, G.J. & PLANT, A.G. (1976): Occurrence of selenide and sulphide minerals in bornite ore of Kidd Creek massive sulphide deposit, Timmins, Ontario. *Geol. Surv. Can. Pap.* 76-1A, 311-317.