THE CANADIAN MINERALOGIST

Journal of the Mineralogical Association of Canada

Volume 22 NOVEMBER 1984 Part 4

Canadian Mineralogist
Vol. 22, pp. 521-542 (1984)

QUANTITATIVE TRACE-ELEMENT ANALYSES OF SULFIDES FROM SUDBURY AND STILLWATER BY PROTON MICROPROBE

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ABSTRACT

Major sulfide ore minerals from mineral deposits in the Sudbury area, Ontario, and from the Stillwater Complex, Montana, have been analyzed with the Heidelberg proton microprobe in a search for trace quantities of the platinum-group elements (PGE). No PGE were detected in Sudbury sulfides, down to minimum detection-levels of 1.2 to 3 ppm for Pd and Rh and 50–60 ppm for Pt. Stillwater pentlandite, on the other hand, contains the following PGE in solid solution: Pd 1870 to 13600 ppm, Rh $<$ 26 to 110 ppm, and Ru $<$ 14 to 80 ppm. Chalcopyrite, pentlandite and pyrrhotite from Sudbury and Stillwater contain Se in solid solution. Sudbury chalcopyrite, in addition, contains Zn in the form of a heterogeneous solid-solution ($<$ 35 to 2570 ppm). The data demonstrate the great potential of the proton microprobe in research on the geochemistry of sulfides and other minerals. The low levels determined for extent of solid solution of the PGE in Sudbury sulfides are helpful in guiding future mineralogical research and in directing improvements in PGE recoveries. The data on Stillwater sulfides help understand distribution of the PGE in other Merensky-type deposits and will also assist metallurgists in improving metal recoveries, should the Stillwater deposit be exploited. Data on other trace-elements are of interest in questions concerning ore genesis and flotation research.

Keywords: platinum-group elements, sulfides, trace elements, minimum detection-levels, solid solutions, Sudbury, Stillwater, proton microprobe, electron microprobe, S/Se ratio, geochemistry, ore genesis, mineral beneficiation.

SOMMAIRE

Les principaux sulfures du minerai des gisements de la région de Sudbury (Ontario) et du complexe de Stillwater (Montana) ont été analysés au moyen de la microsonde protonique de Heidelberg, afin de vérifier la présence de traces des éléments du groupe du platine. Aucun de ces éléments n'est décelé dans les sulfures de Sudbury, à un seuil de détection de 1.2 à 3 ppm pour Pd et Rh, et de 50–60 ppm pour Pt. Par contre, la pentlandite de Stillwater contient en solution solide les éléments suivants: Pd: de 1870 à 13600

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ppm; Rh: de < 26 à 110 ppm, et Ru: de < 14 à 80 ppm. La chalcopyrite, la pentlandite et la pyrrhotine de Sudbury et de Stillwater contiennent du Se en solution solide. De plus, la chalcopyrite de Sudbury contient le Zn sous forme de solution solide hétérogène (entre < 35 à 2570 ppm). Les données démontrent le très grand potentiel de la microsonde protonique dans les études de la géochimie des sulfures et autres minéraux. Les niveaux très faibles des solutions solides des éléments du groupe du platine dans les sulfures de Sudbury serviront de guide dans la recherche minéralogique prévue afin d'améliorer la récupération de ces éléments. Les données sur les sulfures de Stillwater contribuent par contre à une meilleure compréhension de la distribution de ces éléments dans d'autres gisements du type Merensky, et aideront également les métallurgistes à récupérer les métaux, si jamais ce gisement est exploité. Les données sur les autres éléments-traces sont d'intérêt en ce qui a trait aux questions de métallogénie et de recherche en flottation.

Mots-clés: éléments du groupe du platine, sulfures, éléments-traces, seuil de détection, solution solide, Sudbury, Stillwater, microsonde protonique, microsonde électronique, rapport S/Se, géochimie, métallogénie, enrichissement du minerai.

INTRODUCTION

Copper–nickel sulfide deposits commonly contain economically important concentrations of the platinum-group elements (PGE); in some stratiform mafic complexes, the PGE are more valuable than Cu and Ni, which are thus recovered as by-products. Detailed mineralogical studies in the last fifteen years have provided a good understanding of the distribution of the PGE that occur as platinum-group minerals (PGM), but the acquisition of data on the distribution of the PGE as trace elements in other minerals, such as the major sulfides in Cu–Ni deposits, has not progressed as rapidly (Cabri & Laflamme 1981). There is no denying the important contribution of bulk analytical methods, such as neutron activation, especially for the study of Pd and Ir; however, in spite of the careful separation of minerals prior to analysis (Mitchell & Keays 1981), the exact siting of trace elements among the major sulfide minerals is insufficiently known.

Almost routine *in situ* analyses by electron microprobe are performed on sulfides today, and detection limits of 1000 ppm are commonly obtained. More specialized methods of electron-microprobe analysis may lower detection levels for PGE in sulfides to several hundred ppm (Crocket & Cabri 1981). The ion probe (Liebl 1975) and laser probe (Hillenkamp *et al.* 1975) are destructive *in situ* methods because material is sputtered from the sample surface. There are very few reports of the analysis of sulfide minerals by these methods; more work would need to be done for quantitative results (Bhatia & Hagni 1979).

Within the past decade, the Van de Graaff accelerators, initially developed to perform experiments in nuclear physics, have increasingly found new applications, especially as analytical instruments (Ziegler 1975, Cookson 1981). Analyses are possible because of two phenomena: the production of characteristic X-rays induced by energetic ions and the elastic scattering of the ions due to electrical forces between the nuclei. The invention of high-resolution detectors such as Si(Li) has enhanced the exploitation of these phenomena as versatile and formidable tools for analysis.

Thus *in situ,* nondestructive, multielement analysis of minerals by *P*article-*I*nduced *X*-ray *E*mission (PIXE) is comparable to that by X-ray fluorescence (XRF) and electron microprobe, but with much improved detection limits. It is the much higher *bremsstrahlung* background produced by electron bombardment, making a low ratio of characteristic X-ray to *bremsstrahlung,* that is the cause of relatively poor detection-limits for the electron microprobe. The intensity of the background radiation (*i.e., bremsstrahlung)* varies inversely with the square of the mass of the incident particles. Thus the lower primary *bremsstrahlung* flux produced in the PIXE technique gives it the capability of detection levels of the order of 1–10 ppm. Most PIXE analyses, however, have been done on "thin" targets, usually biological and aerosol materials; very few results have been published on "thick" targets such as minerals (Bosch *et al.* 1978, Harris *et al.* 1984). The ability to focus the charged particles down to the dimensions of an electron beam used in the electron probe (< 10 μm), together with good optical and sample-handling facilities, has resulted in a powerful analytical tool for trace-element analyses with mineralogical applications. This analytical technique may be referred to as Micro-PIXE, and the instrument as a proton microprobe (Bosch *et al.* 1980) or a nuclear microprobe (Cookson 1981).

In addition to the PIXE technique, the tandem accelerator has also been used as an ultrasensitive mass-spectrometer. This development improves the measurement of isotopic ratios by several orders of magnitude over those achieved by conventional mass-spectrometry (Litherland 1980). Measurements by this technique of *T*andem-*A*ccelerator *M*ass *S*pectrometry (TAMS) have been reported on mineral samples (Rucklidge *et al.* 1982) and are very promising for providing quantitative estimates of concentrations at the ppb or even sub-ppb levels. Further development is currently underway to reduce the size of the beam spot and make facilities of sample handling more readily suitable to mineral analysis.

PREVIOUS TRACE-ELEMENT STUDIES

A fairly large number of modern trace-element studies, using bulk analytical methods, have been published on Sudbury sulfides and ores (*e.g.,* Keays

& Crocket 1970, Naldrett *et al.* 1982). On the other hand, there have been few published reports of such trace-element studies using *in situ* techniques.

The first attempt at determining whether the PGE, other than occurring as PGM, also occur as a dilute solid-solution in Sudbury minerals, was made with the electron microprobe, but neither Pt, Pd nor Rh was detected in chalcopyrite, pentlandite and pyrrhotite because analyses were limited by minimum detection-limits (MDL) in the range 300–500 ppm (Cabri & Laflamme 1976). However, these three PGE were measured and found to occur as solid solutions in Sudbury arsenides and sulfarsenides (Cabri & Laflamme 1976). Application of further mineralogical research on the distribution of the PGE in the Cu–Ni sulfide ores of the Sudbury area has shown that it is very difficult to achieve a metallurgical balance of mill products (Cabri 1981); further studies indicate that it is possible to account for some PGE better than for others (Cabri & Laflamme 1984; Sizgoric, unpubl. data). It has thus become evident that more powerful *in situ* analytical techniques should be tested on the major sulfides from Sudbury to determine if they are carriers of PGE.

In contrast to the published reports on Sudbury, there are no detailed studies of PGE distribution in a metallurgical material-balance of Stillwater samples. The presence of Pd in solid solution in Stillwater pentlandite, first reported in detail by Cabri & Laflamme (1981) as varying from less than 0.04 to up to 1.5 wt.% Pd, has been confirmed by Todd *et al.* (1982). The high levels of Pd in Stillwater pentlandite, which permit detection by the electron microprobe, make these samples good candidates for comparison of results obtained by a proton microprobe (Micro-PIXE) as well as for determination and measurement of other trace elements, if present.

SAMPLES AND STANDARDS

Chalcopyrite, pentlandite and pyrrhotite concentrates were prepared from −100+200 mesh fractions of mill products from the Copper Cliff secondary mill and are typical of ore from the Sudbury area processed in 1981 by Inco Metals Company. These concentrates were prepared by a combination of heavy liquid and Franz magnetic separations. Assays on these concentrates (Table 1) indicate their high purity and also the concentration of some of their trace elements. Their relative purity was also confirmed by quantitative image-analysis, which showed 98.1% for chalcopyrite, 95.0% for pentlandite, and 92.8% for pyrrhotite.

The accuracy of the PGE assays (Table 1) was considered to be only of the order of ±20% relative; the amount and distribution of PGM in these separates were also not precisely known. The distribution of Pd as a solid solution in pentlandite and of the PGE in sulfarsenides and arsenides (Cabri & Laflamme 1981) had been shown to be typically erratic at levels detected with the electron microprobe. Whereas these mineral separates were low in total PGE, individual grains might contain higher levels of PGE, at concentrations below the sensitivity of the electron microprobe but detectable by proton-microprobe analysis (≈ 1 to 300 ppm).

Splits from each mineral separate were mounted in araldite and made up into a single 2.5-cm polished section together with 14 synthetic standards. The minerals were carefully examined microscopically, in air and in oil, in order to select grains suitable for analysis (free of inclusions and imperfections). The 120 grains selected were photographed and then re-examined by SEM to verify that they are free of inclusions, especially of PGM. The SEM examination used imaging by both secondary and backscattered electrons. The energy-dispersion detector was not used to determine if some "inclusions" might be surface contamination. Thus, if a grain appeared to have more than about three "inclusions" or if such "inclusions" were badly located, the grain was considered unsuitable for analysis. Thirty-seven chalcopyrite, 26 pentlandite, and 35 pyrrhotite grains were found suitable. The grains were also rechecked by SEM after analysis to ensure that the contamination mark caused by the proton beam was well located with respect to the "inclusions".

The sulfides from the Stillwater Complex are from a fraction concentrated by flotation from a bulk sample taken in 1975 from the West Fork adit of the property worked by the Johns–Manville Corporation (*cf.* Cabri *et al.* 1978). Ten pentlandite grains were selected for analysis, 3 of which had been previously analyzed with the electron microprobe. In addition, two grains each of chalcopyrite, pyrrhotite and pyrite were also selected for analysis. The grains were also examined microscopically (after mounting in araldite together with 4 standards) and with the SEM, before and after proton-microprobe analysis.

TABLE 1. ASSAYS OF THREE SUDBURY CONCENTRATES

	Cu	Ni	Co	Fe	S	Totals	Pt	Pd	Se
chalcopyrite	33.6 %	0.12%	<0.02%	29.7%	34.0%	97.44%	0.59ppm	0.56ppm	90ppm
pentlandite	0.07	33.1	1.25	31.4	34.1	99.92	4.4	2.3	85
pyrrhotite	0.15	1.14	0.02	56.0	34.4	91.71	0.31	0.25	73

Synthesis of homogeneous standards, close in composition to the minerals to be analyzed, was also considered an important factor in obtaining accurate quantitative data. Therefore, a series of standards was synthesized from high-purity elements using the standard method of dry synthesis by reaction of the elements in evacuated tubes of silica glass for the most part. Besides synthesizing compounds with minor amounts of Pt, Pd, Rh and Ir and similar compounds without these PGE, compounds with minor Se and Zn were also synthesized because earlier qualitative proton-microprobe analyses by us had indicated their presence in the Sudbury sulfides. The (Pt,Fe) standard (No. 566) was synthesized by initial reaction of Fe (in sheet form) with Pt (sponge) in an evacuated tube of silica glass held at 1000°C for over a month. Then the charge was homogenized by melting in an electric arc furnace under argon. All standards were carefully checked for homogeneity microscopically and by electron microprobe. Those actually used in the proton-microprobe analyses are listed in Table 2, together with their weighed-in compositions and the homogeneity index (HOM index), a measure of the variance, for the trace elements.

ANALYTICAL METHODS

Proton microprobe

The experimental set-up for the Heidelberg proton microprobe, used in these analyses, may be summarized as follows. The proton beam, produced by a 6 MV tandem Van de Graaff accelerator, is collimated by a series of specially designed slits in order to reduce the halo of scattered particles. The final collimated beam is focused by means of a short magnetic quadrupole doublet to produce a lateral width or diameter of 4 to 6 μm. The originally reported resolution of 2 × 2 μm² (Bosch *et al.* 1978) could not be used. The limited brightness of the ion source-accelerator combination required a compromise between lateral resolution and analytical time.

The stage can accommodate a single circular sample 25 or 31 mm in diameter, the usual sizes of a polished section. The sections were carbon-coated in the same manner as for electron-microprobe analysis. The sample can be moved in *x, y* and *z* direction and also rotated around the beam axis. In addition, movement in *x* and *y* directions can be controlled by means of stepping motors with minimum step-length of 0.25 μm. The optical system permits direct observation under reflected light at a magnification of 300×. A much lower magnification is also possible (20×) for rough positioning of the sample. The focused beam of protons is readily observed in the araldite mounting medium in reduced illumination. It is also possible to use a thin film of plastic scintillator, obtained by applying a small drop of toluene (containing dissolved plastic scintillator) to the target's surface (Chen *et al.* 1981). The typical vacuum is about 5×10^{-7} Torr, and the cryogenic pumps are fed liquid He from 3 containers, which last about 72 hours. The time required for a sample change and re-establishment of measurement conditions is about 30 minutes.

The beam current varied throughout the analyses and ranged from 160 to 320 pA at 3 MeV and from 120 to 180 pA at 4 MeV. The beam current is monitored by means of a "Rutherford monitor", which permits hitting the target with a predetermined number of protons, regardless of drift in beam current. Betweeen the collimator and the lens, four gold foils, each with an equivalent thickness of 1 mg/cm², are mounted on a rotating wheel, so that each foil is switched periodically into the beam (about 10% of the run time at frequencies of 10–20 Hz). By means of Rutherford scattering, the protons are measured with a surface barrier detector at 35°, and the X-ray analysis is gated off during normalization of the charge. To prevent the scattered particles from reaching the sample, antiscatter slits are placed after the "Rutherford monitor".

X rays from the sample are detected with a Kevex Si(Li) detector fitted with a 50 μm Be proton shield. In order to suppress the low-energy part of the spec-

TABLE 2. SYNTHETIC STANDARDS

No.	Compound	Weighed-in composition % and (HOM index)										Anneal Temp. °C
		Cu	Fe	Ni	Pt	Pd	Rh	Ir	Zn	S	Se	
181	Cu-Fe-S	30.00	37.00	-	-	-	-	-	-	33.00	-	600
527	Cu-Fe-(S,Se)	32.15(2)	35.32(1)	-	-	-	-	-	-	32.38(1)	0.15(3)	600
528	Cu-(Fe,Zn)-S	32.15(2)	35.24(1)	-	-	-	-	-	0.15(3)	32.46(1)	-	600
533	Fe-(S,Se)+Fe	-	63.47(1)	-	-	-	-	-	-	36.36(1)	0.17(3)	900-650
239	FeS+Fe	-	63.53	-	-	-	-	-	-	36.47	-	1000-600
542	$(Fe,Pd)_9S_{10}$	-	60.92(1)	-	-	0.15(3)	-	-	-	38.93(1)	-	800-650
535	$(Fe,Ir)_9S_{10}$	-	60.96(2)	-	-	-	-	0.12(3)	-	38.92(2)	-	800-650
481	$(Fe,Rh)_7S_8$	-	59.95(1)	-	-	-	0.52(1)	-	-	39.53(1)	-	825
457	$(Fe,Ni,Pd)_9S_8$	-	28.79(1)	37.50(1)	-	0.65(3)	-	-	-	33.06(1)	-	590
440	$(Fe,Ni)_9S_8$	-	32.55	34.22	-	-	-	-	-	33.23	-	570
566	(Fe,Pt)	-	99.82	-	0.18(1)	-	-	-	-	-	-	
-	Fe	-	100.00	-	-	-	-	-	-	-	-	

trum, Al absorbers of different thicknesses were placed in front of the Si(Li) detector: 350 μm at 3 MeV and 1 mm at 4 MeV. Another Be foil (150 μm thick), placed in front of the Al absorbers, stops backscattered protons in order to prevent γ-ray production in the Al absorbers. It is worth noting, however, that the reduced peaks for the major metals, although not providing a quantitative representation of metal concentration, were very important in screening the results for spurious analyses. Significant drops in peak heights (≈ 20%) were considered indicative of an analytical problem such as a thin or imperfect grain and were used as justification to delete the results of the analysis. Further details of the Heidelberg proton microprobe, including diagrams, may be found in Bosch *et al.* (1980) and Chen *et al.* (1981).

Data acquisition was largely done on-line using a program written by Mr. C. Ender. Some analytical results, however, were processed with a conventional multichannel analyzer and data transmission by paper tape. Counting periods varied from about 7 to 120 minutes. At 3 MeV, 60 minutes was generally the longest counting period; 1.8 × that time is required at 4 MeV if the same Rutherford integral is used.

Electron microprobe

A Materials Analysis Company (MAC) electron microprobe was used to determine the homogeneity of the synthetic standards listed in Table 2 and for the analyses of the Stillwater pentlandite. Determinations of the homogeneity index were carried out as described in Cabri & Laflamme (1976). The pentlandite analyses were performed at 25 kV with a specimen current of 0.03 microamperes. The following X-ray lines and synthetic standards were used: Fe*K*α, Ni*K*α, and S*K*α using $(Fe_{4.00}Ni_{5.00})(S_{7.99}Se_{0.01})$, Co*K*α using $(Fe_{0.99}Co_{0.01})S_{1.00}$ and Pd*L*α using $(Fe_{4.00}Ni_{4.95}Pd_{0.05})S_{8.00}$. A trace-element analysis for Pd was done according to the procedures described by Cabri & Laflamme (1976) and Cabri (1981).

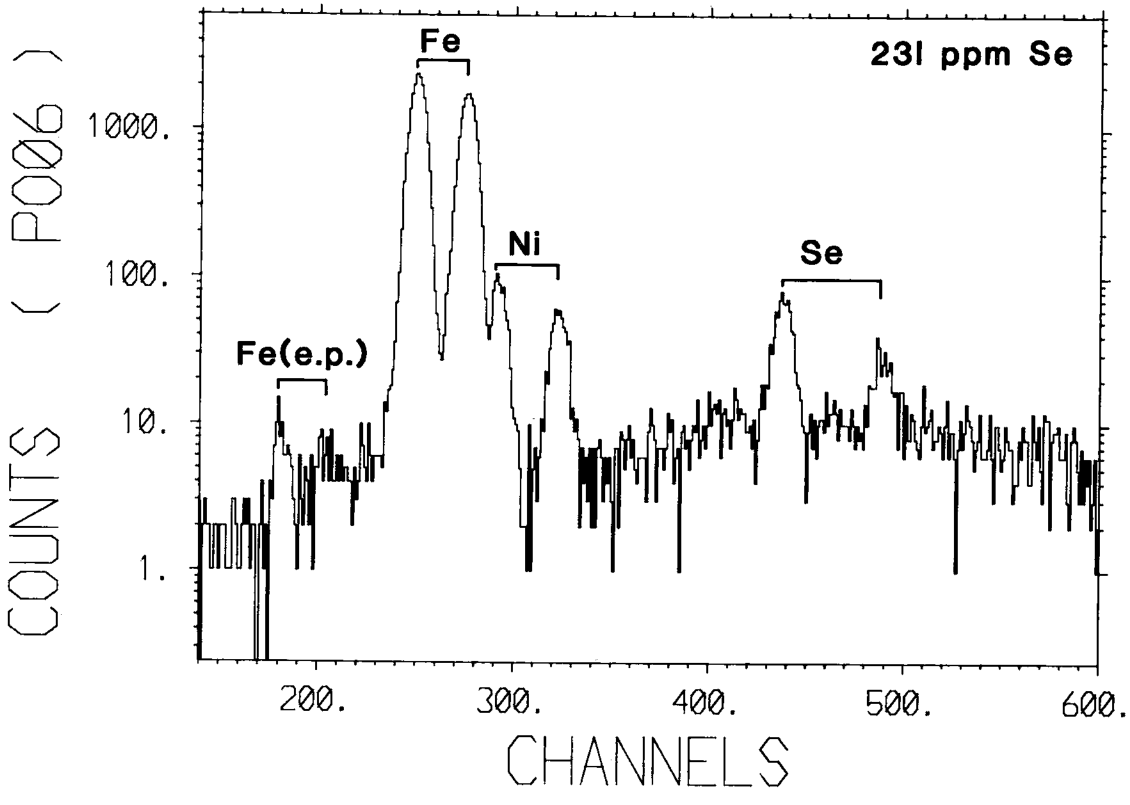

FIG. 1. X-ray spectrum of Sudbury nickeloan pyrrhotite (grain po-6) at 3 MeV proton excitation, showing well-developed Se*K*α and Se*K*β peaks. Fe escape peaks also present in the low-energy part of the spectrum. Note the reduced intensity of the Fe and Ni peaks owing to the Al absorber.

DATA ANALYSIS

The X-ray spectra obtained from each analysis point with the proton microprobe were first treated with a curve-fitting program to obtain the net peak-counts above background. For standards, where the desired trace-element and the matrix were the same as in the mineral to be analyzed, the ppm/count for a specific X-ray peak (*e.g.*, *K*α) was readily calculated. All values are relative to identical proton-charge in standard and unknown by means of the Rutherford monitor.

In cases where the trace element and matrix in the standard did not both correspond with the mineral, a calculation was made according to a matrix-correction program developed by Blank (1982). Equations are given in the Appendix. The usual relationship of net peak-counts > $3\sqrt{\text{Background}}$ was used to determine minimum detection-limits (MDL). All the electron-microprobe analyses were computed with a locally modified version of EMPADR VII (Rucklidge & Gasparrini 1969).

RESULTS

The results of analyses are presented in the following two groups: 1) analyses in which trace elements could be detected and measured, and 2) those analyses where specific elements could not be detected in spite of being specifically sought.

Trace elements measured

Selenium was measured in all analyzed chalcopyrite, pentlandite and pyrrhotite grains from both Sudbury and Stillwater. Both selenium *K*α and *K*β peaks are well resolved in all three sulfides where the selenium content is relatively high (Fig. 1), but only the *K*α peak is well resolved where it is low (Fig. 2). Several chalcopyrite grains and one of pentlandite were reanalyzed in different spots that could later be located easily by the beam-contamination mark (Figs. 3,4). These repeat analyses were done during different beam-times as well as for different accumulated charges (μC) (Table 3). The results indicate a

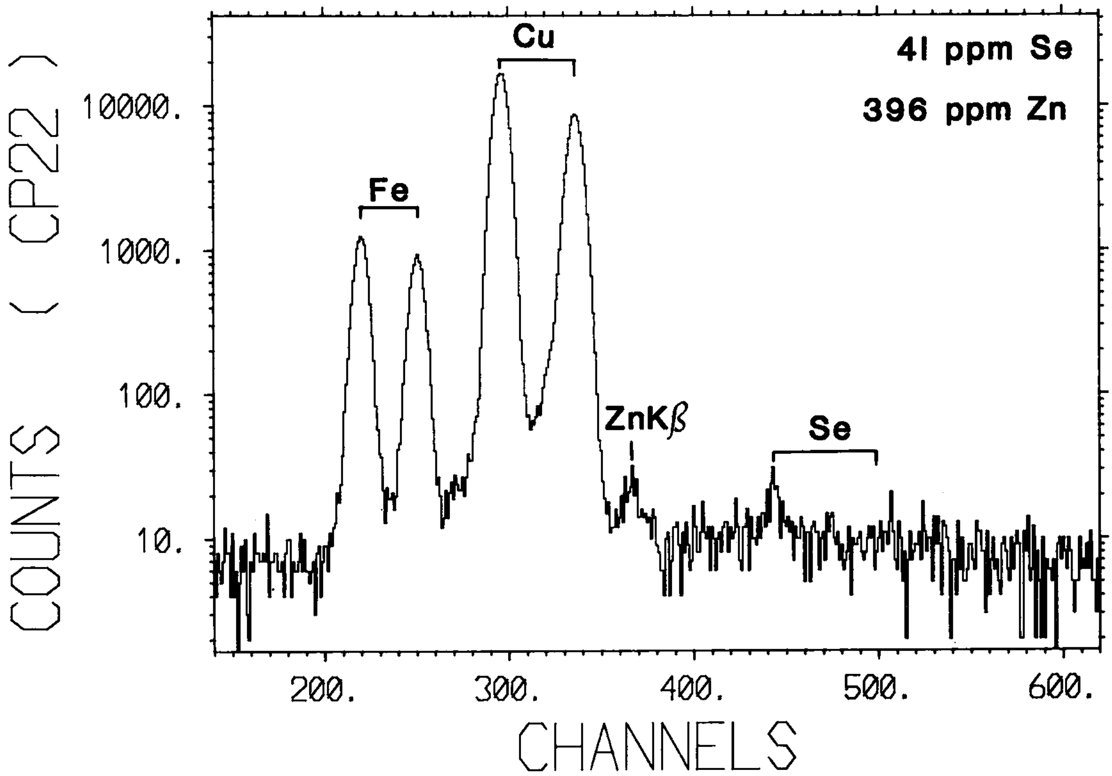

FIG. 2. X-ray spectrum of Sudbury chalcopyrite (grain cp-22) at 3 MeV proton excitation, showing fairly well-developed Zn*K*β and Se*K*α peaks. The Zn*K*α distorts the Cu*K*β slightly, and the Se*K*β peak is not readily discernable.

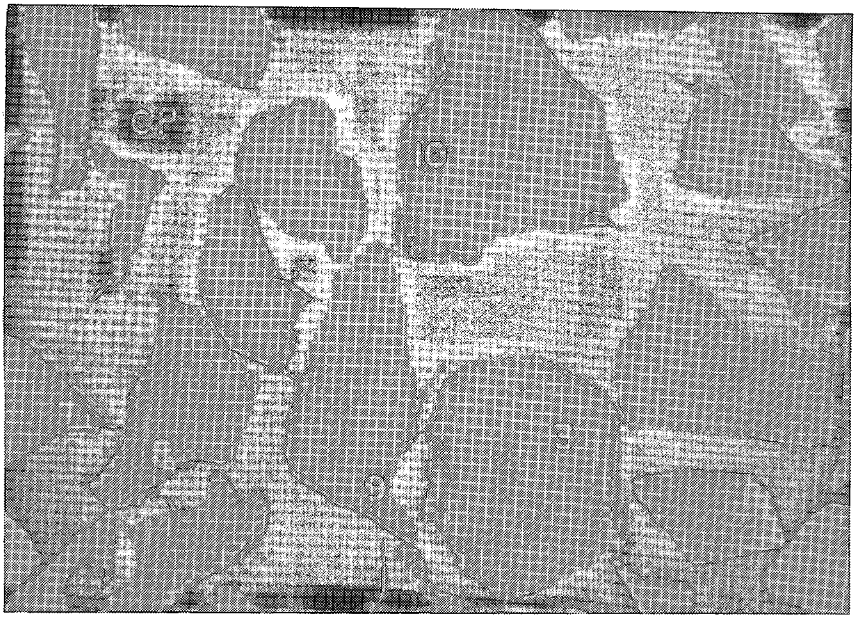

FIG. 3. Scanning-electron micrograph of Sudbury chalcopyrite grains. Five grains show beam marks (cp–3, 7, 8, 9 and 10). The beam contamination mark is rectangular to elliptical or square, depending on the final focusing. Scale: 30 μm = 0.8 cm.

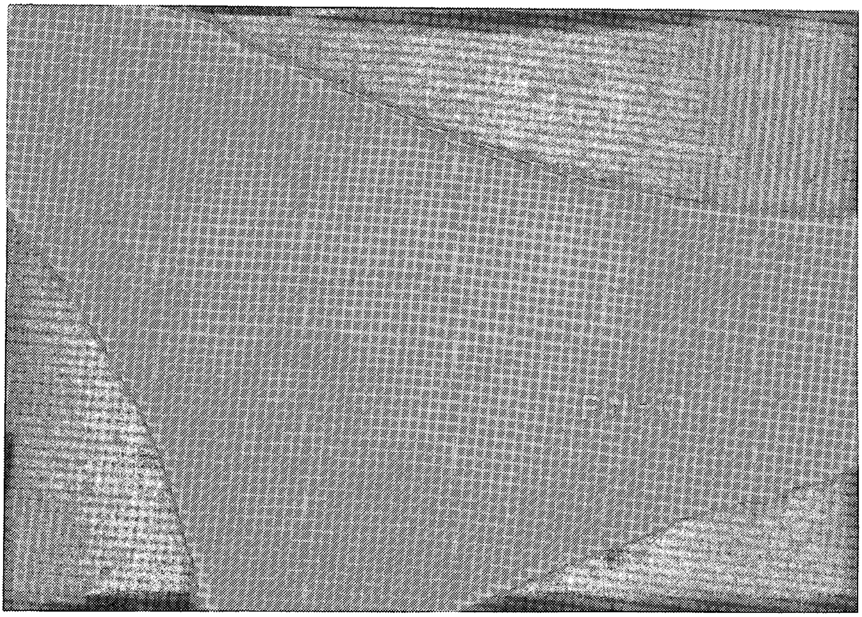

FIG. 4. Scanning-electron micrograph of a grain of Sudbury pentlandite showing detail of a square-shaped beam-contamination mark. Scale: 10 μm = 1.1 cm.

TABLE 3. SELENIUM: REPRODUCIBILITY/HOMOGENEITY IN SUDBURY CHALCOPYRITE AND PENTLANDITE

Analysis*	Accumulated charge (μC)	grains**	net peak counts background	net peak counts Se***	ppm	average
C	0.5	cp-7-2	111	631	227	222
D	0.5	cp-7	168	620	217	
C	1.0	cp-14	208	981	177	185
D	0.5	cp-14	126	552	193	
C	0.5	cp-22	82	115	41	44
C	0.5	cp-22-2	93	126	45	
D	0.5	cp-22	136	132	46	
C	1.0	cp-23	228	1362	245	238
C	0.5	cp-23-2	114	616	222	
D	0.5	cp-23	142	705	247	
D	0.5	pn-29	108	263	92	89
D	0.5	pn-29-2	112	248	86	

*refers to different beam periods for analyses.
**same grains, but different spot analyses for each set of 2 or 3.
***counts above background.

very narrow range of values, suggesting both good reproducibility and homogeneous distribution of selenium in the structure of chalcopyrite and probably also in pentlandite.

The results for sulfides from the two areas are compared in Figures 5, 6 and 7, which show the number of grains analyzed, the mean selenium content for each sulfide, and the range of selenium values obtained. For Sudbury, the mean values are remarkably close to the values obtained from bulk analyses of "nearly pure" separates given in Table 1: chalcopyrite 102 ppm *versus* 90 ppm from bulk analysis, pentlandite 85 ppm *versus* 85 ppm from bulk analysis, pyrrhotite 92 ppm *versus* 73 ppm from bulk analysis. Note that the pyrrhotite separate is the least pure, so that a lower Se content is to be expected from a bulk analysis.

Though the number of grains analyzed was not the same for each mineral or from each area, it is apparent that the three Stillwater sulfides have higher selenium contents than their Sudbury counterparts (Figs. 5–7). Reproducibility and homogeneity of Se in Stillwater pentlandite were found to be very good. Four spot-analyses were made on eight grains and three spot-analyses on two grains. The standard error of the mean ranges from 4 ppm for grain G, which has a mean Se content of 682 ppm, to 30 ppm for grain C, with a mean Se content of 506 ppm. These analyses were all done at an accumulated charge of 0.5 μC during a single period of beam time at 3 MeV.

Zinc was found to occur, in measurable quanti-

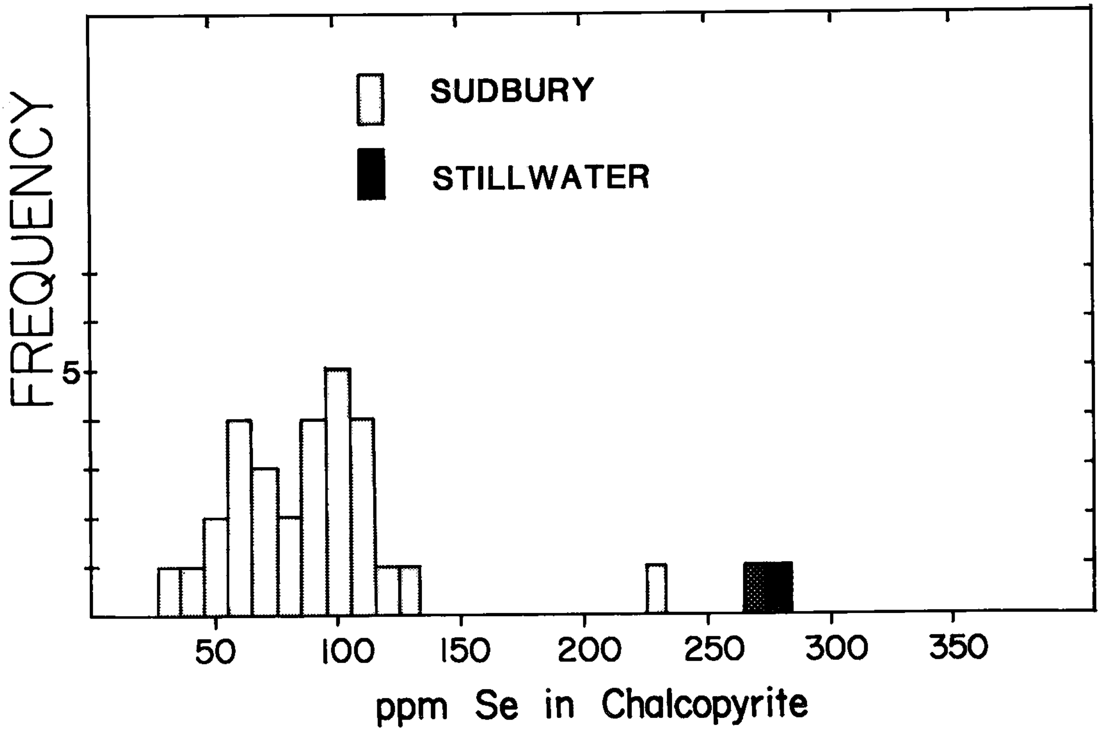

FIG. 5. Histogram illustrating the Se distribution for 32 grains of Sudbury chalcopyrite. Arithmetic mean value and range is 102(40–238) ppm. Two chalcopyrite grains from Stillwater with 278 and 281 ppm are also plotted for comparison.

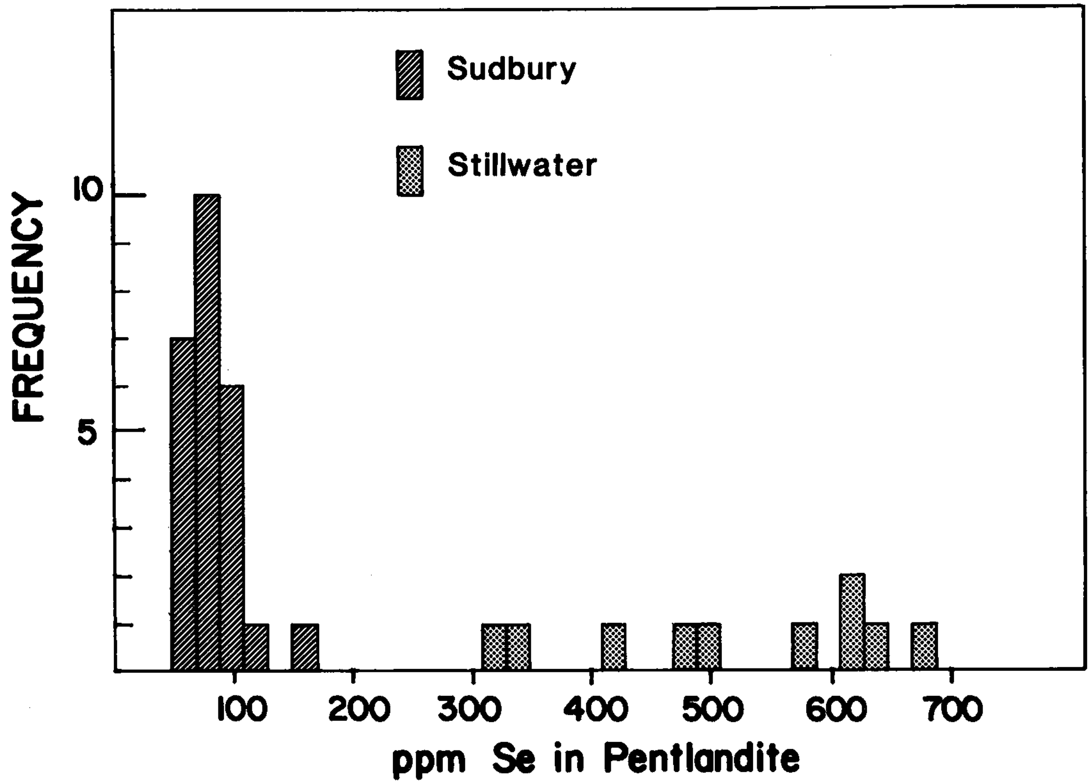

FIG. 6. Histogram illustrating the distribution of Se for 25 grains of Sudbury pentlandite compared with Se in two grains of Stillwater pentlandite. Arithmetic mean values and ranges are 85(51–168) ppm and 523(326–682) ppm for Sudbury and Stillwater, respectively.

ties, in about 90% of grains of Sudbury chalcopyrite. The MDL for zinc ranges from 35 to 39 ppm. The histogram in Figure 8 clearly shows a distribution different to that of selenium. Results of duplicate and triplicate analyses on different areas of the same grains of chalcopyrite also confirm the wide range ($<$ 35 to 2570 ppm) and heterogeneous distribution of Zn in chalcopyrite (Table 4). However, there is an interference between the Zn$K\alpha$ and Cu$K\beta$ peaks, so that all the Zn values were obtained using only the Zn$K\beta$ peak, which limits analytical precision somewhat. The distortion of Cu$K\beta$ by Zn$K\alpha$ is readily seen on an X-ray spectrum of chalcopyrite with a high Zn content (Fig. 9).

Palladium was found in measurable quantities only in the Stillwater pentlandite; this is not unexpected since three of the ten grains previously analyzed had been shown to contain Pd by electron-microprobe analysis. Both Pd$K\alpha$ and Pd$K\beta$ peaks are well resolved in all spectra (Fig. 10), but only the Pd$K\alpha$ was used in the calculations. Four spot-analyses on noncontiguous areas were performed on all ten pentlandite grains, but only three spot-analyses could be used for two of these grains owing to spurious results. The same areas were reanalyzed with the electron microprobe by placing the electron beam at the centre of each of the contamination marks left by the proton beam. The averaged results for each grain are compared in Table 5. The close correspondence (within ±7.7%) between the two analytical methods is considered excellent. We recognize the fact that electron-probe results given to hundreds of ppm are usually rounded off, but we present the raw results in this manner in order to facilitate the comparison with the proton-microprobe results (also not rounded off). A more detailed presentation indicative of the typical values for Pd in two grains is given in Table 6. Such data are indicative of good analytical reproducibility; in addition, they demonstrate a relatively homogeneous distribution of palladium in the pentlandite structure.

The detection of measurable quantities of *rhodium* and *ruthenium*, in addition to palladium, in some

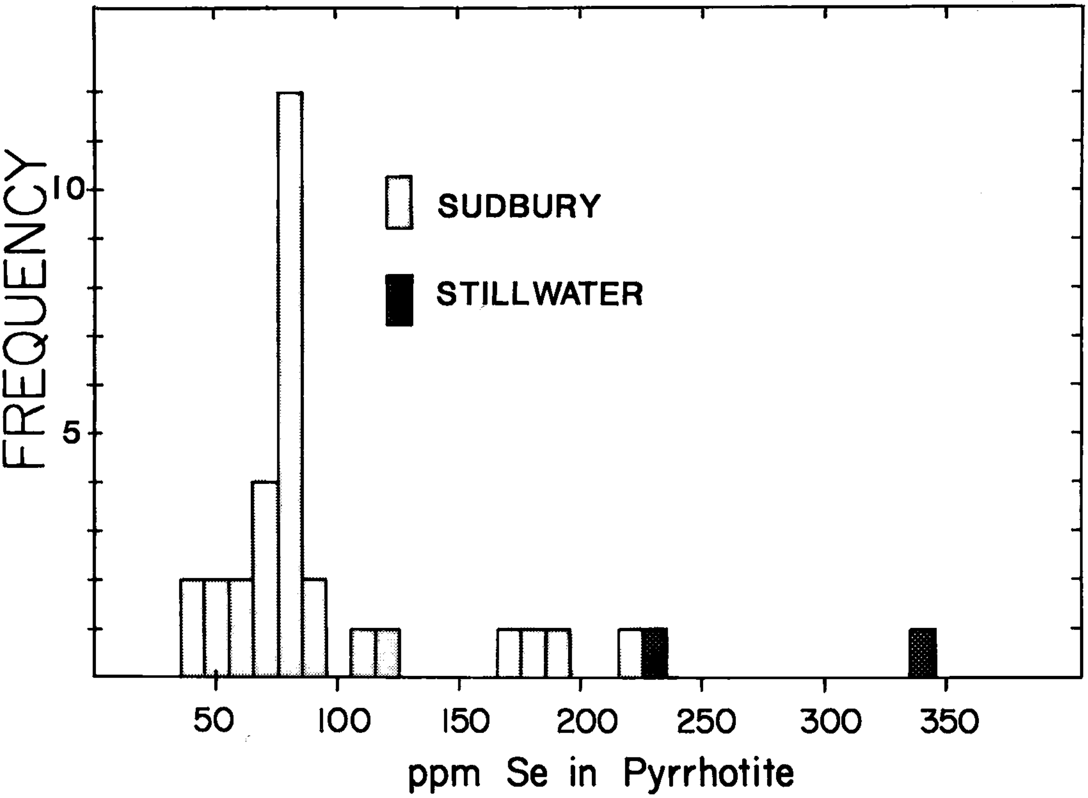

FIG. 7. Histogram illustrating the distribution of Se for 29 grains of Sudbury pyrrhotite compared with Se in two grains of Stillwater pyrrhotite containing 243 and 247 ppm. Arithmetic mean value and range for Sudbury is 92(31–231) ppm.

grains of Stillwater pentlandite is not surprising in view of the similar chemistry of these Group-VIII elements with (Fe,Ni) (Westland 1981). Genkin *et al.* (1974) had reported electron-microprobe data for pentlandite from sulfide-poor serpentinized dunite of the Lower Tagil'sk massif (Urals); these contain high Ru and Rh (9.6 and 4.0 wt.%, respectively), but no Pd. Similarly, Cabri *et al.* (1981) reported a rhodian "pentlandite" from the Yubdo ultramafic complex that contains approximately one Rh atom per unit cell (13.3 wt.% Rh) and also no Pd. Rhodium was detected in four of the ten pentlandite grains, but values can be calculated for three grains only (Table 7) owing to spurious Fe,Ni values in one spot-analysis of the fourth grain. Only two grains have measurable quantities of ruthenium (Table 7). At these low concentrations (< 110 ppm), only the $K\alpha$ peaks are resolved (Fig. 10), but better resolution was obtained in the Rh-bearing synthetic standard (Fig. 11). There appears to be no correlation between Pd and Rh/Ru ratio or between Rh and Ru, except that the two grains of Ru-bearing pentlandite also contain Rh. The lack of correlation is not surprising because these elements probably replace (Fe,Ni) in the pentlandite $Fm3m$ structure (Hall & Stewart 1973, Rajamani & Prewitt 1973), and because the extent of replacement is likely partly a function of the concentration ratio of each element during crystallization.

Arsenic was detected and measured only in the two pyrite grains analyzed from Stillwater. Calculated values of 496 (grain KI) and 856 (grain Ni) ppm arsenic do not compare well with the electron-microprobe values of 210 and 470, respectively, except in their relative proportions. This may be ascribed to a lack of a suitable standard for background in the case of the proton-microprobe analyses.

Trace elements not detected

The major emphasis of this investigation was on the detection of PGE, if present, to the limits of the experimental conditions. Thus, the availability of

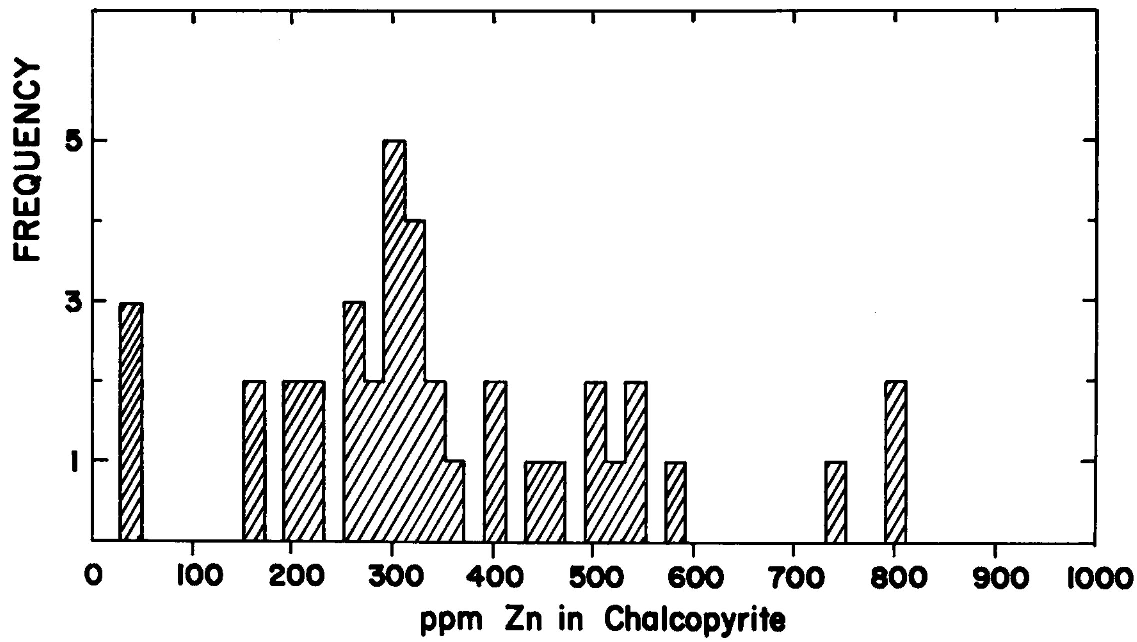

FIG. 8. Histogram illustrating the distribution of Zn for 39 spot analyses on 32 grains of Sudbury chalcopyrite. Arithmetic mean value and range is 353 (< 35–805) ppm, plus an additional value of 2570 ppm. The MDL was 35–39 ppm.

synthetic standards (with and without the PGE) is essential in order to establish good background and ppm/count levels required for the statistical determination of specific minimum levels of detection or MDL.

As listed in Table 2, standards containing one of four PGE (Rh, Pd, Ir and Pt) were prepared in anticipation of the discovery of measurable quantities. As the experiments proceeded, however, we found that determination of Pt would be a particular problem because of the ubiquitous presence of Se in all three sulfides and, in the case of Sudbury chalcopyrite, the common presence of Zn as well. This problem is caused by the interference and close overlap for the three *L* peaks of Pt (which are well resolved in the synthetic standard), *i.e.*, between Pt*L*α and Zn*K*β, Pt*L*β and Se*K*α, and Pt*L*γ and Se*K*β.

TABLE 4. ZINC: HETEROGENEITY IN SUDBURY CHALCOPYRITE

Analyses*	Accumulated charge (μC)	grains**	net peak counts background	net peak counts Zn***	ppm
C	0.5	cp-7-2	94	91	311
D	0.5	cp-7	173	19	n.d.†
C	1.0	cp-14	205	197	339
D	0.5	cp-14	116	143	501
C	0.5	cp-22	80	150	516
C	0.5	cp-22-2	103	234	805
D	0.5	cp-22	130	115	396
C	1.0	cp-23	221	167	585
C	0.5	cp-23-2	124	76	261
D	0.5	cp-23	127	210	735
C	0.5	cp-25	97	102	350
D	0.5	cp-25	140	25	n.d.††

*refers to different beam periods for analyses.
**same grains, but different spot analyses.
***counts above background.
† statistically not detected at MDL of 39 ppm Zn.
†† statistically not detected at MDL of 35 ppm Zn.

The first results, based on preliminary calculations using only analyses on Sudbury sulfides at 3 MeV, were reported by Cabri *et al.* (1983): MDL of 7 ± 2 ppm Pd and 10 ± 3 ppm Rh in chalcopyrite; 6 ± 2 ppm Pd, 9 ± 3 ppm Rh, 60 ± 20 ppm Pt and 50 ± 20 ppm Ir in pentlandite; and 5 ± 2 ppm Pd, 8 ± 3 ppm Rh, 50 ± 20 ppm Pt and 40 ± 15 ppm Ir in pyrrhotite. After further work on optimizing the curve-fitting program for the background calculations, a slight improvement was made in the Pd MDL in chalcopyrite, which decreased to 5 ± 1.75 ppm. It should be noted that these results were obtained by summation of data for several grains. Thus, for pentlandite, data for 10 grains were summed, each of which represented an analysis time of approximately 1 hour (*i.e.*, an accumulated charge of 0.5 μC) for a total of 5 μC. For chalcopyrite and pyrrhotite, the summations represent 6 μC and 4.5 μC, respectively.

In order to lower the MDL further, the last beam-time period was planned so as to run the experiments

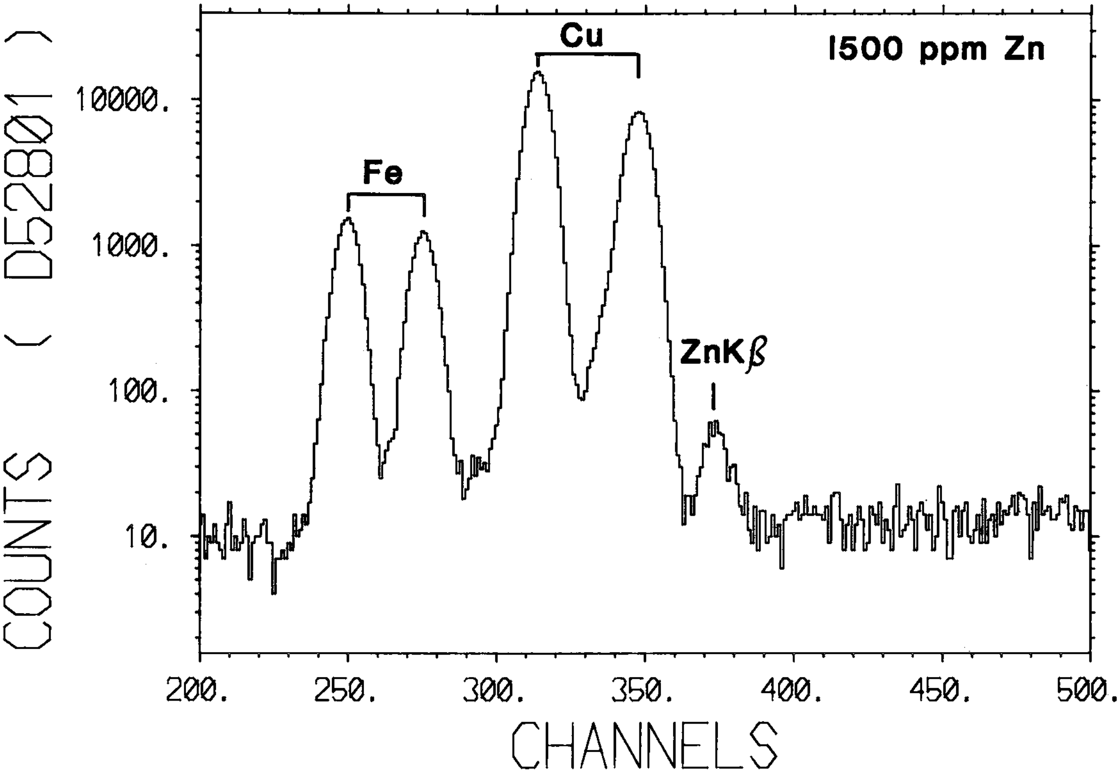

FIG. 9. X-ray spectrum of a synthetic chalcopyrite containing 1500 ppm Zn; the spectrum illustrates the distortion of the Cu$K\beta$ peak by the Zn$K\alpha$ peak.

at 4 MeV. Analysis times were roughly doubled; fewer grains could thus be analyzed, but the MDL were, indeed, lowered as shown in Table 8. The analytical results were also summed, as indicated in Table 8; the summed spectra show absolutely no evidence of trace elements such as Pd, Rh or Pt (Fig. 12). The MDL for Pd in pentlandite and for Rh in pyrrhotite were obtained directly without matrix corrections by using background counts from the PGE-free synthetic standards (3 × $\sqrt{\text{counts}}$) correlated to the equivalent proton charge and ppm/count from the appropriate Pd- or Rh-bearing standards. The other MDL values given in Table 8 were calculated using the matrix-correction program of Blank (1982). This was done by taking the MDL values known directly and calculating for a different matrix. Calculations for the appropriate matrix helped lower the MDL slightly in all cases compared to MDL values estimated without the matrix correction. For example, at 4 MeV, the MDL for chalcopyrite are 2.2 ppm Pd and 3.2 ppm Rh (uncorrected) *versus* 2.1 ppm Pd and 1.9 ppm Rh (matrix-corrected). For pentlandite, at 4 MeV, MDL values are 2.6 ppm Rh (uncorrected) and 1.6 ppm Rh (matrix-corrected). For pyrrhotite, also at 4 MeV, MDL values are 2.0 ppm Pd (uncorrected) and 1.2 ppm Pd (matrix-corrected).

DISCUSSION

Proton-microprobe analyses

Correct or truly quantitative analyses are dependent on the quality of the standards (accuracy) and the experimental conditions (precision). The quality of the synthetic standards is dependent on the care taken during synthesis, including weighing the elements. The weighing error for the trace elements is considered to be less than ±5 wt.% of the trace element in question (Table 2). Additional errors are introduced by an inhomogeneous distribution of the trace element in the sulfide matrix. For electron-microprobe analyses, the latter may usually be overcome by taking a large number of spot analyses and averaging or by using a defocused beam. Observed elemental variations in seven of the standards are compared in Table 9 with the statistical variation based on ± $\sqrt{\text{av.}}$ counts from 10 to 16 spot ana-

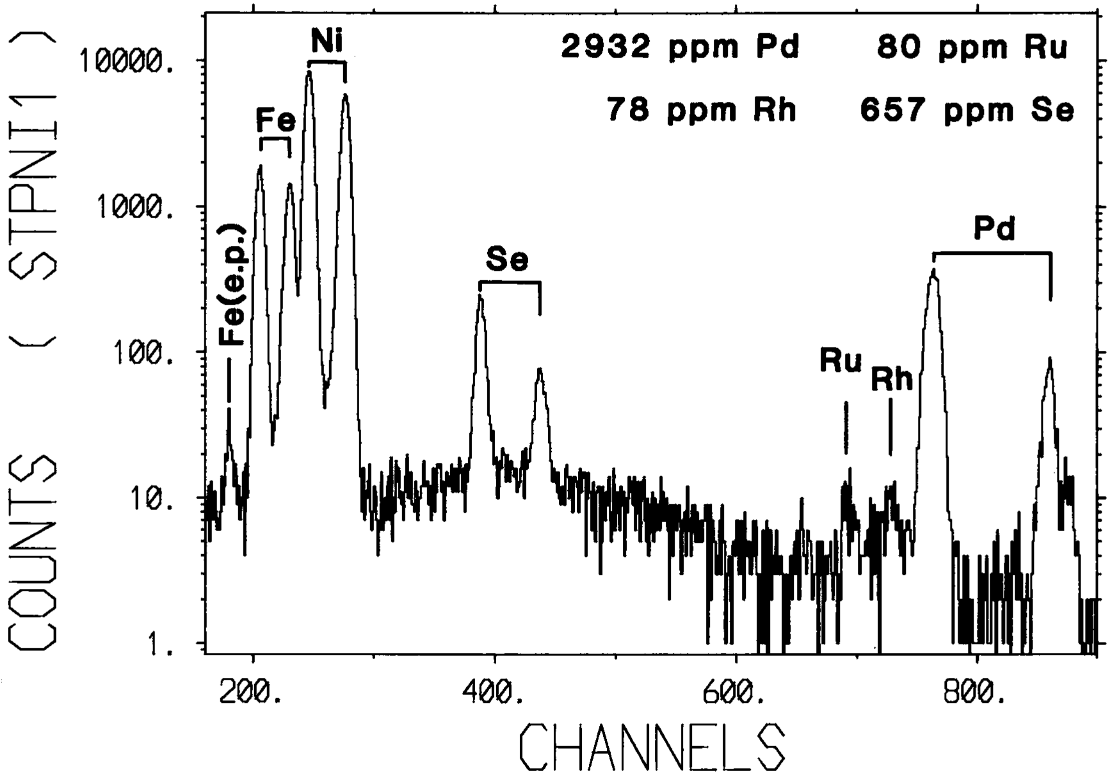

FIG. 10. X-ray spectrum of a Stillwater pentlandite (grain STPNI-1) at 3 MeV proton excitation, showing well-developed Pd*K*α, Pd*K*β, Se*K*α, Se*K*β, and less well-developed Ru*K*α and Rh*K*α peaks.

lyses. It may be seen that, with two exceptions (Nos. 533, 535), the statistical variation is close to or less than the observed variation. This suggests that inhomogeneity in the standards is not a serious problem for most analyses and that the results are accurate to within ±5 wt.% of the individual weighed-in trace-element values in the case of most standards.

Whereas it is not possible to do 10 to 16 spot analyses for each standard with the proton microprobe, owing to the time involved, the variations observed are of the same order of magnitude as those with the electron microprobe. Where several spot-analyses of a standard were taken, the observed variation (in ppm/count) was found to be below ±3% except for No. 528, where it was ±20%. The Pd-pentlandite standard (No. 457) was used to determine the Pd content of the Pd-pyrrhotite standard (No. 542) using the matrix-correction program of Blank (1982). For a weighed-in value of 1500 ± 75 ppm Pd, the calculated value is 1484 ppm, which represents excellent agreement. Using the Rh-pyrrhotite standard (No. 481) to determine the same did not produce as close a result (2075 ppm Pd). This is difficult to explain at this time, especially since standard No. 481 showed the least observed and calculated variation in Rh (Table 9). Finally, taking the Se value from chalcopyrite

TABLE 5. COMPARISON OF ANALYTICAL RESULTS FOR STILLWATER PENTLANDITE

grain	Pd(ppm)* electrons(1)	Pd(ppm)** protons(2)	(1-2)/1
A	14,220	13,648	-4.0%
B	4,050	4,044	-0.2%
C	1,900	1,868	-1.6%
D	2,720	2,933***	+7.7%
E	10,520	10,286	+2.2%
F	3,000	2,793	-7.0%
G	7,750	7,865	+1.4%
H	5,070	5,057	-0.2%
I	3,070	3,215	+4.6%
J	2,830***	2,789***	-1.4%

*Arithmetic mean of 4 spot analyses, except for J. 100 sec at 25kV, 0.05 μamp using synthetic standards.

**Arithmetic mean of same four spots, except for D & J. 1600-2000 sec at 5×10^5 Rutherfords using same synthetic standards.

***Arithmetic mean of 3 spot analyses.

TABLE 6. DETAILED COMPARISON OF ANALYTICAL RESULTS FOR STILLWATER PENTLANDITE

grain	spot#	Pd(%) electrons	Pd(ppm) protons
B	1	0.39	4023
B	2	0.39	3995
B	3	0.42	4176
B	4	0.43	3982
F	1	0.31	2829
F	2	0.30	2821
F	3	0.30	2772
F	4	0.29	2750

TABLE 7. RHODIUM AND RUTHENIUM IN STILLWATER PENTLANDITE

grain	spot #	ppm Rh		ppm Ru	
F	1	75	81	58	44
F	2	75		37	
F	3	86		45	
F	4	87		37	
G	1	80	86	n.d.	<14
G	2	112		n.d.	
G	3	79		n.d.	
G	4	73		n.d.	
I	1	66	68	24	47
I	2	60		35	
I	3	66		49	
I	4	78		80	

n.d. = not detected, MDL < 14 ppm Ru

standard No. 527 as known, the Se content of pyrrhotite standard No. 533 was calculated to be 1611 ppm, which is within 5.2% of the weighed-in value of 1700 ± 65.

At levels of about 200 ppm and less, we estimate the results to be accurate to within ±35% of the amount present. Thus, for replicate analyses, deviation by more than 35% from the mean value is indicative of either inhomogeneity in distribution of elements or contribution from an unresolved mineral impurity. Of all elements analyzed, it appears that Zn is distributed inhomogeneously in Sudbury chalcopyrite and that Ru may also be inhomogeneous in one grain of Stillwater pentlandite (grain I). All other elements detected and measured appear to be homogeneously distributed as solid solutions in their host-mineral matrix. In addition, for replicate analyses, such a distribution is also indicative of good analytical reproducibility.

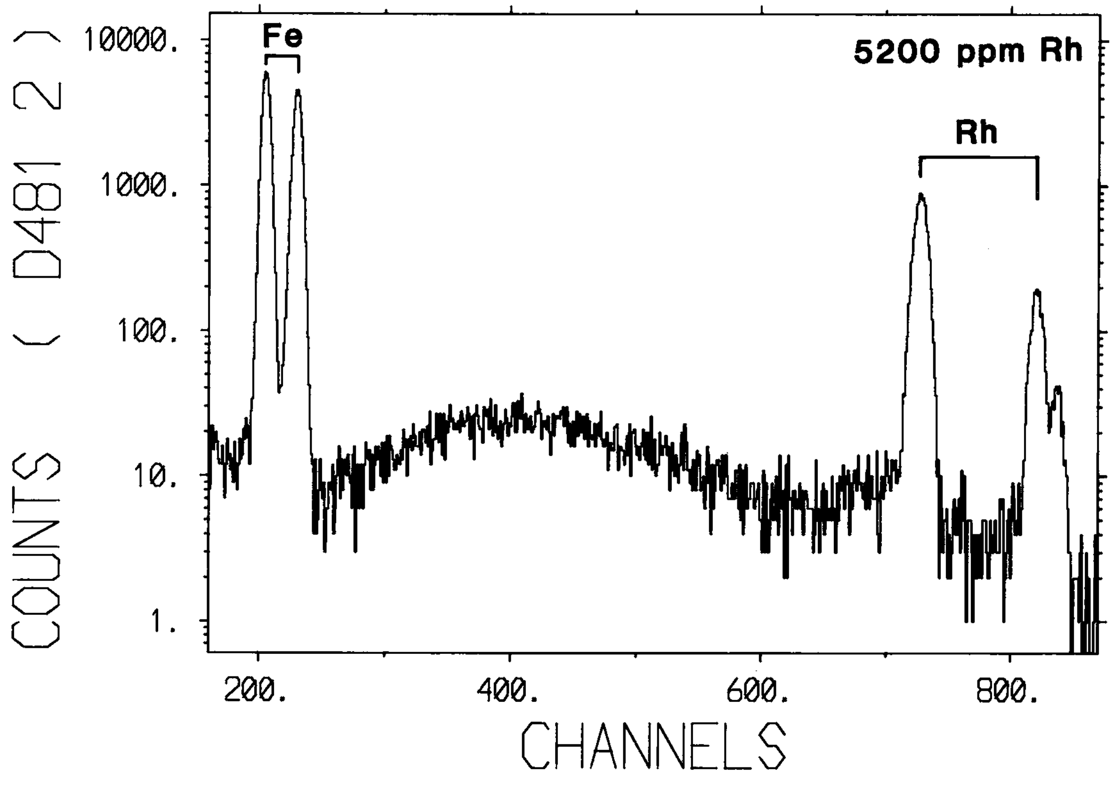

FIG. 11. X-ray spectrum of a synthetic pyrrhotite with 5200 ppm Rh, which illustrates the well-resolved Rh$K\alpha$ and Rh$K\beta$ peaks at 3 MeV proton excitation.

TABLE 8. MINIMUM DETECTION-LIMITS FOR SUDBURY SULFIDES

Mineral	# grains	Accumulated charge (μC)	MeV	MDL(ppm)
chalcopyrite	7	6.0	3	5±1.75 Pd
chalcopyrite	4	7.1	4	2.1±0.7 Pd
chalcopyrite	7	5.0	3	4.7±1.6 Rh
chalcopyrite	4	7.1	4	1.9±0.7 Rh
pentlandite	10	5.0	3	6±2.1 Pd
pentlandite	7	7.1	4	1.8±0.6 Pd
pentlandite	10	5.0	3	4.8±1.7 Rh
pentlandite	7	7.1	4	1.6±0.6 Rh
pyrrhotite	9	4.5	3	5±1.75 Pd
pyrrhotite	4	7.1	4	1.2±0.4 Pd
pyrrhotite	9	4.5	3	4±1.4 Rh
pyrrhotite	4	4.4	4	3.0±1.0 Rh

There also appears to be no indication of any contribution from an unresolved impurity in any of the analyses. This is always a concern because protons penetrate more deeply into sulfides than do electrons. For example, it was calculated that at 3 MeV, the proton beam penetrated into these sulfides to a depth of about 51 to 57 μm and from 82 to 92 μm at 4 MeV. Apparently, if there were unresolved inclusions, the impurity elements were not sufficiently excited to release their characteristic X-rays or the characteristic X-rays could not escape from such depths in the sample to permit their detection.

The sensitivity of the PIXE technique requires great care in sample preparation to avoid misleading results. Two examples of this type of problem were experienced. Silver paint, used to improve contacts between the sample mount and the sample stage, can flake and be redeposited on the sample surface. These flakes may be 0.1 μm in diameter or less and will still be picked up by the proton microprobe (Figs. 13,14). Material used in the polishing process may lodge in microcavities in the sample and be detected. The polycrystalline nature of some synthetic standards results in a somewhat porous surface, which can retain very small particles from the Pb polishing laps. This occurred several times, giving rise to small peaks for Pb in the spectrum of a synthetic standard.

Selenium solid-solution in sulfides

Hawley & Nichol (1959) presented an excellent discussion of the Se content of sulfides, including state-of-the-art data by XRF for Sudbury chalcopyrite and pyrrhotite. They reported values of 100 (33–165) ppm for 21 samples of South-Range chalcopyrite, 54 (18–83) ppm for 50 North-Range and 72 (17–230) ppm for 51 South-Range samples of pyrrhotite. These results compare very favorably with the present proton-microprobe results, but it has not been possible to assign all the Se content from bulk analyses to solid solution of Se in the major sulfides.

Cabri & Laflamme (1976) reported that Se also occurs as a solid solution in altaite, based on four analyses, but in quantities up to only 1.1 wt.%. Intensive studies of Sudbury ores by ore microscopy over many years have led to the discovery (unpublished) of only one occurrence of a selenide mineral (clausthalite), suggesting that essentially all the Se is in solid solution in the major sulfides, a conclusion confirmed by our results. Bulk analyses for Se (unpublished) have also indicated that the Se content is bimodal when one compares Frood-Stobie ore with ore from other parts of the Sudbury basin. Thus, the already narrow range in Se values in all three sulfides reported here may be narrower still. Fewer detailed mineralogical studies have been performed on Stillwater samples; therefore, there are no published data available on Se distribution. The present data suggest that, whereas the same sulfides contain Se as at Sudbury, the Stillwater sulfides have greater Se contents. The two Se-free grains of Stillwater pyrite may be of secondary origin.

S/Se ratios in sulfides

The genetic implications of S/Se ratios apparently lost their earlier promise when it was discovered that sedimentary sulfides were not exclusively low in Se and that some magmatic–hydrothermal sulfides were not high in Se. A brief review of the status of S/Se ratios in ore genesis is given in Stanton (1972, p. 170-176). However, low S/Se ratios are still being quoted in current studies of ore deposits with the proviso that, though consistent with a proposed magmatic–hydrothermal origin, low ratios are not proof of such an origin (Groves *et al.* 1979, Green & Naldrett 1981, McQueen 1981). The more accurate S/Se ratios obtainable by proton-microprobe analyses will reactivate interest in this genetic and geochemical problem by providing more definitive and specific data for individual mineral species. For Sudbury sulfides, therefore, the range of values of the S/Se ratio is as follows:

chalcopyrite	1470 to 8750
pentlandite	1980 to 6510
pyrrhotite	1710 to 12770

For Stillwater sulfides, though representative of fewer grains, the values of the S/Se ratio are:

chalcopyrite	1250 and 1260
pentlandite	490 to 1020
pyrrhotite	1140 and 1630

The large ranges in S/Se ratio may have contributed to problems in genetic interpretation.

Solid solution of Zn in chalcopyrite

Zinc contents of synthetic chalcopyrite and intermediate solid solution (*iss*) (Cabri 1973) have been reported by Wiggins & Craig (1980) and by Hutchison & Scott (1981) as part of their investigations of sphalerite in the Cu–Fe–Zn–S system. At 1 bar the Zn content of *iss* decreases with temperature (with concomitant increase of Fe) but ranges widely, de-

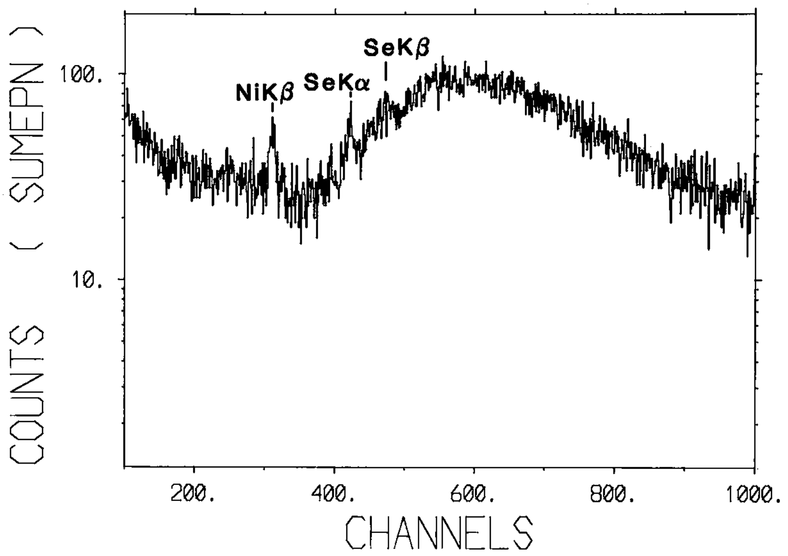

FIG. 12. X-ray spectrum representing the summation of analyses of seven Sudbury pentlandite grains at 4 MeV proton excitation. The only peaks visible are Ni*K*β, Se*K*α and Se*K*β.

pending upon the phase assemblage. For example, Wiggins & Craig (1980) reported ranges of 1.91–18.9 wt.% Zn in *iss* at 800°C and 2.15–8.57 wt.% Zn at 600°C. The lowest Zn contents for *iss* were reported by Hutchison & Scott (1981) at 353°C and 5 kbar pressure: 0.47 and 0.24 wt.% Zn. Hutchison & Scott (1981) also reported that iron-rich chalcopyrite in equilibrium with sphalerite + pyrite + pyrrhotite at 353°C and 5 kbar contains 0.35 wt.% Zn. Linear extrapolation of the 1 bar and 5 kbar curves of experimentally derived Zn contents of Hutchison & Scott (1981) *versus* temperature gives 0% Zn at about 85°C. This suggests that either the experimental data obtained on *iss* are not applicable to natural chalcopyrite or that the experimental curves deviate from linearity at lower temperatures and Zn contents, possibly owing to the change in phase assemblage at 334°C (Yund & Kullerud 1966). A third possibility is that a small quantity of Zn in chalcopyrite, such as at Sudbury, is not at equilibrium. The Zn values were not thought to be due to microscopic inclusions of sphalerite because of the careful microscopic examination coupled with lack of typical trace-elements such as Cd. This whole aspect requires further detailed study.

TABLE 9. OBSERVED AND CALCULATED RANGES FOR ELECTRON MICROPROBE ANALYSES FOR TRACE ELEMENTS IN SYNTHETIC STANDARDS

No.	Compound	weighed % trace element	range obs.	range calc.	HOM Index
527	Cu-Fe-(S,Se)	0.15	±13%	±10%	3
528	Cu-(Fe,Zn)-S	0.15	± 9%	± 6%	3
533	Fe-(S,Se)+Fe	0.17	±62%	±30%	3
542	$(Fe,Pd)_9S_{10}$	0.15	±16%	±11%	3
457	$(Fe,Ni,Pd)_9S_8$	0.65	± 5%	± 3%	3
481	$(Fe,Rh)_7S_8$	0.52	± 3%	± 3%	1
535	$(Fe,Ir)_9S_{10}$	0.12	±53%	±27%	3

Solid solution of platinum-group elements in sulfides

(a) *Sudbury*

Palladium and rhodium could not be detected in chalcopyrite, pentlandite and pyrrhotite at detection levels ranging from 1.2 to 3 ppm (Table 8). As explained above, these detection levels were achieved by summing the data for a series of grains of each species. In order that these minimum levels of detection be correct, one must assume that very dilute solid-solutions of the PGE, if present, would be uniform in grains of the same species so that their presence would be cumulative and additive. Because the detection level decreases only by the square root of the duration of the analysis, it is not realistic to attempt to lower the detection levels much further by Micro-PIXE. Another method, such as TAMS, may be better suited for the Sudbury sulfides, if a microbeam were employed. It would, however, be worthwhile to analyze more grains from Sudbury at 4 MeV in order to make the analytical data more representative statistically.

Platinum could not be detected at a MDL level of about 50–60 ppm. This relatively high MDL was obtained from a direct comparison of the spectra of the synthetic Pt standard against each unknown. We could not use the matrix-correction program of Blank (1982), as it does not calculate *L* lines. Matrix corrections are much more difficult in the case of *L* lines and are also far less accurate (Rogers *et al.* 1984). Therefore, the rough estimate given here is only correct within 50% relative. As mentioned above, peak interferences contribute additional difficulties in Pt detection.

(b) *Stillwater*

The success in measuring trace quantities of Pd, Rh and Ru in Stillwater pentlandite also confirms the potential of Micro-PIXE analyses. Platinum-group-element deposits of the Merensky Reef, the Noril'sk and the Platreef types (*cf.* Cabri & Naldrett 1984) are excellent candidates for Micro-PIXE analyses because electron-microprobe work has already demonstrated solid solution of Pd in pentlandite from these types of deposit (Cabri & Laflamme 1981). For example, the assertion by Kinloch (1982) that all the Rh in the Merensky Reef is in solid solution in pentlandite could easily be proved or further quantified when considered together with the Rh content of Rustenburg sperrylite reported by Kingston & El-Dosuky (1982).

Genetic implications of PGE distribution

As stated earlier, there have been few attempts at determining the PGE distribution by direct analytical methods. The earliest was by Genkin *et al.* (1973), who first reported solid solution of Pd in pentlandite by *in situ* analyses (electron microprobe). They demonstrated that for the Talnakh deposit, the highest Pd content (123–60 ppm) was found in the "flame"-like pentlandite exsolved in early pyrrhotite ores, and the lowest Pd content (59–32 ppm) occurs in phenocryst-like pentlandite grains and large pentlandite phenocrysts in the later cubanite, chalcopyrite and talnakhite ores. Intermediate Pd contents of 110–52 ppm were found in the more massive bands of pentlandite that occur at chalcopyrite–pyrrhotite boundaries. Genkin *et al.* (1973) further observed that the ratio [conc. Pd(ss)]/[conc. Pd(total)] is inversely proportional to [conc. Pd(total)] in the sequence pyrrhotite ores → cubanite ores → talnakhite ores. That is, the solid solution of Pd decreases with a concomitant increase of total Pd with time as Cu increases and $f(S_2)$ decreases.

This study was followed by the analytical and experimental studies of Distler *et al.* (1974, 1977, 1981) and of Skinner *et al.* (1976) on phase relations in ternary portions of the system Pt–Pd–Fe–As–S. The experiments of Distler *et al.* and Skinner *et al.* indicate that for magmatic Cu–Ni sulfide ores, the Pd will be concentrated in the final liquid, which is also favored by Cu over monosulfide solid solution (*mss*) (Craig & Kullerud 1969). Distler *et al.* (1977) have also demonstrated that the *mss* structure initially be-

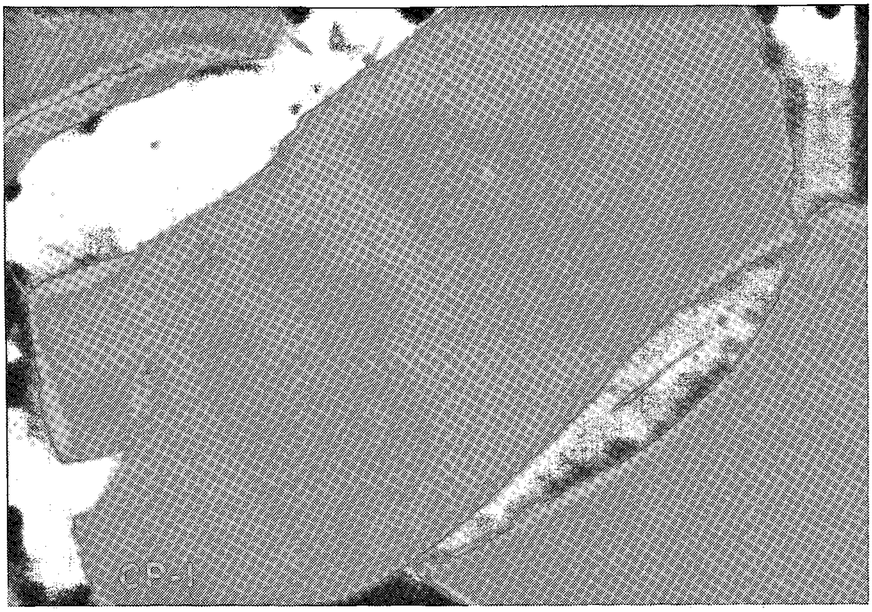

FIG. 13. Scanning-electron micrograph of Sudbury chalcopyrite (grain cp–1) showing several proton-beam contamination marks, including a white spot (< 1 μm wide) of silver-rich surface impurity at the edge of one of the contamination marks (see Fig. 14). Scale: 10 μm = 0.9 cm.

comes enriched in Rh, and especially in Ru, with respect to Pd. The early pentlandite, which forms irregular band-like aggregates, apparently crystallizes with Fe > Ni and, on cooling, gradually changes in composition to Ni > Fe with an accompanying increase of Pd in solid solution. The later pentlandite, which exsolves from pyrrhotite in a subsolidus reaction, was found to cause no redistribution of Pd (after exsolution) and is characterized by a Fe > Ni composition. These experimental results were discussed by Distler *et al.* (1977, 1981) in terms of the PGE distribution in the Noril'sk ores as follows. The early pyrrhotite ores, formed under higher $f(S_2)$, are always enriched in Rh, Ru, Ir and Os, whereas the PGE (except for Pt) occur mainly as dilute solid-solutions rather than as PGM. The Cu-rich cubanite, talnakhite and mooihoekite in the later ores, formed under low $f(S_2)$, are enriched in Pd and Pt, which occur mainly as PGM, rather than as a solid solution. They also concluded that the composition of pentlandite is directly proportional to the S content for the different ores, *i.e.*, high-Ni and Pd-bearing pentlandite is found in high-S ores. In contrast, Kinloch (1982) concluded that in the Merensky Reef ores, PGE solid solution is highest for ores formed under low $f(S_2)$ [and high $f(O_2)$], as determined by an abundance of Pt–Fe alloys and paucity of Pt–Pd sulfides.

None of the pentlandite grains analyzed from Sudbury and Stillwater are of the exsolution type because coarse-grained pentlandite was specially selected to provide grains with the largest contamination-free areas. These would, therefore, correspond to type-I pentlandite of Distler *et al.* (1977), which changed from an original composition of Fe > Ni to Ni > Fe and also whose Pd content in solid solution increased on cooling. Since we have not found measureable quantities of the PGE in Sudbury pentlandite, we can only compare values of the Fe/Ni ratio (Table 10). All grains of Sudbury pentlandite have Ni > Fe, with a Ni/Fe ratio ranging from 1 to 1.11 (atomic). This is comparable to a ratio of 1 to 1.22 for pentlandite from the Inco ores (unpublished electron-microprobe data). This relatively narrow range contrasts markedly with the extreme range of the Ni/Fe ratio in pentlandite, *e.g.*, 0.58 for that in

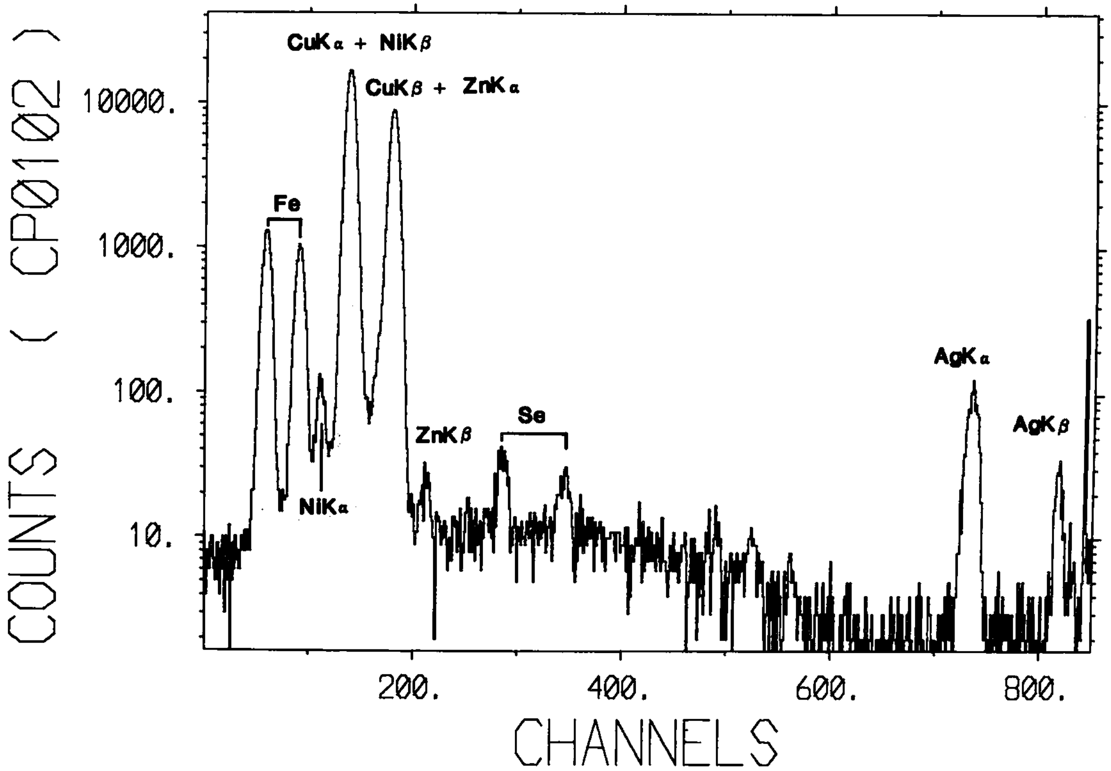

FIG. 14. X-ray spectrum of Sudbury chalcopyrite (grain cp–1, analysis cp–1–2) with well-resolved Ag peaks due to surface contamination shown in Figure 13. This is the only chalcopyrite spectrum showing Ni. The Ni is therefore also attributed to the silver paint rather than to an impurity of pentlandite or other Ni-bearing mineral. Minor effects due to peak pile-up are visible between Se*K*β and Ag*K*α.

TABLE 10. ELECTRON-MICROPROBE ANALYSES OF PENTLANDITE

	Weight per cent						Atomic proportions						
Sudbury	Fe	Ni	Co	Pd	S	Totals	Fe	Ni	Co	Pd	Σ	S	Ni/Fe
pn-1	30.4	34.3	2.3	n.d.	33.1	100.1	4.22	4.53	0.30	-	9.05	8.00	1.07
pn-3	32.0	33.8	1.4	"	33.2	100.4	4.43	4.45	0.19	-	9.07	8.00	1.00
pn-11	30.8	34.3	2.0	"	33.1	100.2	4.28	4.52	0.26	-	9.06	8.00	1.06
pn-29	31.0	34.4	1.7	"	33.1	100.2	4.30	4.54	0.23	-	9.07	8.00	1.06
pn-30	31.6	34.2	1.6	"	33.4	100.8	4.35	4.48	0.21	-	9.04	8.00	1.03
pn-34	30.6	35.4	0.98	"	33.3	100.28	4.22	4.64	0.13	-	8.99	8.00	1.10
pn-38	30.6	35.0	2.0	"	33.4	101.0	4.21	4.58	0.26	-	9.05	8.00	1.09
Stillwater													
pn-F	30.6	35.2	0.50	0.30	33.9	100.50	4.15	4.54	0.06	0.02	8.77	8.00	1.09
pn-G	29.7	35.7	1.1	0.08	33.7	100.28	4.05	4.63	0.14	0.01	8.83	8.00	1.14
pn-H	31.0	35.2	0.37	0.51	33.9	100.98	4.20	4.54	0.05	0.04	8.83	8.00	1.08
pn-I	31.8	34.0	0.67	0.31	33.7	100.48	4.33	4.41	0.08	0.02	8.84	8.00	1.02

n.d. = not detected. The seven Sudbury pentlandite grains had been analyzed with the proton microprobe at 4MeV.

mooihoekite + cubanite massive ores to 1.76 for that in bornite + chalcopyrite massive ores at Noril'sk (Genkin *et al.* 1981). The Ni/Fe ratio for four grains of Stillwater pentlandite overlap the Sudbury values, but reach a maximum of 1.14 (Table 10). There does not, however, appear to be any correlation of Ni/Fe ratio with Pd content. This is confirmed by a Ni/Fe ratio of 1.02 determined for another grain of Stillwater pentlandite containing 1.37 wt.% Pd. Unpublished electron-microprobe data on 23 pentlandite grains from the Platreef-type Lac-des-Iles deposit (*cf.* Cabri & Laflamme 1979) indicate a Ni/Fe ratio in the range from 1.06 to 1.60. Whereas there is no clear-cut relationship between the Ni/Fe ratio and Pd content, the pentlandite containing the most Ni has the lowest Pd content. It is, therefore, not possible at this time to relate the extent of solid solution of PGE in Sudbury and Stillwater pentlandite to the value of the Ni/Fe ratio or to its genesis, as has been done for the Noril'sk ores.

Importance of MDL values in mineral beneficiation

In order to achieve the best recovery of elements of economic interest, it is essential to know their distribution as precisely as possible. A case in point is the ability to assign only about 40% of the Pd in a particular fraction of Sudbury ore to specific minerals, in contrast to about 91% of the Pt (Cabri & Laflamme 1984). It is essential to know whether the unassigned Pd occurs as a dilute solid-solution [and in which mineral(s)] or as PGM. Only then can further research be directed at improving recoveries.

We can apply the present MDL for Pd in Sudbury pentlandite to Cabri's & Laflamme's (1984) detailed mineralogical study of the Clarabelle bulk concentrate. The +325 mesh fraction had been assigned calculated contents of 12.96% Ni and 2.75 ppm Pd, but 1.64 ppm Pd (or ~ 60%) could not be accounted for on the basis of the observed mineralogy. Taking an average Ni content of 34.5% for pentlandite (Table 10) and 0.7% Ni (based on numerous unpublished data) for the estimated 15% pyrrhotite present in this particular +325 mesh fraction, we calculate that this fraction contains 37.3% pentlandite. If all the unaccounted-for Pd is in solid solution in the 37.3% of pentlandite, the pentlandite would then contain an average of 4.4 ppm Pd. This is well above our MDL of 1.8 ± 0.6 and the 2.3 ppm Pd content in the pentlandite separate (Table 1). This study indicates, therefore, that at least 60% of the unaccounted-for Pd (or 36% of the total Pd) in the Clarabelle bulk concentrate does *not* occur as a solid solution in pentlandite and that much more detailed mineralogical research is required to locate this missing fraction.

CONCLUSIONS

1. Quantitative proton-microprobe analyses, down to ~ 1 ppm for some elements, are feasible for sulfide minerals. The method shows great potential, with many applications in the fields of mineralogy and geochemistry of sulfides and other minerals.
2. Chalcopyrite, pentlandite and pyrrhotite from Sudbury and Stillwater contain Se in solid solution in quantities consistent with the expected low S/Se ratios and the lack of selenide minerals.
3. Sudbury chalcopyrite also contains a heterogeneous solid-solution of Zn, which ranges from < 35 to 2570 ppm.
4. The effects, if any, on the flotability of sulfides, owing to the presence of trace elements such as Se or Zn, should be investigated.
5. The PGE were not detected in the three Sudbury sulfides investigated; however, additional proton-microprobe analyses at 4 MeV of pyrrhotite and pentlandite, especially of exsolution pentlandite, are warranted for better statistical treatment of the MDL.
6. At Sudbury, pentlandite remains the most likely site for the location of dilute Pd solid-solution (if any), but the MDL determined in this study has considerably reduced the significance of the solid solu-

tion of Pd in pentlandite as a consideration for improvements in mineral beneficiation and, by implication, has increased the need for further detailed mineralogical research on the nature of the PGM present in the ores.

7. Stillwater pentlandite contains variable quantities of Pd, Rh and Ru in solid solution. More detailed work could provide a detailed understanding of the distributions of PGE in the Stillwater Complex.

8. There is no apparent correlation between the Ni/Fe ratio in pentlandite and its PGE content, either at Sudbury or Stillwater.

ACKNOWLEDGEMENTS

The authors are grateful to A. Mandel and J. Janicke for help with some proton-microprobe analyses, to C. Ender for on-line data collection, and to R.G. Pinard for the quantitative image-analyses. One of us (L.J.C.) is particularly grateful to the Max-Planck-Institut für Kernphysik for the opportunity of working with the Heidelberg proton microprobe and for many courtesies. We also acknowledge the support and encouragement of the Inco Metals Company at Copper Cliff, Toronto and at the J. Roy Gordon Research Laboratory. We also record our appreciation for critical comments to R.A. Alcock, R.M. Buchanan and P.R. Mainwaring, Editor R.F. Martin, Associate Editor S.D. Scott, B.J. Skinner and two other referees.

REFERENCES

BHATIA, D.M.S. & HAGNI, R.D. (1979): Laser probe determinations of trace element concentrations in sulfide minerals from the Magmont Mine, Viburnum Trend, southeast Missouri. *Trans. AIME* **268**, 1847-1855.

BLANK, H. (1982): *Spurenelemente in Koexistierenden opaken Oxyden lunarer gesteine gemessen mit einer Protonenmikrosonde.* Ph.D. thesis, Univ. Heidelberg, West Germany.

BOSCH, F., EL GORESY, A., HERTH, W., MARTIN, B., NOBILING, R., POVH, B., REISS, H.D. & TRAXEL, K. (1980): The Heildelberg proton microprobe. *Nucl. Sci. Appls.* **1**, 33-35.

______, ______, MARTIN, B., POVH, B., NOBILING, R., SCHWALM, D. & TRAXEL, K. (1978): The proton microprobe: a powerful tool for nondestructive trace element analysis. *Science* **199**, 765-768.

CABRI, L.J. (1973): New data on phase relations in the Cu–Fe–S system. *Econ. Geol.* **68**, 443-454.

______ (1981): Mineralogy and distribution of the platinum-group in mill samples from Cu–Ni deposits from the Sudbury, Ontario area. *In* Precious Metals, Proc. 4th International Precious Metals Inst. Conf., Pergamon Press, Toronto, 23-34.

______, 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.

______, CRIDDLE, A.J., LAFLAMME, J.H.G., BEARNE, G.S. & HARRIS, D.C. (1981): Mineralogical study of complex Pt–Fe nuggets from Ethiopia. *Bull. Minéral.* **104**, 508-525.

______ & LAFLAMME, J.H.G. (1976): The mineralogy of the platinum-group elements from some copper–nickel deposits of the Sudbury area, Ontario. *Econ. Geol.* **71**, 1159-1195.

______ & ______ (1979): Mineralogy of samples from the Lac des Iles area, Ontario. *Can. Centre for Mineral and Energy Tech., Rep.* **79–27.**

______ & ______ (1981): Analyses of minerals containing platinum-group elements. *In* Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **23**, 151-173.

______ & ______ (1984): Mineralogy and distribution of platinum-group elements in mill products from Sudbury. *2nd Int. Conf. Appl. Mineral., Proc.* (in press).

______, ______, STEWART, J.M., TURNER, K. &. SKINNER, B.J. (1978): On cooperite, braggite, and vysotskite. *Amer. Mineral.* **63**, 832-839.

______ & NALDRETT, A.J. (1984): The nature of the distribution and concentration of platinum-group elements in various geological environments. *Int. Geol. Congress 27th (Moscow), Proc.* **10**, 17-46.

CHEN, J.R., KNEISS, H., MARTIN, B., NOBILING, R., PELTE, D., POVH, B. & TRAXEL, K. (1981): PIXE microprobe analysis with the Heildelberg proton microprobe. *Nucl. Instr. Methods* **181**, 141-148.

COOKSON, J.A. (1981): The use of the PIXE technique with nuclear microprobes. *Nucl. Instr. Methods* **181**, 115-124.

CRAIG, J.R. & KULLERUD, G. (1969): Phase relations in the Cu–Fe–Ni–S system and their application to magmatic ore deposits. *In* Magmatic Ore Deposits (H.D.B. Wilson, ed.). *Econ. Geol., Mon.* **4**, 344-358.

CROCKET, J.H. & CABRI, L.J. (1981): Analytical methods for the platinum-group elements. *In* Platinum-Group Elements: Mineralogy, Geology, Recovery. (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **23**, 71-81.

DISTLER, V.V., CHIRINA, N.A. & BELOUSOV, G. YE. (1974): Rhodium in pyrrhotite from copper–nickel ore of the Noril'sk deposits. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **214**, 205-208.

______, GENKIN, A.D., & GLADYSHEV, G.D. (1981): Conditions of formation of copper–nickel ores. *In* Copper–Nickel Sulphide Ores of the Noril'sk Deposits (T.N. Shadlun, ed.). Nauka, Moscow (in Russ.).

______, MALEVSKIY, A.YU & LAPUTINA, I.P. (1977): Distribution of platinoids between pyrrhotite and pentlandite in crystallization of a sulfide melt. *Geochem. Int.* **146**, 30-40.

GENKIN, A.D., DISTLER, V.V., LAPUTINA, I.P. & FILIMONOVA, A.A. (1973): Geochemistry of palladium in copper–nickel ores. *Geochem. Int.* **10**, 1007-1013.

______, EVSTIGNEEVA, T.L., FILIMONOVA, A.A., KOVALENKER, V.A. & LAPUTINA, I.P. (1981): Mineralogy of the Noril'sk copper–nickel ores. *In* Copper–Nickel Sulphide Ores of the Noril'sk deposits (T.N. Shadlun, ed.). Nauka, Moscow (in Russ.).

______, LAPUTINA, I.P. & MURAVITSKAYA, G.N. (1974): Ruthenium- and rhodium-containing pentlandite – an indicator of hydrothermal mobilization of platinum metals. *Geol. Rudnykh Mestorozh., No. 6,* 102-106 (translation (1976): *Int. Geol. Rev.* **18**, 723-728).

GREEN, A.H. & NALDRETT, A.J. (1981): The Langmuir volcanic peridotite-associated nickel deposits: Canadian equivalents of the Western Australian occurrences. *Econ. Geol.* **76**, 1503-1523.

GROVES, D.I., BARRETT, F.M. & MCQUEEN, K.G. (1979): The relative roles of magmatic segregation, volcanic exhalation and regional metamorphism in the generation of volcanic-associated nickel ores of Western Australia. *Can. Mineral.* **17**, 319-336.

HALL, S.R. & STEWART, J.M. (1973): The crystal structure of argentian pentlandite $(Fe,Ni)_8AgS_8$, compared with the refined structure of pentlandite $(Fe,Ni)_9S_8$. *Can. Mineral.* **12**, 169-177.

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**, 497-502.

HAWLEY, J.E. & NICHOL, I. (1959): Selenium in some Canadian sulfides. *Econ. Geol.* **54**, 608-628.

HILLENKAMP, F., UNSOLD, E., KAUFMANN, R. & NITSCHE, R. (1975): A high-sensitivity laser microprobe mass analyzer. *Appl. Phys.* **8**, 341-348.

HUTCHISON, M.N. & SCOTT, S.D. (1981): Sphalerite geobarometry in the Cu–Fe–Zn–S system. *Econ. Geol.* **76**, 143-153.

KEAYS, R.R. & CROCKET, J.H. (1970): A study of precious metals in the Sudbury Nickel Irruptive ores. *Econ. Geol.* **65**, 438-450.

KINGSTON, G.A. & EL-DOSUKY, B.T. (1982): A contribution on the platinum-group mineralogy of the Merensky Reef at the Rustenburg platinum mine. *Econ. Geol.* **77**, 1367-1384.

KINLOCH, E.D. (1982): Regional trends in the platinum-group mineralogy of the Critical Zone of the Bushveld Complex, South Africa. *Econ. Geol.* **77**, 1328-1347.

LIEBL, H. (1975): Ion probe microanalysis. *J. Phys.* **E8**, 797-808.

LITHERLAND, A.E. (1980): Ultrasensitive mass spectrometry with accelerators. *Ann. Rev. Nucl. Part. Sci.* **30**, 437-473.

MCQUEEN, K.G. (1981): The nature and metamorphic history of the Wannaway nickel deposit, Western Australia. *Econ. Geol.* **76**, 1444-1468.

MITCHELL, R.H. & KEAYS, R.R. (1981): Abundance and distribution of gold, palladium and iridium in some spinel and garnet lherzolites: implications for the nature and origin of precious metal-rich intergranular components in the upper mantle. *Geochim. Cosmochim. Acta* **45**, 2425-2442.

NALDRETT, A.J., INNES, D.G., SOWA, J. & GORTON, M.P. (1982): Compositional variations within and between five Sudbury ore deposits. *Econ. Geol.* **77**, 1519-1534.

RAJAMANI, V. & PREWITT, C.T. (1973): Crystal chemistry of natural pentlandites. *Can. Mineral.* **12**, 178-187.

ROGERS, P.S.Z., DUFFY, C.J., BENJAMIN, T.M. & MAGGIORE, C.J. (1984): Geologic applications of nuclear microprobes: progress and problems. *3rd Int. Conf. on PIXE, Proc., Nucl. Instr. Methods* (in press).

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

______, GORTON, M.P., WILSON, G.C., KILIUS, L.R., LITHERLAND, A.E., ELMORE, D. & GOVE, H.E. (1982): Measurement of Pt and Ir at sub-ppb levels using tandem-accelerator mass spectrometry. *Can. Mineral.* **20**, 111-119.

SKINNER, B.J., LUCE, F.D., DILL, J.A., ELLIS, D.E., HAGAN, H.A., LEWIS, D.M., ODELL, D.A., SVERJENSKY, D.A. & WILLIAMS, N. (1976): Phase relations in ternary portions of the system Pt–Pd–Fe–As–S. *Econ. Geol.* **71**, 1469-1475.

STANTON, R.L. (1972): *Ore Petrology.* McGraw-Hill, New York.

TODD, S.G., KEITH, D.W., LE ROU, L.W., SCHISSEL, D.J., MANN, E.L. & IRVINE, T.N. (1982): The J–M platinum–palladium reef of the Stillwater Complex, Montana. I. Stratigraphy and petrology. *Econ. Geol.* **77**, 1454-1480.

WESTLAND, A.D. (1981): Inorganic chemistry of the platinum-group elements. *In* Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **23**, 5-18.

WIGGINS, L.B. & CRAIG, J.R. (1980): Reconnaissance of the Cu-Fe-Zn-S system: sphalerite phase relationships. *Econ. Geol.* **75**, 742-751.

YUND, R.A. & KULLERUD, G. (1966): Thermal stability of assemblages in the Cu-Fe-S system. *J. Petrology* **7**, 454-488.

ZIEGLER, J.F., ed. (1975): *New Uses of Ion Accelerators.* Plenum Press, New York.

Received September 20, 1983; revised manuscript accepted January 11, 1984.

APPENDIX

To correct for thick targets the formula used is:

$$C_u = \frac{N_u \cdot A_u \cdot R_k \cdot \sigma_k}{N_k \cdot A_k \cdot R_u \cdot \sigma_u} \cdot C_k \cdot f \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

symbols:	u	unknown, k known
	C	concentration in ppm
	N	number of counts
	A	atomic weight of element
	R	value from equation (3)
	σ	density of matrix

$$f \begin{cases} 1, \text{ if u and k are measured at the same energy} \\ 9/16, \text{ if u was at 4 MeV and k at 3 MeV} \\ 16/9, \text{ if u was at 3 MeV and k at 4 MeV} \end{cases}$$

Equation (1) is derived from the well-known formula

$$N = n_p \frac{cN_L}{A} \cdot \frac{\Delta\Omega}{4\pi} \cdot R \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

symbols:	N	number of detected X-ray quanta
	n_p	number of arriving protons
	c	concentration in g/cm^3
	N_L	Avogadro's number in parts/Mol
	$\Delta\Omega$	solid angle of the detector
	A	atomic weight in g/Mol
	R	value from equation (3)

The change in proton energy, in the ionization cross-section and in absorption of the X rays by the target, as a function of penetration depth, has to be taken into account because the protons penetrate deeply into the samples (20–100 μm). This is done by integrating over the sample thickness with a computer program that gives the R values (equation 3).

$$R = \epsilon w k \int_0^\infty \delta\, [E_p(z)] T(z) dz \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

symbols:	ϵ	detector efficiency
	w	fluorescence yield
	k	transition probability
	δ	ionization cross-section
	E_p	energy of the protons
	z	penetration depth
	T	transmission