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SILVER-BEARING CHALCOPYRITE, A PRINCIPAL SOURCE OF SILVER IN THE IZOK LAKE MASSIVE-SULFIDE DEPOSIT: CONFIRMATION BY ELECTRON- AND PROTON-MICROPROBE ANALYSES

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ABSTRACT

Detailed *in situ* analyses by electron and proton microprobes have confirmed the presence of silver in solid solution in chalcopyrite from the Izok Lake Zn–Cu–Pb deposit, Northwest Territories, and in that from the Ag–Pb–Zn orebodies 1–7 at the Hilton mine in northwestern Queensland, Australia. Silver content in chalcopyrite ranges from 266 to 560 ppm for an Izok Lake sample and from 1414 to 2900 ppm for a Hilton mine sample. Minimum levels of detection were established at about 200 and < 10 ppm Ag for the electron and proton microprobes, respectively. Proton-microprobe analyses also indicate that the Izok Lake chalcopyrite contains between 38 and 72 ppm indium.

Keywords: silver-bearing chalcopyrite, silver, indium, electron microprobe, proton microprobe (micro-PIXE), Izok Lake, Northwest Territories, Hilton mine, Queensland, Australia.

SOMMAIRE

Des analyses détaillées *in situ* par microsondes électronique et protonique ont permis de constater la présence d'argent en solution solide dans la chalcopyrite du gisement de Zn–Cu–Pb d'Izok Lake dans les Territoires du Nord-Ouest, de même que dans celle des veines métallifères de Ag–Pb–Zn 1–7 de la mine Hilton dans le Nord-Ouest du Queensland (Australie). La teneur en argent de la chalcopyrite d'Izok Lake varie de 266 à 560 ppm tandis que celle de l'échantillon de la mine Hilton varie de 1414 à 2900 ppm. Les limites de détection sont établies à environ 200 et < 10 ppm d'argent, respectivement, pour les microsondes électronique et protonique. La microsonde protonique démontre aussi la présence de 38 à 72 ppm d'indium dans la chalcopyrite d'Izok Lake.

Mots-clés: chalcopyrite argentifère, argent, indium, microsonde électronique, microsonde protonique (micro-PIXE), Izok Lake, Territoires du Nord-Ouest, mine Hilton, Queensland (Australie).

INTRODUCTION

Minor elements in sulfide ores have been investigated intensively for over a century. Fleischer (1955) summarized the available widely scattered information for those sulfides for which the most data had been obtained, namely galena, sphalerite and wurtzite, chalcopyrite, pyrite, marcasite, pyrrhotite and arsenopyrite. For the bulk silver content of chalcopyrite, he tabulated the results of 8 determinations, which cover the range 10 to 2300 ppm. In addition to these analyses, Hawley & Nichol (1961) determined the trace-element content of a number of chalcopyrite samples from copper deposits and of one sample from a gold mine. They obtained mean concentrations of silver of 91 to 310 ppm in chalcopyrite from the copper deposits and 165 ppm in that from the gold mine. In a study of ore deposits of the Rossland area, British Columbia, Thorpe (1967) summarized available information on the precious-metal contents of chalcopyrite. Most of the information available was related to investigations of its gold content, with minor data on silver. However, in several cases, the correlations of silver *versus* copper are very good, and led Thorpe to the conclusion that silver, as well as gold, had been deposited as a solid solution in chalcopyrite. The calculated average total concentration of precious metals in chalcopyrite from the Rossland area is about 1200 ppm. Information from two of the mines, namely Le Roi No. 2 and Centre Star, indicate a silver content in chalcopyrite of approximately 900 ppm.

Unfortunately, these earlier investigations of minor elements in sulfides were based on bulk-composition data obtained on ore samples, concentrates and mineral separates, with no knowledge of whether the elements occur in solid solution or within discrete mineral impurities. The use of the electron microprobe for *in situ* analysis has minimized the need for mineral separation, but routine wavelength-dispersion analysis will not give better than 500 ppm sensitivity for most elements. Increased operating current and longer counting times lower these detection limits. Some modern instruments are capable of 100–200 ppm for certain elements in sulfide minerals. Recently, new instruments, namely the ion and proton microprobes (Micro-PIXE), have become available. These can provide *in situ* analyses with detection levels better than 10 ppm. One of us (LJC) has been investigating the presence of trace quantities of platinum-group elements (PGE) in sulfide minerals and recently had the opportunity to use the proton microprobe at the Max-Planck-Institut für Kernphysik in Heidelberg for analysis of silver in chalcopyrite (Cabri *et al.* 1983).

The purpose of this paper is to report the trace silver contents of chalcopyrite using electron- and proton-microprobe data. These data show that silver-bearing chalcopyrite is a major source of silver in the Izok Lake massive-sulfide deposit, Northwest Territories (Harris 1982), and is confirmed in the Hilton mine, northwestern Queensland. There are various methods used to indicate minor and variable isomorphous substitution in minerals. Hey & Gottardi (1980) outlined the two kinds of terms currently used in mineralogical nomenclature: names and adjectival modifiers. An *adjectival modifier* is an adjective that gives some information on the chemistry of the mineral. Examples are: "argentian", "silver-rich" or "silver-bearing" in English. Argentiferous chalcopyrite, on the other hand, is not recommended in the report of Hey & Gottardi (1980). For chalcopyrite with low contents of silver, argentian or silver-bearing are appropriate. We have preferred the latter modifier, although longer, as it clearly defines the chemistry.

ANALYTICAL METHODS

Electron microprobe

Material Analysis Company (MAC) microprobes were used at the Canada Centre for Mineral and Energy Technology (CANMET) and the Geological Survey of Canada (GSC) to carry out the analyses of silver-bearing chalcopyrite from the Izok Lake deposit and the Hilton mine. The instruments were operated at 25 kV with a specimen current on chalcopyrite of 0.07×10^{-6} amperes and a counting time of 100 seconds. The X-ray line used was Ag $L\alpha$; standards of synthetic PbS with 0.4 wt.% Ag and synthetic $Cu_4Fe_5S_8$ with 0.12 wt.% Ag were used. Background counts were determined from a silver-free chalcopyrite with the wavelength spectrometer positioned on the Ag$L\alpha$ peak. The minimum detection-limit (MDL) was established as $3\sqrt{N_B}$, where N_B is total background counts on the chalcopyrite.

Proton microprobe

The Heidelberg proton microprobe (Bosch *et al.* 1978, 1980) was used for a few analyses of silver-bearing chalcopyrite from the Izok Lake deposit and the Hilton mine. Pieces of ore cut from drill core from both deposits were mounted in araldite as a 2.5 cm polished section together with the standards, synthesized at CANMET, that were used in the electron-microprobe analyses. The analyses were performed at a beam current ranging from 120 to 180 pA at 4 MeV using a 1 mm Al absorber (to suppress the low-energy part of the spectrum) in addition to the 150-μm Be foil, placed in front of the Al absorber (to stop backscattered protons in order to prevent X-ray production in the Al absorber). The X rays from the target are detected with a Kevex Si(Li) detector fitted with a 50-μm proton shield. Data acquisition was done with an on-line computer, and analysis times were about one hour each at an accumulated charge of about 0.9 μC. In contrast to the electron-microprobe analyses, the Ag$K\alpha$ line was used.

The grains for analysis were carefully selected by microscopic observation followed by SEM study to confirm, in particular, the *absence* of inclusions of silver minerals. It should be stressed that no silver minerals were found in this particular polished section, thus making it highly unlikely that inclusions of silver minerals occur below the surface. This is an important considerations, since protons probably penetrate about 50 μm into this type of material. The beam-contamination spot, about 6 × 6 μm, was checked by SEM study again after analysis. Electron-microprobe analyses were later made in the contamination area caused by the proton beam in order to compare results for the same area. Further details on typical contamination spots made by the proton beam are given in Cabri *et al.* (1984).

SILVER-BEARING CHALCOPYRITE

On the basis of detailed ore-microscopic investigations of Ag–Pb–Zn orebodies 1–7 at the Hilton mine in northwestern Queensland, J.F. Riley (*in* Knights 1983) was the first to report, by electron-microprobe analysis, silver-bearing chalcopyrite as a major silver contributor in an ore deposit. This was found to be so in orebodies 1–3, and the mineral was also identified as a minor contributor of silver in orebodies 4–7. Analyses indicate an average of 2000 ppm silver in solid solution. There has not been, however, a thorough published documentation of quantitative *in situ* analyses of the silver-bearing chalcopyrite to demonstrate the presence of the silver in solid solution. The phenomenon of tarnishing of sulfide minerals such as chalcopyrite and tennantite has long been recognized, and 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 on chalcopyrite from the Heath Steele mine, New Brunswick. In 1980, Chen *et al.* undertook a study to ascertain the nature of the tarnish products and to correlate the rate of tarnishing with silver concentration. This study showed that when chalcopyrite is in contact with silver minerals, especially native silver, it undergoes rapid tarnishing that appears to be caused by the surface diffusion of silver onto the chalcopyrite, followed by a reaction to form an Ag_2S film. Using AES (Auger Electron Spectroscopy) combined with ion-sputter depth-profiling techniques and optical microreflectometry, Remond *et al.* (1982) investigated color changes and Ag diffusion in chalcopyrite inclusions within an Ag_2S matrix. Their observations are consistent with the results published by Chen *et al.* (1980).

IZOK LAKE

Occurrence and mineralogy

Izok Lake is located at 65°39′N, 112°49′W, in the northern part of the Slave structural province, Northwest Territories, about 366 km north of Yellowknife and 300 km south-southeast of Coppermine, the two nearest major settlements. The geology and exploration history of the massive-sulfide deposit are given by Money & Heslop (1976) and Bostock (1980). Briefly, the deposit occurs in Archean metavolcanic rocks of the Precambrian Shield. The rocks are highly metamorphosed and recrystallized and have undergone at least three major phases of folding. The deposit consists of a stratabound volcanogenic massive-sulfide ore, metamorphosed to the amphibolite facies. To date more than 12 million tonnes of indicated ore grading 13.7% Zn, 2.82% Cu, 1.42% Pb and 70.3 g/tonne Ag have been established by drilling. In 1981, one of us (DCH) undertook a detailed study of the ore microscopy of the Izok ore to define its mineralogy, particularly the silver minerals and their distribution. The major ore minerals are pyrite, pyrrhotite, sphalerite, chalcopyrite, magnetite and galena, with minor to trace amounts of gahnite, tetrahedrite, gudmundite, arsenopyrite, pyrargyrite, native bismuth, meneghenite, bournonite, boulangerite, two new sulfosalts, cosalite, nuffieldite, tennantite, stannite, electrum, allargentum, dyscrasite, native silver, acan-

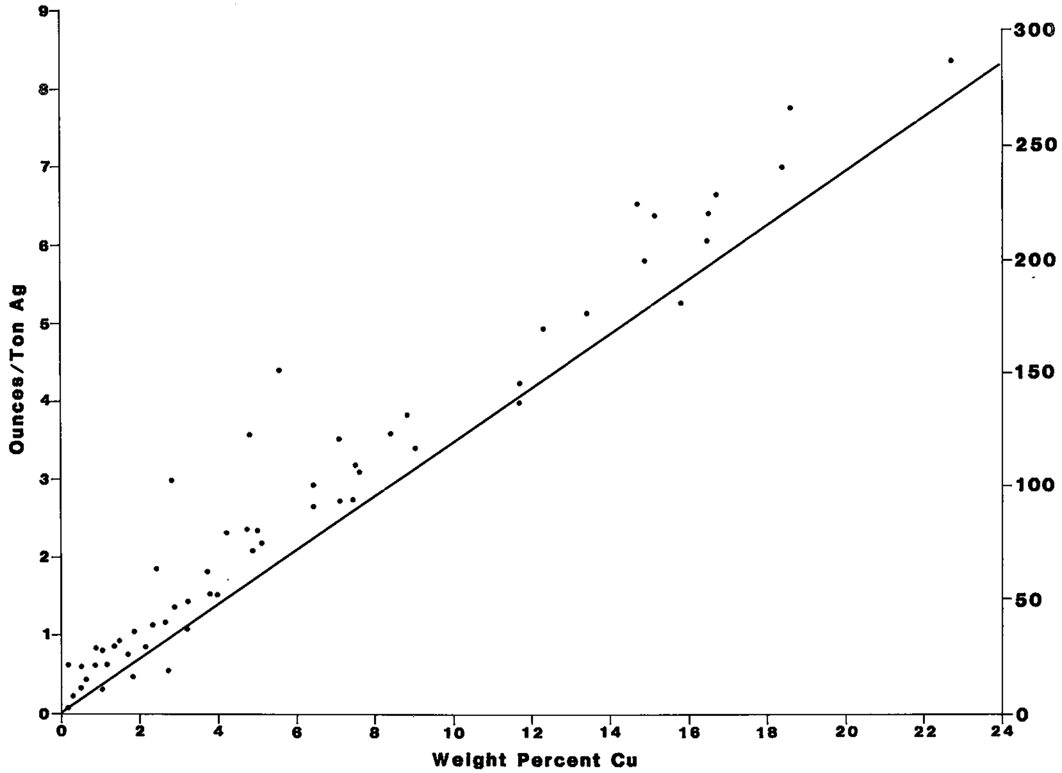

FIG. 1. Correlation between the copper and silver contents of ore from the central zone, hole 33, Izok Lake deposit, N.W.T. Each dot represents the assay value for a five-foot interval.

thite, polybasite, stephanite, molybdenite, valleriite, breithauptite, cassiterite, covellite, digenite, cubanite, sternbergite and cobaltite. The principal minerals that account for the silver content are chalcopyrite, galena, tetrahedrite, pyrargyrite, native silver and silver–antimony compounds.

HILTON MINE (ORE)

As outlined by Knights (1983), the Hilton ore consists of abundant spheroidal and euhedral pyrite, in addition to pyrrhotite, sphalerite and galena, and minor amounts of chalcopyrite, marcasite, arsenopyrite and numerous silver-bearing minerals. Although more highly deformed, the ore is very similar to the lead–zinc ores at the Mount Isa mine. Silver minerals, in approximate order of importance, include pyrargyrite, freibergite, native silver, silver-bearing chalcopyrite, stephanite, argentopyrite and dyscrasite.

ANALYTICAL

Assay data

The presence of silver-bearing chalcopyrite in the Izok Lake deposit was suggested by a correlation between the copper and silver contents of drill core as determined by assay data. Figure 1 illustrates the assay values for each five-foot interval for Hole 33. This drill hole is located in the central part of the ore zone and intersected 318.3 feet of massive-sulfide ore containing 5.58% Cu, 0.56% Pb, 14.14% Zn, 2.55 oz/ton (87.4 g/tonne) Ag. Detailed ore-microscopy of samples representing each five-foot assay interval established either the absence of, or the presence of only trace amounts of, known silver minerals, *e.g.*, silver-bearing galena, tetrahedrite–freibergite, and pyrargyrite. These observations and the absence of a tarnished surface (*e.g.*, an Ag_2S film) strongly suggested that silver-bearing chalcopyrite is the principal source of silver. Based on the detailed mineralogical observations, a line was established to pass through or close to those data points for which the silver values could only be correlated with chalcopyrite (Fig. 1). The line corresponds to a silver content of 500 ppm in chalcopyrite. Most of the data points above this line represent sections of core in which the ore was found to contain traces of silver-bearing galena, tetrahedrite or pyrargyrite. Microprobe analyses of associated silver-bearing galena gave values from 0.07 to 0.29 wt.% Ag, average 0.15 wt.%. Because galena is the principal lead-bearing mineral in the drill core, mineral distribution and assay data show that chalcopyrite accounts for 76% of the silver and galena for 9%, with the remainder accounted for by tetrahedrite and pyrargyrite. Other parts of the ore deposits give similar trends, although with chalcopyrite apparently accounting for a lesser proportion of the total silver.

ELECTRON- AND PROTON-MICROPROBE ANALYSES

Results of the electron- and proton-microprobe analyses are given in Table 1. All analyses represent the same areas examined with both instruments. During the earlier stages of this study, pure Ag metal was used as a standard, but the results were consistently lower than those obtained using other standards containing low contents of silver. In our opinion, the use of pure metals as standards for the determination of trace amounts does not yield results of the greatest possible accuracy, largely due to uncertainties in matrix corrections.

It was determined, after many electron-micro-

TABLE 1. ELECTRON- AND PROTON-MICROPROBE DATA* ON SILVER-BEARING CHALCOPYRITE

		Electron microprobe		Proton microprobe	
		1.	2.	3.	4.
IZOK	IZCP1	291 ± 116	266 ± 106	467 ± 70	382 ± 57
IZOK	IZCP2	612 ± 245	560 ± 224	451 ± 68	369 ± 55
IZOK	IZCP4	433 ± 173	390 ± 156	427 ± 64	349 ± 52
IZOK	IZCP5	452 ± 181	413 ± 165	436 ± 65	357 ± 54
Hilton	HCP1	1759 ± 264	1609 ± 241	1729 ± 173	1414 ± 141
Hilton	HCP2	3170 ± 476	2900 ± 435	2630 ± 263	2151 ± 215
Hilton	HCP3	2349 ± 352	2149 ± 322	1762 ± 176	1441 ± 144

1. Using synthetic (Pb,Ag)S with 0.4% Ag, uncorrected.
2. Using synthetic $(Cu,Ag)_4Fe_5S_8$ with 0.12% Ag, uncorrected.
3. Using synthetic $(Cu,Ag)_4Fe_5S_8$ with 0.12% Ag, uncorrected.
4. Using synthetic $(Fe,Ni,Pd)_9S_8$ with 0.65% Pd, corrected with matrix correction program of Blank (1982).

* All values are Ag ppm.

MDL 3σ for electron microprobe is 200 ppm. MDL 3σ for proton microprobe analyses ranged from 8.4 to 8.6 ppm for Izok and from 9.0 to 9.7 ppm for Hilton.

probe analyses, that the synthetic (Cu, Ag)$_4$Fe$_5$S$_8$ standard was not as homogeneous as originally thought. Therefore, for the electron microprobe, a larger number of spot analyses than is usual (*i.e.,* 8–12) were made on this standard, thus giving greater confidence in the values reported in Table 1. Matrix corrections were not applied to the electron-microprobe values reported in Table 1 because data corrections, using a modified version of the EMPADR VII computer program of Rucklidge & Gasparrini (1969), did not produce significantly different results when compared to the uncorrected electron-microprobe data. On the other hand, the proton-microprobe analyses reported are, unfortunately, calculated by reference to only one spot analysis on the standard, subsequently found to be heterogeneous. This may explain the slight unsystematic variation between electron- and proton-microprobe results, though we are unable to evaluate the effects, if any, of temperature changes during the analyses. Lower concentrations of silver, however, were obtained for the proton-microprobe analyses by using a homogeneous Pd-doped synthetic standard and applying the matrix-correction program of Blank (1982). Another mechanism possibly accounting for only fair agreement between all the results might be related to the mobility of Ag in a chalcopyrite matrix (Chen *et al.* 1980), also reflected by the inability to quench a homogeneous Ag-bearing isometric solid-solution (Cabri, unpubl. data). Comparison of analytical results for Pd contained in solid solution in pentlandite, on the other hand, shows excellent correspondence between electron- and proton-microprobe results, to within ±8% (Cabri *et al.* 1984).

Indium was determined in the Izok chalcopyrite and sphalerite, and the latter also contains Cd (Figs. 2, 3). Interestingly, no In was detectable in the three analyses of chalcopyrite from the Hilton mine (MDL In = < 10 ppm), for which one spectrum is shown in Figure 4. The presence of Cd and In in the Izok sphalerite are not unexpected, but silver was not detected (MDL Ag = < 10 ppm). Though no standards for In or Cd were available, the concentrations of these elements (Table 2) were calculated using the matrix-correction program of Blank (1982). Both In and Cd were calculated with reference to Pd in the synthetic pentlandite standard.

CONCLUSIONS

Detailed *in situ* analyses by electron- and proton-microprobes have confirmed the solid solution of silver in chalcopyrite. Owing to its greater sensitivity, the proton microprobe shows great promise for studying trace-element geochemistry of minerals, and of sulfides in particular.

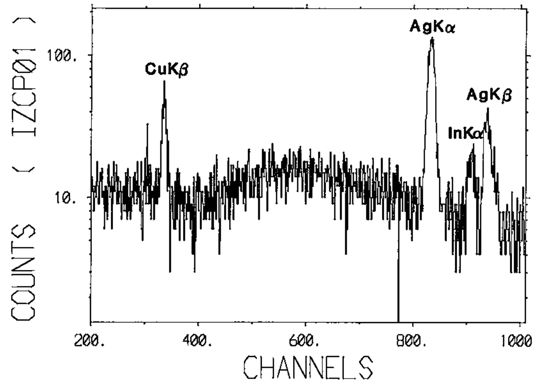

FIG. 2. X-ray spectrum of silver-bearing chalcopyrite from the Izok Lake deposit with 4 MeV proton excitation using a Si(Li) detector and Al and Be as absorbers for Fe and Cu (which now appear at much reduced intensities). Note the high peak-to-background ratio for Ag and In peaks. IZCPO1 analysis.

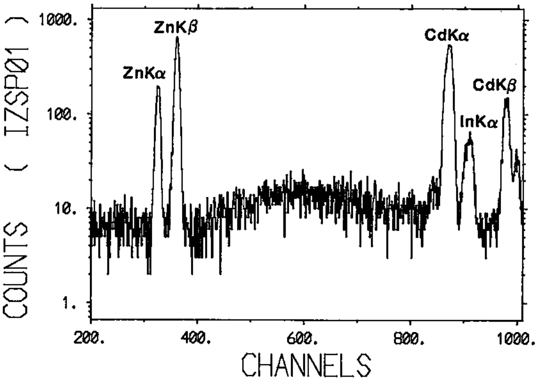

FIG. 3. X-ray spectrum of sphalerite associated with the silver-bearing chalcopyrite from the Izok lake deposit. Operating conditions as given in Figure 2. Presence of Cd and In readily detectable, but no silver. Note that the Zn*Kα* peak is less than the *Kβ* due to the Al absorber. IZSPO1 analysis.

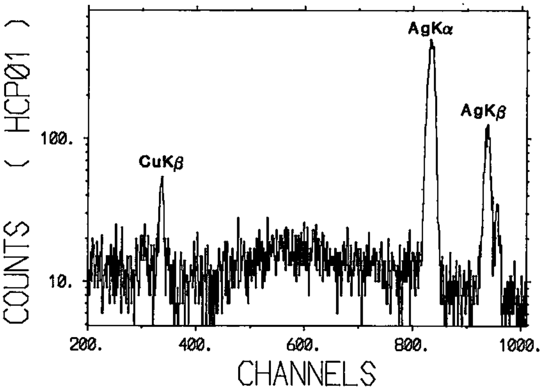

FIG. 4. X-ray spectrum of silver-bearing chalcopyrite from the Hilton mine produced using conditions as specified in Figure 2. The spectrum clearly shows that there is no In peak. HCPO1 analysis.

TABLE 2. PROTON-MICROPROBE DATA* (IZOK)

	In	Cd
chalcopyrite		
IZCP1	38 ± 13	n.d.**
IZCP2	72 ± 25	n.d.
IZCP4	62 ± 22	n.d.
IZCP5	41 ± 14	n.d.
sphalerite		
IZCP(SP)3	228 ± 46	2084 ± 417
IZSP1	263 ± 53	2228 ± 445

* all values are in ppm; ** n.d. = not detected

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REFERENCES

BLANK, H. (1982): *Spurenelemente in Koexistierenden Opaken Oxyden Lunarer Gesteine Gemessen mit einer Protonenmikrosonde.* Ph.D. thesis, Univ. Heidelberg, W. Germany.

BOSCH, F., EL GORESY, A., MARTIN, B., POVH, B., NOBILING, R., SCHWALM, D. & TRAXEL, K. (1978): The proton microprobe: a powerful tool for non-destructive trace element analysis. *Science* **199**, 765-768.

——, ——, HERTH, W., MARTIN, B., NOBILING, R., POVH, B., REISS, H.D. & TRAXEL, K. (1980): The Heidelberg proton microprobe. *Nucl. Sci. Appls.* **1**, 33-35.

BOSTOCK, H.H. (1980): Geology of the Itchen Lake area, District of Mackenzie. *Geol. Surv. Can. Mem.* **391.**

CABRI, L.J., BLANK, H., EL GORESY, A., LAFLAMME, J.H.G., NOBILING, R., SIZGORIC, M.B. & TRAXEL, K. (1983): Quantitative proton microprobe analyses of major sulphides in ore deposits of the Sudbury area. *Geol. Assoc. Can. - Mineral. Assoc. Can., Program Abstr.* **8**, A9.

——, ——, ——, ——, ——, —— & —— (1984): Quantitative trace-element analysis of sulfides from Sudbury and Stillwater by proton microprobe. *Can. Mineral.* **22**, (in press).

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 & Res.* Ottawa.

FLEISCHER, M. (1955): Minor elements in some sulfide minerals. *Econ. Geol. 50th Anniv. Vol.*, 971-1024.

HARRIS, D.C. (1982): Unusual ore mineral assemblage from the Izok Lake deposit, Northwest Territories, Canada. *Int. Mineral. Assoc., 13th Gen. Meet. (Varna), Program Abstr.*

HAWLEY, J.E. & NICHOL, I. (1961): Trace elements in pyrite, pyrrhotite and chalcopyrite of different ores. *Econ. Geol.* **56**, 467-487.

HEY, M.H. & GOTTARDI, G. (1980): On the use of names, prefixes and suffixes, and adjectival modifiers in the mineralogical nomenclature. *Can. Mineral.* **18**, 261-262.

KNIGHTS, J.G. (1983): Hilton Mines silver mineralogy - its distribution, textural associations and metallurgical significance. *Geol. Soc. S. Afr., Spec. Publ.* **7**, 275-286.

MONEY, P.L. & HESLOP, J.B. (1976): Geology of the Izok Lake massive sulphide deposit. *Can. Mining J.* **97(5)**, 24-27.

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.

RUCKLIDGE, J.C. & GASPARRINI, E. (1969): Specifications of a computer program for processing electron microprobe analytical data: EMPADR VII. *Dep. Geol., Univ. Toronto.*

THORPE, R.I. (1967): *Controls of Hypogene Sulphide Zoning, Rossland, British Columbia.* Ph.D. thesis, Univ. Wisconsin, Madison, Wisc.

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

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