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PROTON-MICROPROBE ANALYSIS OF TRACE ELEMENTS IN SULFIDES FROM SOME MASSIVE-SULFIDE DEPOSITS

LOUIS J. CABRI

Canada Centre for Mineral and Energy Technology, 555 Booth Street, Ottawa, Ontario K1A 0G1

JOHN L. CAMPBELL

Department of Physics, University of Guelph, Guelph, Ontario N1G 2W1

J.H. GILLES LAFLAMME

Canada Centre for Mineral and Energy Technology, 555 Booth Street, Ottawa, Ontario K1A 0G1

ROBERT G. LEIGH AND JOHN A. MAXWELL

Department of Physics, University of Guelph, Ontario N1G 2W1

J. DOUGLAS SCOTT

Kidd Creek Mines Limited, P.O. Box 175, Suite 5000, Commerce Court, Toronto, Ontario M5L 1E7

ABSTRACT

We have determined the amount of Ge, As, Se, Ag, Cd, In, Sn and Sb present in solid solution in major sulfides such as bornite, chalcopyrite, galena, pyrite, pyrrhotite and sphalerite from three massive-sulfide deposits (Kidd Creek, Geco and Mattagami-Norita) and one carbonate-hosted Pb-Zn-Ag deposit (Nanisivik). The analyses were performed mainly by proton microprobe (down to levels of ~ 7 to 20 ppm) and were corroborated, for concentrations above ~ 200-300 ppm, by electron microprobe. Silver, selenium and indium concentrations in sulfides from the Kidd Creek deposit vary with ore type. In general, galena and chalcopyrite are important Ag carriers, but sphalerite is of secondary importance. Occasionally, pyrrhotite and pyrite have also been identified as Ag carriers, but an evaluation of their significance requires further work. Tin is an important trace constituent in much of the Kidd Creek chalcopyrite, as is arsenic in much of the pyrite. More accurate material-balances may be obtained in future for elements such as silver by combining the results of *in situ* trace-element analysis of all major minerals with quantitative mineralogy.

Keywords: trace elements, proton microprobe, MicroPIXE, electron microprobe, base-metal sulfides, Ge, As, Se, Ag, Cd, In, Sn, Sb, Kidd Creek, Geco, Mattagami-Norita, Nanisivik.

SOMMAIRE

On a déterminé la teneur en Ge, As, Se, Ag, Cd, In, Sn et Sb sous forme de solution solide dans les principaux sulfures, tels bornite, chalcopyrite, galène, pyrite, pyrrhotite et sphalérite, provenant de trois gisements à sulfure massif (Kidd Creek, Geco, Mattagami-Norita) et d'un gisement Pb-Zn-Ag (Nanisivik), à roche-mère carbonatée. Les analyses ont été effectuées principalement par microsonde protonique (seuil minimum ~ 7 à 20 ppm); celles qui accusaient une concentration supérieure à ~ 200-300 ppm ont été corroborées à la microsonde électronique. La concentration en argent, sélénium ou indium dans les sulfures du gisement de Kidd Creek varie selon le type de minerai. La galène et la chalcopyrite sont généralement porteurs d'argent importants, tandis que la sphalérite est d'importance secondaire. Pyrrhotite et pyrite aussi ont parfois été identifiées comme porteurs d'argent, mais leur évaluation nécessitera une étude plus approfondie. A Kidd Creek, l'étain est un constituant-trace important de la chalcopyrite, comme l'est l'arsenic de la pyrite. Des bilans plus précis des matériaux pourraient être obtenus en combinant à la minéralogie quantitative l'analyse *in situ* des éléments-traces dans les principaux minéraux.

Mots-clés: éléments-trace, microsonde protonique, MicroPIXE, microsonde électronique, sulfures des métaux de base, Ge, As, Se, Ag, Cd, In, Sn, Sb, Kidd Creek, Geco, Mattagami-Norita, Nanisivik.

INTRODUCTION

The proton microprobe (Micro-PIXE technique) was used to determine quantities of trace elements in major sulfide minerals from some Canadian silver-bearing Zn-Pb-(Cu) sulfide ores. The work reported here is a follow-up of the encouraging earlier results (Cabri *et al.* 1984a, b, Harris *et al.* 1984) with this analytical technique, which is considered a method complementary to already established methods of quantitative mineralogical investigation. The major objectives of this investigation are (a) to demonstrate the credibility of the data obtained and (b) to illustrate the usefulness of such data in quantitative mineralogy and mass-balance calculations involving minor elements in massive-sulfide deposits currently in production.

All but one sample analyzed came from massive base-metal sulfide ores, mostly from the Kidd Creek mine, Timmins, Ontario (Walker & Mannard 1974). Whereas the major emphasis of this study concerns the identification of the silver carriers, it is also of practical importance to know more precisely the partitioning of selenium because of the deleterious effect of high concentrations of selenium in copper concentrates.

SAMPLES

Kidd Creek mine

Thirty samples, consisting of twenty-five hand

samples and five drill-core samples, were studied. The samples are considered to form a complete suite representative of run-of-mine types of ore collected in January, 1983, with mill heads uniformly about 250 ppm Ag for "C" ore and 30 ppm for "A" ore; however, most of the samples are not precisely located in the mine as they were taken from the rod-mill feed belts.

Figure 1 shows the location of the five diamond-drill-core samples and the geology in the vicinity of the bornite zone on the 2000 level. The samples are classified either as Zn-Pb-Ag-(Cu) "C" ore (massive, banded and breccia ores, North orebody), Cu-(Zn) "A" ore (stringers, both North and South orebodies), bornite zone (South orebody, Thorpe *et al.* 1976, Pringle & Thorpe 1980) or bornite-zone halo (mainly massive chalcopyrite). This classification, together with mineralogical descriptions, is followed in Table 1.

Mattagami-Norita

A +100-mesh fraction of zinc concentrate (14/03/ZnC) from the Mattagami and Norita mines of Mines Noranda Ltée, near Matagami, Quebec (MacGeehan *et al.* 1981) was examined mineralogically. Sphalerite and chalcopyrite grains were selected for analysis; no silver minerals were found.

Geco

A head sample (-4 mesh) from Noranda's Geco

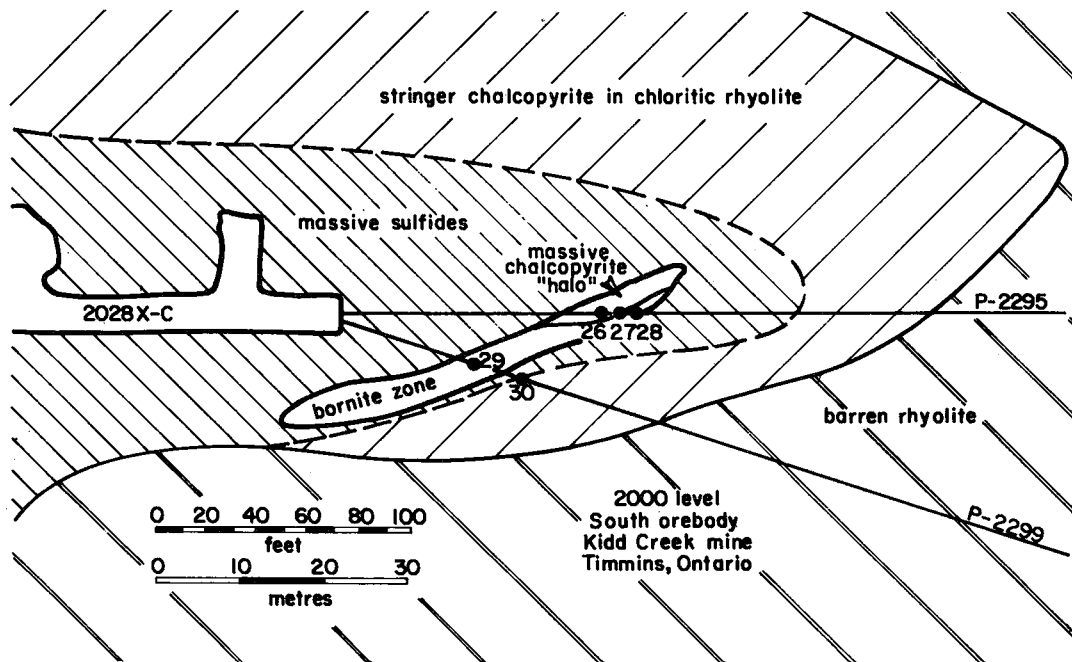


FIG. 1. Plan view of 2000 level, South orebody, Kidd Creek mine, showing sample locations.

TABLE 1. KIDD CREEK MINE SAMPLES

Number	Mineralogy: macroscopic	Mineralogy: microscopic
"C" ore (massive, banded and breccia ores)		
83-1	Massive coarse sp with trace cp and gn.	Sp>G>py>cp>cas, po, gn>asp. Trace Ag found in po.
83-2	Massive fine-grained sp with py bands.	Sp, py>G>>cp, po>>asp, gn. Trace Ag found in po and py.
83-3	Massive fine-grained sp with py breccia and trace cp.	Sp, py>G>cp, po>asp. Trace tt found in sp, and Ag in po, py and G.
83-4	Massive sp with coarsely crystalline pyrite breccia.	Sp, py>G>>cp, gn, asp. Ag found in py and G, and trace tt in sp.
83-5	Banded fine-grained sp and py with coarse gn in the sp.	Py, sp>>G>gn>>po, cas>asp. Large areas of hi-Ag tt>my?>>dy? in gn.
83-7	Coarse-grained gn and py with minor sp.	Py>sp>G>>gn>>cp>cas, asp. Trace tt in gn and py.
83-9	Granular pyrite in "chert".	Py, G>>sp>>cp, gn, po.
83-10	Fine-grained pyrite with disseminated sp.	Py>>sp>>G, gn, cp>po, asp.
83-11	Fine-grained pyrite breccia masses with recrystallized borders of cubic crystals and minor gn in cherty rhyolite with disseminated sp.	Py, G>>gn, po, asp.
83-13	Fine-grained pyrite breccia with interstitial sphalerite and trace cp and gn.	Py>sp, G, cp>gn, cas, po. Trace Ag in po, py and cp.
83-14	Coarse-grained py breccia with minor interstitial sp.	Py>>sp>>G, gn, cp.
83-15	Massive intermediate-grained pyrite with thin quartz veins.	Py>>sp>G>gn>cas.
83-18	Fine-grained pyrite breccia invaded around grain boundaries by cp and minor sp.	Cp>py>>po, G>sp.
83-19	Alternately banded (5mm) fine-grained py and cp with minor sp in py bands.	Cp>py>G>>sp>po, cas. Trace Ag in po.
83-22	Partly tarnished cp with trace bn and sp cut by fine-grained py bands.	Cp>>py>G, sp, cas. Trace Ag found in py and cp.
83-24	Gn vein in coarsely-banded fine-grained sp and py.	Py>sp>>gn, G, po, cas>asp. Trace Ag-rich tt>dy found in gn.
83-25	Massive gn.	Gn>>py>sp>po>G, cp>asp. Ag-rich tt>dy found in gn.
"A" ore (stringers)		
83-6	Fine-grained sp with py "rosettes" to 1 cm.	Py>>G>cp, gn>asp. Trace Ag in py.
83-8	Coarse-grained shiny "cleavable" py with trace sp.	Py>G>>sp>cp>cas, asp, po.
83-12	Coarse-grained py breccia with trace intergranular gn.	Py>>G>>gn, sp>po, cp.
83-16	Coarse-grained py "rosettes" to 1 cm with cp veinlets in fine-grained black matrix (28310 stope, near bornite zone).	Py>>G>cp>po>asp.
83-17	Coarsely-disseminated granular py with cp stringers in chloritic rhyolite.	Py>>G, cp, sp.
83-21	Fine-grained banded cp in dark rhyolite.	Cp>>G>po, py, cas. Trace stn finely disseminated in the cp.
83-23	Massive coarse-grained cp with euhedral albite crystals to 8 mm (1622 L stope).	Cp>>>py, G>cbt, cas, monazite?

TABLE I Continued

Bornite zone halo		
83-20	Coarse-grained cp-in-rhyolite stringer ore with trace disseminated sp. 1631 M stope, near bn zone.	Cp>>G>>stn, asp, sp. Trace tt in G.
83-26	Massive cp marginal to bn zone; DDH 2295 @ 100.5'.	Cp>>G>>sp>mk?, py.
83-27	Massive cp immediately adjacent to bn zone; DDH 2295 @ 107'.	Cp>>G>>stn/kes, sp>>py.
83-30	Stringer cp in rhyolite near bn zone; DDH 2299 @ 66.5'.	G>>cp>>py.
Bornite zone		
83-28	Stringer cp in bn zone; DDH 2295 @ 113'.	Cp>>G>>bn>maw, stnd, py>crl, and trace nm.
83-29	Massive cp in bn zone with trace bn; DDH 2299 @ 54'.	Cp>>bn, G>di>col>tn. Trace en, crl, boh, cv, eu, clu.

Abbreviations used: ac acanthite, Ag native silver, asp arsenopyrite, bn bornite, boh bohdanowiczite, cas cassiterite, cbt cobaltite, clu clausenthalite, cp chalcopyrite, col colusite, crl carrollite, cv covellite, di digenite, dy dyscrasite, en enargite, eu eucairite, G gangue, gn galena, kes kesterite, maw mawsonite, mk mackinawite, my miargyrite, nm naumannite, po pyrrhotite, py pyrite, sp sphalerite, stn stannite, stnd stannoidite, tn tennantite, tt tetrahedrite

mine in the Manitowadge mining camp, Thunder Bay mining district of northwestern Ontario (Friesen *et al.* 1982) was prepared for analysis of chalcopyrite, sphalerite, pyrrhotite and pyrite; no silver minerals were observed.

Nanisivik

Sphalerite grains from a hand sample of ore from the Nanisivik zinc-lead deposit, near the northern tip of Baffin Island, N.W.T. (Clayton & Thorpe 1982, Olson 1984), were analyzed because sphalerite is known to be a silver carrier in that deposit (McIntyre *et al.* 1984).

ANALYTICAL TECHNIQUES

Ore microscopy

Polished sections (3 cm in diameter) were prepared for all the samples and carefully examined microscopically. Grains of chalcopyrite, galena, pyrite, pyrrhotite and sphalerite, free of inclusions, were selected and sawed from the sections as 2-4 mm cubes. These essentially monomineralic cubes were reset in araldite, together with appropriate synthetic standards (Table 2), to make new 2.5-cm-diameter polished sections so that all suitable grains of a selected sulfide were located in one section. The new sections were, once again, carefully re-examined with

TABLE 2a. X-RAY LINES AND STANDARDS USED FOR ELECTRON-MICROPROBE ANALYSES

MINERAL	AgLa	SbLa	SeKa	X-ray line				
				ZnKa	FeKa	CdLa	InLa	SnLa
Galena	(Pb,Ag)S	metal	Fe(S,Se)	-	-	-	-	-
Sphalerite	(Zn,Ag,In)S	-	-	(Zn,Fe)S	(Zn,Fe)S	CdS	(Zn,Ag,In)S	-
Pyrite	"	-	-	Cu ₄ (Fe,Zn) ₅ S ₈	-	-	-	metal
Chalcopyrite	"	-	Cu ₄ Fe ₅ (S,Se) ₈ or Fe(S,Se)	"	-	-	(Zn,Ag,In)S	"
Bornite	-	-	"	-	-	-	-	-

Weighed-in trace-element contents and calculated "homogeneity" values (in parentheses) for these synthetic standards are as follows: (Pb,Ag)S: 0.40 wt% Ag(0.78); Fe(S,Se): 0.17 wt% Se(0.66); (Zn,Ag,In)S: 0.114 wt% Ag(0.46) and 0.119 wt% In(0.39); Cu₄(Fe,Zn)₅S₈: 0.15 wt% Zn(0.40); Cu₄Fe₅(S,Se)₈: 0.15 wt% Se(0.55). (Zn,Fe)S had 6.4 wt% Fe. The following standards were used for background corrections: PbS, ZnS and (Zn,Fe)S, pyrite (Elba), Cu₄Fe₅S₈ and Cu₅FeS₄.

TABLE 2b. X-RAY LINES AND STANDARDS USED FOR MICRO-PIXE ANALYSES

Mineral	AgK α	X-ray lines SeK α	InK α
Galena	(Pb,Ag)S	Fe(S,Se)	-
Sphalerite	(Zn,Fe,Ag,In)S series*	"	(Zn,Fe,Ag,In)S series
Pyrite	see disc.*	"	-
Chalcopyrite and bornite	(Zn,Fe,Ag,In)S series	Fe(S,Se) or Cu ₄ Fe ₅ (S,Se) ₈	(Zn,Fe,Ag,In)S series

*See discussion. Trace-element contents for these synthetic standards are given below Table 2a, as well as the list of standards used for background corrections.

the ore microscope and an SEM in order to locate inclusion-free areas for the proton-microprobe analyses.

Electron-microprobe analyses

A Materials Analysis Company (MAC) model 400 electron microprobe was used to obtain the iron content of the sphalerite and the antimony content of the galena as well as to verify the proton-microprobe results, where applicable. For quantities above the detection levels by electron microprobe, we were able to either confirm the proton-microprobe results or to reject them owing to contamination from adventitious inclusions below the surface of the polished section.

All the analyses were performed at 25 kV, with exception of the galena analyses, which were carried out at 20 kV, according to analytical procedures described by Cabri & Laflamme (1976). The X-ray lines and standards used are listed in Table 2a. Raw data were reduced with a locally modified version of EMPADR VII (Rucklidge & Gasparrini 1969). The standards were tested for homogeneity according to the homogeneity test of Buseck & Goldstein

(1969), in which a standard is considered homogeneous if $H \leq 1$ ($H = S/2\sigma_c$, where S is the measured standard-deviation and σ_c is the minimum standard-deviation, $\sqrt{N_x}$, or the square root of the mean counts).

Proton-microprobe analyses

The Heidelberg proton microprobe (Bosch *et al.* 1978, Cabri *et al.* 1984a, b, Harris *et al.* 1984) was used. All analyses were done at 4 MeV with different thicknesses of Al absorbers placed in front of the Si(Li) detector: 350 μ m for chalcopyrite, bornite, pyrrhotite and pyrite, 750 μ m for sphalerite, and 1050 μ m for galena. In spite of deep penetration of the protons at 4 MeV, the resultant higher count-rate was deemed to have justified the choice. Table 3 lists penetration depths for 90% X-ray production for

TABLE 3. CALCULATED DEPTHS OF X-RAY PRODUCTION

Trace element	Matrix	Al absorber thickness (μ m)	Penetration depth* (μ m)
Se	PbS	1050	43
Se	ZnS	750	33
Se	(Zn,Fe)S	750	33
Se	FeS	350	35
Se	FeS ₂	350	33
Ag	PbS	1050	49
Ag	ZnS	750	49
Ag	(Zn,Fe)S	750	48
Ag	FeS ₂	350	39
Ag	FeS	350	44
Ag	CuFeS ₂	350	47
In	PbS	1050	49
In	ZnS	750	50
In	(Zn,Fe)S	750	49
In	FeS ₂	350	39
In	FeS	350	44

*Calculated for 90% X-ray production at 4 MeV

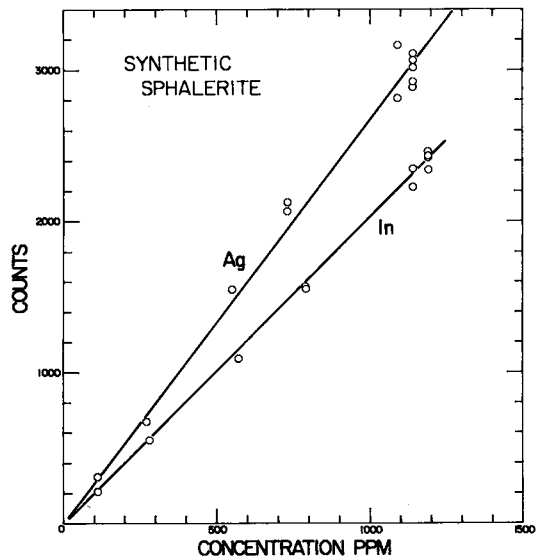


FIG. 2. Least-squares fits of proton microprobe data for Ag- and In-bearing ZnS standards.

some elements of interest in different matrices, calculated with a program of Dr. K. Traxel (University of Heidelberg). The majority of analyses took about 25 minutes each with a beam current of about 150 pA.

The analyses were planned and conducted using similar procedures to those described by Cabri *et al.* (1984a). Thus, synthetic standards were used whenever possible to provide trace-element-free background counts as well as experimental data for known trace-element concentrations. In the case of sphalerite, synthetic (Zn,Fe,In,Ag)S standards were used (Fig. 2). Details on the synthesis procedure for these standards are given by McIntyre *et al.* (1984). The procedure eventually selected for calculating trace-element concentrations is discussed below (under *Determination of H*).

The accuracy of the proton-microprobe results was verified, wherever possible, by analysis of precisely the same area with the electron microprobe. The precision of the proton-microprobe results was obtained by repeated analyses at different points within the same grains. Analyses of different grains of the same sample give an indication of trace-element homogeneity with an implied precision.

PIXE DATA COLLECTION AND DATA PROCESSING

The data were collected on-line in Heidelberg onto a hard disk and then transferred onto floppy disks for reading at Guelph. The continuum background was suppressed from both the model spectra and the data by the top-hat digital-filter technique (Schamber 1977), enabling us to avoid any assumptions about the functional shape of the background. Integrated areas (intensities) of characteristic X-ray peaks in the PIXE spectra were obtained using a nonlinear least-squares fitting program implemented on a MINC 11/23 computer. Each peak was represented by a Gaussian whose height was a variable of the fit; the centroid and width of the k^{th} Gaussian corresponding to energy E_k (keV) were determined by the relationships

$$(X_o)_k = P_1 + P_2 E_k \quad (1)$$

$$\sigma_k^2 = P_3 + P_4 E_k \quad (2)$$

TABLE 4. H VALUES FROM STANDARDS

Trace Element	(Cu ₄ Fe ₅ (S,Se) ₈) (Cu,In,Ag) ₄ Fe ₅ S ₈	(Zn,Fe,In,Ag)S	(Pb,Ag)S	Fe(S,Se)
Se	0.0343			0.0341
Ag	0.0313	0.0354*	0.0397	
In	0.0396	0.0390*		

*Derived from least squares fit (Fig. 2).

which are inherent in the physics of the spectrometer. The parameters P_1 to P_4 were variables of the fit. In each case, separate fits were done for the energy region containing the strong lines of FeK α , β , CuK α , β or ZnK α , β and the two regions containing, respectively, SeK α , β , AsK α , β and AgK α , β' , β'_2 , InK α , CdK α , SnK α .

The resulting intensities were converted to concentrations using the expression

$$Y(Z,M) = HC_z I(Z,M) \epsilon_z \exp(-\mu x)_{Al} \quad (3)$$

derived from a recent study of data-analysis techniques in thick-target PIXE (Campbell *et al.* 1983). In equation (3), $Y(Z,M)$ is the intensity of a particular characteristic X-ray (*e.g.*, K α) from a trace element Z of concentration C_z in a known matrix M; it is quoted for a standard proton-charge incident on the specimen. The quantity I is the integral of X-ray production along the proton path and thus involves the ionization cross-section, the stopping power of the matrix for protons, the matrix attenuation of the emergent photons, fluorescence yields and X-ray branching ratios. It was computed using the data-base recommended by Campbell *et al.* (1983), with the exception that the more accurate 'ECPSSR' cross-sections of Brandt & Lapicki (1981) were used. The exponential in (3), the attenuation factor of the aluminum foil, was calculated using the known thickness and the attenuation coefficients recommended in (3); ϵ_z , the relative efficiency of the detector, was calculated from the nominal 3.0-mm-thick silicon crystal. The quantity H incorporates those factors that are common to all X-ray energies and all matrices, *i.e.*, the solid angle of the detector, fundamental constants and the fixed correlation between number of protons incident on the target and the number of counts actually recorded by a rotating vane Rutherford backscattered-beam monitor. The approach taken here was to determine H from results obtained with a variety of synthetic standards.

ANALYTICAL RESULTS

Determination of H

Table 4 shows the values of H observed by substituting the standard data, *i.e.*, known concentrations, measured X-ray intensities per unit proton charge and computed $I(Z,M)$ values in equation (3). There is considerable variation, $2\sigma \pm 12\%$, and it is greater than expected from counting statistics and errors in $I(Z,M)$ (see later). However, electron-microprobe studies indicate that the distribution of Ag and In in the Cu-Fe-Se standards is not homogeneous, allowing us to eliminate two of the three extreme points. It was decided to adopt the

result on In in sphalerite since this element clearly is homogeneous (slightly more than the Ag) and since the ratio of X-ray intensity to concentration was derived from an extensive suite of synthetic standards, six in all, with In concentration ranging from 0.011 to 0.119 wt.%; these results are shown in Figure 2. The resulting value of H is 0.0390, as obtained from a least-squares fit of the In data.

Determination of concentrations

Substitution of the known H, the relevant $I(Z,M)$, and the X-ray intensities derived from the least-squares procedure, gave the concentrations listed in tabular form. Computer tests were done to ensure that, over the observed ranges of trace-element concentration, the relation of X-ray intensity to concentration is linear, or, in other words, that the matrix behaves consistently for small variations in trace-element concentrations; no departures from a linear response were predicted or found.

In those cases where there was no visible evidence for an element in a particular spectrum, the tables state that its concentration is below the minimum detection-limit (MDL). Synthetic blanks were used in ascertaining the values of the MDL for some of the specimens. Where the relevant peak is not perturbed by overlap with others, the MDL was estimated simply as three standard deviations of the continuum count in the region normally occupied by the peak. However, matters are less straightforward where peak overlaps occur; an example is the limit for $\text{Sn}K\alpha$ where Ag is present, since the $\text{Ag}K\beta'_1$ and $K\beta'_2$ lines straddle the $\text{Sn}K\alpha$ energy. In this case, standards of silver-bearing sphalerite were used to measure the $\text{Ag}K\beta/K\alpha$ intensity ratio; then the $\text{Ag}K\beta$ intensity for a given specimen was deduced by multiplying the observed $K\alpha$ intensity by this ratio; finally this deduced $\text{Ag}K\beta$ intensity was subtracted from the measured intensity in the $\text{Ag}K\beta + \text{Sn}K\alpha$ region and the remainder, if any, assigned to $\text{Sn}K\alpha$; by carrying statistical errors through this procedure, an estimate of either the uncertainty, or the MDL, for Sn could be made.

Estimation of errors

The high degree of linearity of the indium and silver X-ray intensity *versus* concentration for the sphalerite standards (Fig. 2) suggests that systematic errors in the measuring equipment are small.

The uncertainties shown in the tables are the statistical errors in peak areas given by the spectrum-fitting procedure. The computer program calculates an error matrix whose diagonal entries are related to the parameter errors $\sigma(P_k)$, where $\sigma^2(P_k)$ is equal to ϵ_{kk} , provided that the fit is good. Since the

reduced chi-squared values were found to be generally close to 1.0, this approach is valid. The error in peak area is calculated directly from these parameter errors by the program.

Errors arise in the derivation of the expressions $I(Z,M)$ for a thick-target matrix because the data-base used, although good, is not perfect. However, these errors will be minimized since all values of $I(Z,M)$ are, in effect, used relative to the corresponding value for $\text{In}K\alpha$ X rays in sphalerite. For example, the data-base cross-section for In in the range of 3 to 4 MeV may be a few percent high (Campbell *et al.* 1983) compared to reality, but those of the neighboring elements Ag, Cd and Sn would be similarly high, so that the errors would, to some extent, cancel. The same is true of errors in attenuation coefficients; however, since typically μ/ρ equals $10\text{--}20\text{ cm}^2\text{g}^{-1}$, these would be small given the low values. For relatively lighter trace-elements, *e.g.*, Zn, Se and As, the cancellation is likely to be less effective, and the attenuation coefficients are a factor of ten greater; it is difficult to estimate the associated errors, but they are unlikely to exceed 10%.

Comparison of the proton-microprobe results with those from the electron microprobe (in cases where the latter exist) gives some indication of the real uncertainties. For example, in 20 out of 21 grains of sphalerite, Cd is lower in the case of the proton microprobe, the relative difference being 9.4%. The concentrations are high (~ 3000 ppm), so that statistical and fitting errors are at the 1–2% level; hence there is real evidence of a 10% discrepancy between the two techniques, but no reason to attribute this to either one in particular. In contrast to this example, that of Ag in galena shows much larger discrepancies occurring with both signs; their mean magnitude is 29%, but their overall mean is almost zero. This would either indicate poor statistics in the electron-microprobe data or specimen inhomogeneity.

MINERALOGICAL RESULTS

Galena

(i) Kidd Creek

The only trace elements detected are Ag, Se and Sb (the Sb data determined with the electron microprobe only). Eight samples of "C" ore galena have a mean of 638 ppm Ag with a range from 87 to 1167 ppm. One sample of "A" ore galena has 446 ppm Ag. Precision for two grains was found to be better than $\pm 3\%$ but increased to $\pm 33\%$ for a third grain. Correspondence between proton- and electron-microprobe results for Ag is good, except for the grains in the sample with poorest precision (83–11,

TABLE 5. SUMMARY OF DATA FOR KIDD CREEK SPHALERITE, CHALCOPYRITE & PYRITE

	"C" ORE	"A" ORE	BORNITE ZONE HALO
	sphalerite [15 samples]	sphalerite [2 samples]	sphalerite [1 sample]
Fe wt. %	6.1(5.0-6.7) [15]	3.4, 4.8 [2]	2.4 [1]
Se ppm	181(110-292) [4]; n.d. [11]	144 [1]; n.d. [1]	108 [1]
Ag ppm	90(25-308) [7]; n.d. [8]	n.d. [2]	36 [1]
Cd wt. %	0.33(0.14-0.63) [15]	0.22, 0.35 [2]	0.18 [1]
In ppm	629(61-2059) [9]; n.d. [6]	29, 135 [2]	362 [1]
	chalcopyrite [6 samples]	chalcopyrite [4 samples]	chalcopyrite [4 samples]
Zn ppm	233(190-512) [5]; n.d. [1]	203 [1]; n.d. [3]	n.d. [4]
As ppm	n.d. [6]	n.d. [4]	n.d. [4]
Se ppm	138(101-192) [3]; n.d. [3]	253(76-542) [4]	606(83-1308) [4]
Ag ppm	1047(224-1579) [6]	112(30-197) [4]	36(25-57) [3]; n.d. [1]
In ppm	248(12-414) [5]; n.d. [1]	442(270-747) [4]	463(5-1085) [4]
Sn ppm	variable (see text)	variable (see text)	663(210-1345) [4]
	pyrite [14 samples]	pyrite [6 samples]	pyrite [1 sample]
Zn ppm	1286(216-3334) [3]; n.d. [9]	n.d. [6]	n.d. [1]
As ppm	237(54-415) [12]; n.d. [2]	216(36-710) [6]	536 [1]
Se ppm	20(14-27) [4]; n.d. [10]	66(18-149) [4]; n.d. [2]	282 [1]
Ag ppm	see text [4]; n.d. [10]	n.d. [6]	n.d. [1]
In ppm	n.d. [14]	n.d. [6]	n.d. [1]
Sn ppm	see text [2]; n.d. [12]	n.d. [6]	n.d. [1]

Fe analyses are by electron microprobe, Cd analyses by electron- and proton-microprobe and the rest by proton microprobe.
n.d. = not detected at the calculated MDL. MDL (ppm) @ 3 σ for proton microprobe are: sphalerite Se(43), Ag(12), In(16); chalcopyrite Zn(128), As(17), Se(13), Ag(10), In(13), Sn(17 with no Ag present, otherwise variable); pyrite Zn(91), As(9), Se(7), Ag(7), In(10), Sn(11).

Appendix, Table I). Concentration of antimony, as expected, correlates well with that of Ag.

Selenium cannot be detected at low levels in galena, because of overlap from the $PbL\epsilon$ X-ray line; the MDL is calculated to be about 500 and 700 ppm for proton and electron microprobes, respectively. Only one sample of galena from the "C" ore has high Se values (83-11, with an average 1367 ppm). The other samples, however, gave values just above or at the MDL; this indicates that the true level of Se in Kidd Creek samples is probably at least a few hundred ppm.

(ii) Nanisivik

Three galena grains were analyzed. One has a measurable Ag content (118 ppm). The Ag MDL was calculated to be 29 ppm at 3σ .

Sphalerite

(i) Kidd Creek

Besides the ubiquitous presence of Fe and Cd, variable quantities of Se, Ag and In were detected in 22 sphalerite grains from eighteen samples (15 of "C" ore, 2 of "A" ore, and one bornite-zone halo). Though there is overlap, sphalerite from "C" ore samples typically contains more Fe, Se, Ag, Cd and In (Table 5) than sphalerite from "A" ore or from the bornite-zone halo. Careful note should be made that a significant number of samples have statisti-

cally no detectable Se, Ag or In; these are not included in the calculation of the "average" values (Table 5).

Reproducibility of the proton-microprobe results was tested by analysis of two areas for five grains and three areas for two grains. Cadmium and indium gave very reproducible results, suggesting a homogeneous distribution of these elements. For Cd, the maximum spread is ~3%; for In it is $\pm 6\%$ for low values (33 ppm) and drops to $\pm 1\%$ for higher values (2000 ppm). Selenium reproducibility is $\pm 20\%$ for about 110 ppm and for Ag, the reproducibility is $\pm 6.8\%$ for about 300 ppm. One sphalerite grain, however, has a heterogeneous distribution of Ag, with three analyses giving 72 ppm, not detected and 125 ppm.

(ii) Mattagami-Norita

Five sphalerite grains were found to contain variable quantities of Cd and In (Appendix, Table II). Selenium (387 ppm) was only found in one grain, whereas a different grain contains 19 ppm Ag. Selenium and Ag were not detected in the other grains. The proton- and electron-microprobe results for Cd are within 10% of each other in the worst case.

(iii) Geco

Seven sphalerite grains from three different samples also contain variable quantities of Cd and In (Appendix, Table II). Silver and Se were not detected

in any grain. As for the Mattagami-Norita sphalerite, the correspondence between proton- and electron-microprobe values is very good.

(iv) *Nanisivik*

One of three grains analyzed contains Ge (86 ppm) and Se (149 ppm), besides the Ag and Cd found in the other two grains (Appendix, Table II). Indium was not detected in any grain.

Chalcopyrite

(i) *Kidd Creek*

Variable quantities of Zn, Se, Ag, In and Sn were measured in sixteen samples (6 of "C" ore, 4 of "A" ore, 4 of bornite-zone halo and 2 from the bornite zone). The results for samples from the first three types of ore are summarized in Table 5 and were obtained by first averaging the results of the number of grains analyzed for each sample. Table 6 lists the samples analyzed more than once; either more than one grain or more than one analysis per grain. Data for the two samples of chalcopyrite from the bornite zone are also given in Table 6.

Zinc in chalcopyrite is difficult to determine because of a relatively high detection-limit (128 ppm) coupled with the possibility of adventitious inclusions of sphalerite. Some Zn values were easily attributed to sphalerite inclusions if Cd was also detected, whereas others were also ascribed to sphalerite inclusions where results could not be confirmed with the electron microprobe, even though the concentrations by proton microprobe were above the MDL for the electron microprobe. The reliability of Zn concentrations in the range between 128 and ~200 ppm is uncertain; nevertheless, a majority of the samples have no detectable Zn.

The Sn content of the chalcopyrite is also difficult to determine because the SnK α peak coincides with the AgK β peak and because the Ag content in these samples is highly variable. However, Sn may well be present in all the chalcopyrite grains because concentrations as low as 15 ppm have been measured for Ag-poor grains. High contents of Sn (up to 1345 ppm) have also been found in samples of the bornite-zone halo, and confirmed with the electron microprobe.

The results for Se, Ag and In, reported in Table

TABLE 6. CONTENT OF SELENIUM, SILVER AND INDIUM IN CHALCOPYRITE FROM KIDD CREEK

Sample Grain	Se		Ag		In		
	No.	P(ppm)	E(wt.%)	P(ppm)	E(wt.%)	P(ppm)	E(wt.%)
"C" ore							
83-3	1	n.d.	n.d.	1569 \pm 42	0.17 \pm 0.03	n.d.	-
83-3	2	n.d.	n.d.	1589 \pm 42	0.19 \pm 0.03	24 \pm 16	-
83-18(D)	2	127 \pm 14	n.d.	217 \pm 19	0.04 \pm 0.02	336 \pm 29	0.04 \pm 0.01
83-18(F)	1	125 \pm 14	n.d.	191 \pm 18	0.03 \pm 0.02	325 \pm 28	0.03 \pm 0.01
83-18(F)	2	114 \pm 14	n.d.	264 \pm 23	0.03 \pm 0.02	416 \pm 35	0.05 \pm 0.01
83-19(D)	1	112 \pm 14	n.d.	1536 \pm 57	0.19 \pm 0.03	384 \pm 28	0.04 \pm 0.01
83-19B	1	105 \pm 13	n.d.	1336 \pm 52	0.17 \pm 0.03	404 \pm 28	0.04 \pm 0.01
83-19(F)	1	92 \pm 14	n.d.	1465 \pm 54	0.17 \pm 0.03	405 \pm 28	0.06 \pm 0.01
83-19(F)	1	98 \pm 14	n.d.	1472 \pm 31	0.17 \pm 0.03	415 \pm 18	-
83-19(F)	2	99 \pm 14	n.d.	1411 \pm 53	0.16 \pm 0.03	463 \pm 30	0.05 \pm 0.01
83-22(D)	1	195 \pm 14	n.d.	1260 \pm 52	0.13 \pm 0.03	278 \pm 25	0.02 \pm 0.01
83-22(F)	1	186 \pm 17	n.d.	1049 \pm 47	0.12 \pm 0.03	312 \pm 25	0.04 \pm 0.01
83-22(F)	2	196 \pm 15	n.d.	1161 \pm 50	0.14 \pm 0.03	312 \pm 25	n.d.
"A" ore							
83-21	1	210 \pm 15	n.d.	33 \pm 2	n.d.	258 \pm 27	n.d.
83-21	1	210 \pm 14	n.d.	23 \pm 11	n.d.	255 \pm 27	n.d.
83-21A	2	156 \pm 15	n.d.	35 \pm 10	n.d.	276 \pm 34	n.d.
83-23	1	202 \pm 15	n.d.	162 \pm 18	0.03 \pm 0.02	513 \pm 24	0.04 \pm 0.01
83-23A	1	208 \pm 15	n.d.	169 \pm 11	n.d.	473 \pm 39	0.04 \pm 0.01
83-23(F)	1	204 \pm 15	n.d.	187 \pm 25	0.03 \pm 0.02	501 \pm 32	0.04 \pm 0.01
83-23(F)	2	200 \pm 17	n.d.	151 \pm 15	n.d.	467 \pm 31	0.05 \pm 0.01
bornite zone halo							
83-26	1	899 \pm 25	0.08 \pm 0.02	23 \pm 12	n.d.	624 \pm 34	0.05 \pm 0.01
83-26	2	875 \pm 25	0.06 \pm 0.02	26 \pm 11	n.d.	561 \pm 33	0.05 \pm 0.01
83-27	1	1323 \pm 28	0.12 \pm 0.03	n.d.	n.d.	1074 \pm 43	0.11 \pm 0.01
83-27	1	1296 \pm 28	0.12 \pm 0.03	n.d.	n.d.	1119 \pm 42	0.10 \pm 0.01
83-27	2	1305 \pm 28	0.14 \pm 0.03	n.d.	n.d.	1062 \pm 42	0.11 \pm 0.01
83-30	1	83 \pm 14	n.d.	34 \pm 13	n.d.	n.d.	n.d.
83-30	1	76 \pm 14	n.d.	25 \pm 11	n.d.	n.d.	n.d.
83-30	1	85 \pm 14	n.d.	18 \pm 11	n.d.	19 \pm 15	n.d.
83-30	1	89 \pm 14	n.d.	28 \pm 11	n.d.	n.d.	n.d.
bornite zone							
83-28	1	3871 \pm 47	0.40 \pm 0.03	553 \pm 34	0.03 \pm 0.02	327 \pm 27	0.04 \pm 0.01
83-28	2	4383 \pm 50	0.46 \pm 0.03	496 \pm 33	n.d.	298 \pm 26	0.02 \pm 0.01
83-29	1	2780 \pm 141	0.33 \pm 0.03	n.d.	n.d.	221 \pm 23	0.03 \pm 0.01
83-29	2	3124 \pm 144	0.36 \pm 0.03	48 \pm 12	n.d.	194 \pm 21	0.02 \pm 0.01

n.d.=not detected at the calculated MDL.

P=proton microprobe; MDL(ppm) @ 3 σ are Se(13), Ag(10), In(13).

E=electron microprobe; MDL(wt%) @ 3 σ are Se(0.05-0.04), Ag(0.03), In(0.02).

Parentheses highlight multiple analyses on the same grain.

TABLE 7. TRACE-ELEMENT CONCENTRATIONS OF PYRITE FROM KIDD CREEK

Sample Grain No.	Zn		As	Se	Ag		Sn		
	P (ppm)	E (wt.%)	P (ppm)	P (ppm)	P (ppm)	E (wt.%)	P (ppm)	E (wt.%)	
"C" ore									
83-1	1	308±82	0.05±0.01	114±12	n.d.	20±8	-	22±10	-
83-2	1	216±70	0.04±0.01	54±12	n.d.	*10±8	-	n.d.	-
83-3	1	n.d.	-	n.d.	14±9	n.d.	-	n.d.	-
83-4	1	n.d.	-	n.d.	24±10	n.d.	-	n.d.	-
83-5	1	3334±82	0.08±0.01	351±10	n.d.	n.d.	-	n.d.	-
83-7	1	***	-	253±15	n.d.	n.d.	-	n.d.	-
83-9	2	n.d.	-	156±12	n.d.	n.d.	-	n.d.	-
83-11	1	n.d.	-	405±54	n.d.	n.d.	-	n.d.	-
83-13	1	n.d.	-	103±40	27±21	*15±8	-	n.d.	-
83-14	1	***	-	168±12	n.d.	n.d.	-	n.d.	-
83-15	1	n.d.	-	284±49	n.d.	n.d.	-	n.d.	-
83-22	1	n.d.	-	114±34	61±22	**341±20	n.d.	2866±80	0.31±0.02
83-22	1	n.d.	-	641±21	n.d.	41±10	n.d.	1505±57	0.07±0.01
83-22	2	n.d.	-	55±31	n.d.	68±11	n.d.	623±39	0.04±0.01
83-22	3	n.d.	-	69±35	n.d.	8±8	n.d.	245±25	0.04±0.01
83-24	1	n.d.	-	325±10	n.d.	n.d.	-	n.d.	-
83-25	4	n.d.	-	415±38	n.d.	n.d.	-	n.d.	-
"A" ore									
83-6	1	n.d.	-	710±67	60±24	n.d.	-	n.d.	-
83-8	1	n.d.	-	51±11	18±10	n.d.	-	-	n.d.
83-12	1	n.d.	-	140±13	n.d.	n.d.	-	n.d.	-
83-16	1	n.d.	-	152±45	36±8	n.d.	-	n.d.	-
83-17	1	n.d.	-	204±39	149±30	n.d.	-	n.d.	-
83-23	1	n.d.	-	36±10	n.d.	n.d.	-	n.d.	-
bornite zone halo									
83-30	1	n.d.	-	571±57	283±36	n.d.	-	n.d.	-
83-30	2	n.d.	-	500±54	282±37	n.d.	-	n.d.	-

*Other pyrite grains in sample contain native Ag inclusions; **see text for details; ***Zn concentration attributed to subsurface sphalerite inclusions.
n.d.=not detected at calculated MDL.
P=proton microprobe; MDL (ppm) @ 3σ are Zn(91), As(9), Se(7), Ag(7) and Sn(11).
E=electron microprobe; MDL (wt.%) @ 3σ are Zn(0.02), Ag(0.03) and Sn(0.02).

6, give an indication of the reproducibility (precision) and of the homogeneity of the trace elements in the chalcopyrite matrix by multiple analyses for four different grains. Indium (± 0.6 to ± 2.6)%, closely followed by Se (0 to ± 7)%, are more homogeneously distributed (more reproducible) than Ag, whose reproducibility ranges from $\pm 2\%$ (at 1468 ppm) to a high of $\pm 31\%$ (at 26 ppm).

Also of interest is the restricted range of values obtained for different grains of the same sample, in cases analyzed at a different time in a different polished section. The largest variation in Se concentrations between different grains of a sample is $\pm 15\%$ (83-21); for Ag it is less than the $\pm 31\%$ obtained for four grains in sample 83-30 and for In it does not exceed $\pm 30\%$ (83-22).

Finally, Table 6 also lists results of the electron-microprobe analyses of the same areas as were analyzed with the proton microprobe. Where the elemental concentrations are above the electron microprobe MDL, there is good correspondence between both sets of data for the majority of cases.

(ii) Mattagami-Norita

Two chalcopyrite grains were analyzed and found to contain variable quantities of Zn, Se, Ag, In and Sn (Appendix, Table III). The Zn concentrations are quite high, but most must be real since they are confirmed with the electron microprobe. Selenium concentrations show little variation, in the 400 to 500 ppm range, but there is a marked but consistent difference in the Ag and In content of the two grains. The Sn content is low.

(iii) Geco

Two chalcopyrite grains were analyzed and found to contain variable concentrations of Zn, Ag and In; Se and Sn were not detected (Appendix, Table III). The Zn found in sample 1, grains 1 and 2, however, is probably due to subsurface inclusions of sphalerite because it could not be confirmed with the electron microprobe. Silver appears to be homogeneously present at the 130-ppm level; the In concentration is in the 40 to 80 ppm range.

TABLE 8. ELECTRON MICROPROBE DATA OF SN- AND AG-BEARING PYRITE

Spot #	Ag (wt.%)	Sn (wt.%)	Spot #	Ag (wt.%)	Sn (wt.%)
1	0.05	0.25	10	n.d.	0.13
2	0.05	0.29	11	n.d.	0.03
3	0.12	0.36	12	n.d.	0.03
4	0.11	0.40	13	n.d.	0.03
5	0.05	0.32	14	n.d.	0.04
6	0.04	0.26	15	n.d.	0.33
7	n.d.*	0.13	16	n.d.	0.40
8	n.d.	0.22	17	n.d.	0.41
9	n.d.	0.38	18	n.d.	0.39

Analyses done on re-polished sample @ 25 kV, 0.050 μ amp for 100 sec using Elba pyrite for background, (Zn, Fe, Ag, In)S for Ag, Cu_2FeSn_4 for Sn.
*n.d. = not detected (MDL 0.03 for Ag and 0.02 for Sn).

Pyrite

(i) *Kidd Creek*

Trace elements, including one or more of Zn, As, Se, Ag and Sn, were found in the 21 samples examined (14 of "C" ore, 6 of "A" ore and 1 of bornite-zone halo, Table 7). Variable quantities of As, usually a few hundred ppm, were measured in

all but two samples of pyrite. Selenium is generally not present in quantities above the detection limit, where found; "C" ore pyrite averages less Se than "A" ore pyrite (Table 7).

Silver and Sn were rarely found (only in "C" ore) but it is not clear, at present, whether the Ag concentrations obtained are due to solid solution or adventitious inclusions. Very small quantities of Ag (10-20 ppm) were found in three samples, one of which also contains 22 ppm Sn (Table 7). Though the grains analyzed were very carefully checked to be free of inclusions, two of the three samples are known to contain other pyrite grains containing inclusions of native silver (Table 1). The third sample also contains such inclusions, but only in pyrrhotite. It is, therefore, not unreasonable to view these results with extreme caution. The interpretation of the Ag and Sn concentrations observed in the fourth sample (83-22) is, however, more complex (Tables 7, 8).

A detailed re-examination of the Ag- and Sn-bearing pyrite grain in sample 83-22 with a JEOL

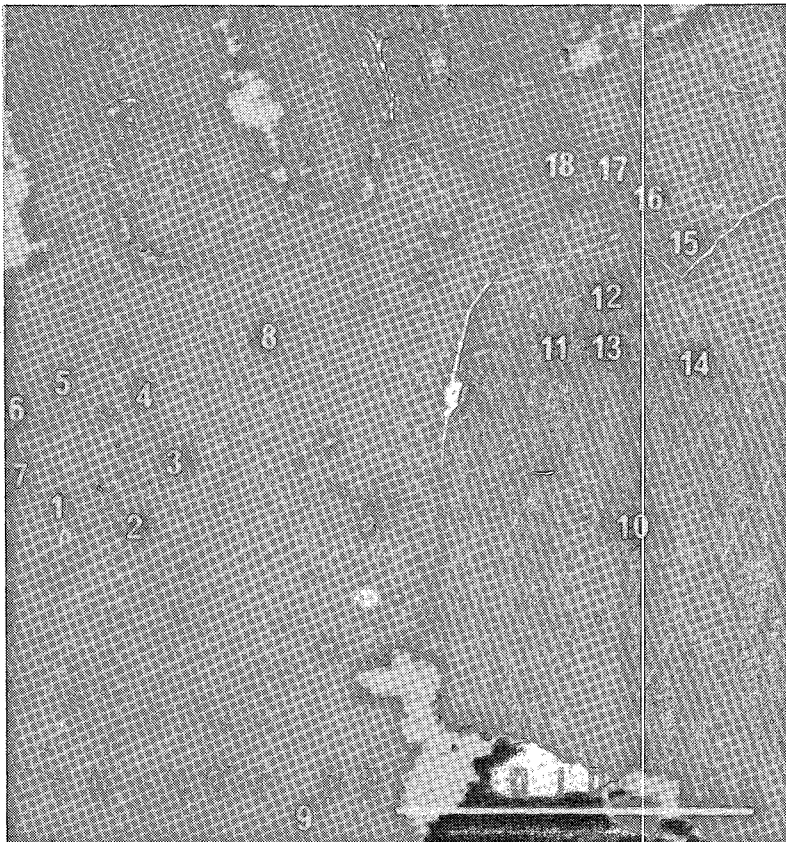


FIG. 3. SEM micrograph of pyrite sample 83-22, Kidd Creek. The light grey areas are Sn-rich and white areas are chalcopyrite inclusions. The numbers refer to electron microprobe spot-analyses (Table 8). Scale bar: 100 μ m.

733 superprobe-SEM and the electron microprobe revealed that Sn-rich areas (up to 0.40 wt.%) and fewer Ag-rich areas (up to 0.13 wt.%) occur in this pyrite as irregular patches (Fig. 3). This confirmation on the nature of the Sn and Ag distribution demonstrates that both the Sn and Ag occur as a solid solution and not as possible submicroscopic inclusions of minerals such as stannite, cassiterite or native silver. Also of interest, most of the Sn-rich zones were found to be Ag-free at the detection levels of the MAC electron microprobe (Table 8).

(ii) Geco

Six pyrite grains from 4 samples give variable amounts of As; both grains of one sample are Se-bearing, and one grain contains 217 ppm Cu, which could be due to a subsurface inclusion of chalcopyrite (Appendix, Table IV). The following elements were not detected (with MDL at 3σ in ppm): Ag(8), In(17) and Sn(18).

Bornite and pyrrhotite

(i) Kidd Creek

Only two grains of bornite were analyzed; both are from the same sample (83-29) and were found to contain high Se values: 7253 ppm or 0.84% and 6710 ppm or 0.71% by proton and electron microprobes, respectively. The MDL (ppm) for other trace elements in those grains are: Ag(11), In(16) and Sn(19); none of these was detected in either sample.

Only two pyrrhotite grains proved suitable for analysis; most of the pyrrhotite grains are too thin or contain inclusions of native silver. Of these two grains, one has a Se concentration of 462 ppm (sample 83-16), the other (83-25) has no Se detected with an MDL of 10 ppm. No other trace elements were detected.

(ii) Geco

Two pyrrhotite samples were analyzed; one of these contains some Ag. Three different spot-analyses on this pyrrhotite grain yielded 21 ppm, 70 ppm and "not detected". The other sample has no detectable Se (MDL 10 ppm), As(12), Ag(7), In(8) and Sn(9).

DISCUSSION

As pointed out by Fleischer (1955), it is very difficult to predict isomorphism in sulfides simply on the basis of ionic or covalent radii or using a similar approach, owing to the complicated nature of bonding in sulfides. Thus, modern crystal-chemical studies dealing with minor elements in sulfides apply appropriate aspects of crystal field, molecular orbital or band theory to knowledge of the crystal structure in attempts to explain their

presence (Vaughan & Craig 1978). Because most trace-element data for sulfides in the literature are based on bulk analyses of uncertain reliability, the present results will be discussed from an analytical rather than a theoretical point of view.

Silver

Silver concentrations were measured in galena, sphalerite, chalcopyrite, pyrite and pyrrhotite, but not in bornite. The presence of silver in galena from New Brunswick ores is already well documented by electron microprobe: for Caribou [0.102 (n.d. - 0.66) wt.%, MDL = 0.04%] by Jambor & Laflamme (1978), for Brunswick Mining & Smelting [0.084 (n.d. - 0.60) wt.%, MDL = 0.035%] by Owens (1980) and for Heath Steele [0.148 (n.d. - 0.9) wt.%, MDL = 0.05%] by Chen & Petruk (1980). It is, therefore, not surprising that Ag was measured in all Kidd Creek samples analyzed. Results suggest that Ag content, though variable from sample to sample in galena, is within analytical precision ($\sim \pm 33\%$).

Sphalerite, however, is not widely recognized as a Ag carrier (Cabri *et al.* 1984b); high Ag values had recently been reported for Nanisivik sphalerite (McIntyre *et al.* 1984) and these are now confirmed. About half the grains of Kidd Creek sphalerite analyzed contain Ag (25-308) ppm, with an MDL of 12 ppm. The average value is 42 ppm Ag (taking "not detected" to be 0) or 45 ppm Ag (taking "not detected" to be $\frac{1}{2}$ MDL, *i.e.*, 6 ppm). There was an insufficient number of multiple analyses to determine whether the Ag distribution within individual grains is homogeneous, but it is variable from sample to sample.

Whereas chalcopyrite was considered to be a Ag carrier for a long time (Fleischer 1955), it has only recently been proven to be so (Harris *et al.* 1984). A recent review (Amcoff 1984) suggests that whereas part of the Ag content of complex base-metal sulfide ores is "connected with chalcopyrite", "the correlation in Cu/Ag ratios is to a large degree masked by the higher silver contents associated with galena". Thus, the proton microprobe is the ideal tool to determine the Ag content of chalcopyrite.

There is still the problem of surface Ag_2S tarnish (Chen *et al.* 1980), which may account for reports in the literature of some high contents of Ag for so-called "green" chalcopyrite (Cabri & Harris 1984). The chalcopyrite grains analyzed in this study were carefully examined to avoid cases with such surface contamination by Ag. Whereas chalcopyrite apparently is a significant carrier of Ag in the Kidd Creek samples, confirming the suggestions of Thorpe *et al.* (1976), it also appears to be so in other massive sulfide deposits, as shown by the few determinations on Mattagami-Norita and Geco samples.

Except for bulk analyses (Fleischer 1955), Ag has

not yet been shown to occur in pyrite. As reported above, 10–20 ppm Ag was found in three pyrite samples from Kidd Creek, but further work is required to ascertain that the Ag content is not due to adventitious subsurface inclusions of, say, native silver. Kidd Creek sample 83–22, which also has a high Sn content, contains a lesser amount of Ag that does not correlate with the Sn, except insofar as all Ag-bearing areas also contain Sn. Further study of this sample of pyrite is also required.

Though few grains of pyrrhotite were analyzed, the low Ag contents measured in multiple analyses of one Geco pyrrhotite suggest that pyrrhotite may also be a Ag carrier in massive-sulfide deposits. It is interesting to note that the two bornite grains from Kidd Creek contain no Ag (MDL 11 ppm), in contrast to the electron-microprobe results of Thorpe *et al.* (1976) on other bornite grains from the bornite zone (1200 level), which showed 1.2 wt. % Ag.

Selenium

Selenium was found, in variable quantities, in all sulfides examined from Kidd Creek (galena, sphalerite, chalcopyrite, pyrite, pyrrhotite and bornite). Selenium also occurs in sphalerite and chalcopyrite from Mattagami–Norita, in sphalerite from Nanisivik, in sphalerite and pyrite from Geco, but not in chalcopyrite (MDL 15 ppm) and pyrrhotite (MDL 10 ppm).

The selenium distribution between Kidd Creek ore-types shows some interesting trends. Average Se values for chalcopyrite and pyrite (calculating grains with no detected Se as 0) increase from “C” ore (69 and 6 ppm) to “A” ore (253 and 44 ppm) to bornite-zone halo (606 and 282 ppm) to bornite zone (3540 ppm in cp only). This appears to be the opposite of the trend for the average Ag concentration in chalcopyrite, which decreases from “C” ore (1047 ppm) to “A” ore (123 ppm) to bornite-zone halo (27 ppm). Recalculating the average Se values for chalcopyrite and pyrite using grains with no detected Se as $\frac{1}{2}$ the MDL gives: “C” ore (72 and 10 ppm), “A” ore (253 and 45 ppm); for Ag values in chalcopyrite, recalculation gives 28 ppm Ag for the bornite-zone halo. Because the MDL is so close to 0, there is no significant difference in the methods of averaging.

Selenium partitioning between Kidd Creek sulfides is difficult to evaluate because few coexisting grains (*i.e.*, from the same sample) were analyzed. Galena could be the principal Se carrier for “C” ore, but the high detection-level impedes the quantification of this type of information. The next highest carrier of Se is sphalerite, followed closely by chalcopyrite. The least amount of Se occurs in pyrite.

Indium

Indium concentrations were measured in nearly all

samples of sphalerite and chalcopyrite from all deposits except from Nanisivik (MDL 16 ppm). The latter finding is understandable, since McIntyre *et al.* (1984) reported ~1 ppm In by SIMS analyses. Indium was not detected in galena (MDL 31 ppm), pyrite (MDL 10 ppm), pyrrhotite (MDL 8 ppm) and bornite (MDL 16 ppm). In those samples from Kidd Creek and Geco, in which sphalerite and chalcopyrite coexist, there appears to be partitioning. Indium is much higher in sphalerite than in chalcopyrite. However, overall, levels of In are higher in chalcopyrite than in sphalerite. Though there is overlap of ranges of values between the different types of sample, there is an apparent increase of In concentration in chalcopyrite from “C” ore to “A” ore to bornite-zone halo (Table 5).

It is also worth noting that no correlation exists between In and Ag in sphalerite. This was unexpected, as McIntyre *et al.* (1984) were able to synthesize homogeneous (Zn,Fe,In,Ag)S *only* by using the coupled substitution $\text{Ag}^+ + \text{In}^{3+} = 2\text{Zn}^{2+}$ in a dry system. This lack of correlation may imply that Ag or In solid solution in sphalerite is partly or wholly interstitial, rather than substitutional as it is in the synthetic equivalent.

Tin

Tin concentrations were only found in chalcopyrite from Kidd Creek and Mattagami–Norita and in only one Sn-rich pyrite sample from Kidd Creek. As discussed above, Sn may well be present in all Kidd Creek chalcopyrite, but is difficult to quantify in the presence of high Ag values. Tin was not detected in galena (MDL 33 ppm), sphalerite (MDL 18 ppm), pyrrhotite (MDL 9 ppm) and bornite (MDL 19 ppm), nor was it detected in any of the 6 Geco chalcopyrite grains analyzed (MDL 17 ppm).

The lack of Sn in the Geco chalcopyrite is in contrast with the findings of Banerjee (1972) who, on the basis of electron-microprobe data on 5 chalcopyrite grains, concluded that chalcopyrite from Geco contains a mean value of 0.10% Sn. Three spot analyses were reported on each of the 5 chalcopyrite grains and gave between 0.08 and 0.15% Sn. However, Banerjee's analyses also revealed Pb in all grains analyzed (range from 0.11 to 0.32% Pb), suggesting that the samples that he examined need re-evaluation.

CONCLUSIONS

This study has confirmed the value of the MicroPIXE technique in increasing our knowledge of trace-element distributions in sulfide minerals in a quantitative manner. Whereas many more samples need to be analyzed for mass-balance calculations,

the data obtained so far permit the following generalizations.

Chalcopyrite and, to a lesser extent, sphalerite have been identified as important Ag carriers. This should be taken into consideration in mass-balance calculations of ore from massive-sulfide deposits. Solid solution of silver in pyrite, particularly from Kidd Creek, is not identified as a significant factor, but more work needs to be done on this aspect. Solid solution of silver in pyrrhotite is another new finding that requires further evaluation. Whereas Se commonly substitutes for S in sulfides, it has been demonstrated that the high Se content of Kidd Creek chalcopyrite, together with an unknown quantity in galena, are probably the major sources of Se in "A" ore, rather than the numerous selenides known to occur in the deposit (Thorpe *et al.* 1976). Further, the significance of Sn solid solution in chalcopyrite should also be considered in any calculations involving Sn recovery since one cannot ascribe all the Sn solely to cassiterite.

Finally, it may be predicted that future mass-balance calculations, based on proton-microprobe analysis of a statistically significant number of samples, could be done by first establishing the mean trace-element contents of all the major minerals, then ascribing the balance to the rarer minerals that comprise the ore assemblage for individual zones of a particular deposit. This will still require careful and detailed quantitative mineralogical studies, such as those of Petruk & Schnarr (1982), but will also result in more precise quantification. This approach, of trace-element analysis by both proton and electron microprobes, will be particularly useful for trace elements such as Ag, which are usually distributed in such a large number of different minerals (Cabri *et al.* 1984b).

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APPENDIX

TABLE I. TRACE-ELEMENT CONTENTS IN GALENA

Sample	Grain No.	Ag		Se		Sb	
		P (ppm)	E (wt.%)	P (ppm)	E (wt.%)	P (ppm)	E (wt.%)
"C" ore							
83-1	1	781±51	0.06±0.02	n.d.*	n.d.	n.d.	0.08±0.02
83-1	1	738±50	0.06±0.02	567±443	n.d.	n.d.	0.06±0.02
83-5	1	937±54	0.08±0.02	n.d.	n.d.	n.d.	0.13±0.02
83-7	1	1167±58	0.10±0.02	534±449	n.d.	n.d.	0.14±0.02
83-7	1	1108±57	0.13±0.03	n.d.	n.d.	n.d.	0.11±0.02
83-11	1	292±39	0.04±0.02	1531±605	0.24±0.05	0.04±0.02	
83-11	1	430±43	0.10±0.02	1254±560	0.19±0.05	0.08±0.02	
83-11	1	243±37	0.03±0.02	1316±553	0.23±0.05	0.03±0.02	
83-13	2	127±33	n.d.*	n.d.	n.d.	n.d.	
83-13	3	87±33	n.d.	n.d.	n.d.	n.d.	
83-15	1	202±32	n.d.	n.d.	n.d.	n.d.	
83-15	2	118±33	n.d.	n.d.	n.d.	n.d.	
83-24	1	738±50	0.06±0.02	495±443	n.d.	n.d.	0.10±0.02
83-25	1	978±55	0.10±0.02	n.d.	n.d.	n.d.	0.11±0.02
83-25A	1	902±49	0.09±0.02	n.d.	n.d.	n.d.	0.09±0.02
"A" ore							
83-12	2	446±43	0.03±0.03	n.d.	n.d.	n.d.	0.04±0.02

*n.d.=not detected at the calculated MDL.
 p=proton microprobe; MDL (ppm) @ 3σ are Se(521), In(31).
 e=electron microprobe; precision given as ±2σ; MDL (wt.%)
 @ 3σ are Se(0.07), Ag(0.03), Sb(0.03).

APPENDIX

TABLE II. TRACE ELEMENT CONTENT OF SPHALERITE FROM MATTAGAMI-NORITA, GECO AND NANISIVIK

Sample	Grain No.	Se		Ag		Cd		In
		P(ppm)	E(wt.%)	P(ppm)	E(wt.%)	P(ppm)	E(wt.%)	P(ppm)
Mattagami/ Norita	1	n.d.*	n.d.	-	-	1101±45	0.11±.03	n.d.
	3	387±57	n.d.	-	-	1720±55	0.16±.03	67±19
	4	n.d.	n.d.	-	-	904±41	0.10±.03	11±13
	5	n.d.	19±11	-	-	1222±48	0.12±.03	44±19
	6	n.d.	n.d.	-	-	1400±49	0.13±.03	79±18
Geco-2	1	n.d.	n.d.	-	-	5096±92	0.53±.04	329±32
	-3	1	n.d.	n.d.	-	2909±71	0.30±.03	56±19
	-3	2	n.d.	n.d.	-	3370±76	0.35±.03	53±19
	-3	3	n.d.	n.d.	-	2872±71	0.32±.03	31±17
	-4	1	n.d.	n.d.	-	5093±92	0.50±.04	172±25
	-4	2	n.d.	n.d.	-	5088±94	0.49±.04	168±23
	3	n.d.	n.d.	-	5057±93	0.51±.04	158±24	
Nanisivik	1**	149±51	704±35	0.05±.03	4433±122	0.51±.04	n.d.	
	3	n.d.	650±33	0.06±.03	6035±142	0.63±.05	n.d.	
	6	n.d.	650±34	0.05±.03	3317±104	0.15±.03	n.d.	

*n.d.=not detected at the calculated MDL.

**also contains 86±39 ppm Ge.

P=proton microprobe; MDL (ppm) @ 3σ are Ge(28), Se(43), Ag(13.5), In(16).

E=electron microprobe; MDL (wt.%) @ 3σ are Ag(0.04), Cd(0.04).

TABLE III. TRACE-ELEMENT CONTENT OF CHALCOPYRITE FROM MATTAGAMI-NORITA AND GECO

Sample	Grain No.	Zn		Se		Ag		In		Sn
		P(ppm)	E(wt.%)	P(ppm)	E(wt.%)	P(ppm)	E(wt.%)	P(ppm)	E(wt.%)	P(ppm)
Mattagami/ Norita	1	1872±370	0.37±0.02	429±19	n.d.	n.d.	-	22±15	n.d.	21±12
	1	1611±329	0.34±0.02	387±19	n.d.	n.d.	-	25±14	n.d.	28±16
	2	1983±341	0.23±0.02	497±19	521±33	0.07±0.02	381±30	0.04±0.02	n.d.*	
	2	1404±315	0.18±0.02	411±19	519±30	0.06±0.02	369±28	0.04±0.02	n.d.*	
	2	4058±495	0.19±0.02	572±19	528±33	0.06±0.02	358±29	0.03±0.02	n.d.*	
	2	4431±478	0.20±0.02	479±19	486±32	0.05±0.02	343±28	0.02±0.01	n.d.*	
Geco-1	1	891±128	n.d.	n.d.	134±15	-	-	59±18	-	n.d.
	-1	2	236±105	n.d.	n.d.	129±15	-	78±15	-	n.d.
	-1	3	n.d.	-	n.d.	135±15	-	68±15	-	n.d.
	-2	1	n.d.	-	n.d.	131±15	-	44±14	-	n.d.
	-2	2	n.d.	-	n.d.	123±15	-	50±15	-	n.d.
	-2	3	308±108	0.03±0.01	n.d.	130±15	-	39±15	-	n.d.

n.d.=not detected at the calculated MDL.

P=proton microprobe; MDL ppm @ 3σ are Zn(131), Se(15), Ag(11), In(10), Sn(17 if no Ag present).

E=electron microprobe; MDL (wt.%) @ 3σ are Zn(0.02), Ag(0.03), In(0.02).

*high Ag content increases Sn MDL up to 147 ppm in some cases.

TABLE IV. PROTON MICROPROBE DATA FOR PYRITE FROM GECO

Sample	Grain No.	As (ppm)	Se (ppm)
1	1	n.d.	n.d.
1	3	63±10	n.d.
2	1	65±10	n.d.
3	1	32±9	n.d.
4	1	51±10	37±11
4	3	93±11	32±9

n.d.=not detected at the calculated MDL
MDL (ppm) @ 3σ are As(9), Se(8).