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TRACE ELEMENT ANALYSIS OF SULFIDE CONCENTRATES FROM SUDBURY BY ACCELERATOR MASS SPECTROMETRY

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ABSTRACT

All the platinum-group elements (PGE), plus silver and gold (Pd, Rh, Ru, Pt, Ir, Os, Ag and Au) have been detected at background levels in concentrates of chalcopyrite, pyrrhotite and pentlandite derived from the mines of Sudbury, Ontario. There is clear evidence of partitioning of all the elements among these phases, though in no cases except Ag do concentrations reach ppm levels. Hence these sulfides are unlikely targets for metallurgical extraction of PGE in these samples. Measurements of pressed concentrate grains by accelerator mass spectrometry may best be described as semiquantitative because of the wide range of composition of the mineral grains, and also because of difficulties in calibration. However, the extraordinarily low levels of detection (sub-ppb) on microgram quantities of material and short data-collection times (100 to 500 seconds per element) show this to be among the most sensitive of analytical methods.

Keywords: platinum-group elements (PGE), trace elements, accelerator mass spectrometry (AMS), secondary ion mass spectrometry (SIMS), proton induced X-ray emission (PIXE), sulfide concentrates, Sudbury, Ontario.

SOMMAIRE

Tous les éléments du groupe du platine ainsi que l'or et l'argent ont été détectés à un niveau de trace dans des concentrés de chalcopyrite, de pyrrhotite et de pentlandite provenant des mines à Sudbury, Ontario. Tous les éléments sont répartis parmi ces phases, bien que dans aucun cas, à l'exception de l'argent, les concentrations atteignent le niveau du ppm. Ainsi, ces sulfures sont des choix improbables pour l'extraction métallurgique viable des éléments du groupe du platine dans ces échantillons de minerai. L'étude de grains compressés par spectrométrie de masse avec accélérateur est une méthode semi-quantitative à cause de la grande diversité de composition des minéraux ainsi que des difficultés de calibrage. Par ailleurs, les très faibles niveaux de détection (sub-ppb) dans des échantillons de quelques microgrammes, ainsi que le court laps de temps requis pour l'analyse (100 à 500 secondes par élément), démontrent que cette méthode d'analyse est l'une des plus sensibles.

Mots-clés: éléments du groupe platine, éléments traces, spéctrometrie de masses avec accélérateur, spectrométrie de masses des ions secondaires (SIMS), emission des rayons X induit par les protons (PIXE), concentrés de sulfures, Sudbury, Ontario.

INTRODUCTION

The determination of the precious metal content of individual mineral phases has been the goal of many investigations. The bulk analysis of a mineral separate for trace constituents always runs the risk that a few highly enriched phases are included in the analyzed material. These may be inclusions in the host mineral or individual grains in which the element of interest is a major phase. As an example, a single grain of sperrylite ($PtAs_2$) in a million equally sized grains of pyrite would yield a 1.2 ppm Pt content for the concentrate. It is virtually impossible to ensure that such levels of impurity do not exist; although bulk analytical methods have adequate sensitivity to measure at the sub-ppm level, the results thus cannot reliably be used to infer the trace-element content of the major mineral phase.

Microprobe analysis of individual grains avoids the problem of inclusions and impurities, but now sensitivity becomes the difficulty. The 100–400 ppm range is the detection limit with the electron probe (beam size 1–10 μm), mainly because of the background contribution from the X-ray continuum generated from the electron excitation. Micro-PIXE (Proton Induced X-ray Emission), which uses a proton probe (beam size 5–20 μm), has a smaller X-ray continuum, thus yielding a sensitivity 3 to 30 times better than the electron probe (Remond *et al.* 1987). In the region of the periodic table containing the elements of interest in this paper, the "30" end of the range is probably appropriate. Details of

TABLE 1. Pt AND Pd CONTENTS (PPM) OF THREE SUDBURY SULFIDE CONCENTRATES

	Pt	Pd
Chalcopyrite	0.59	0.56
Pentlandite	4.4	2.3
Pyrrhotite	0.31	0.25

trace-element analysis of minerals by micro-PIXE have been given by several authors, of whom Cabri *et al.* (1984) were among the first. These authors attempted to analyze individual grains in concentrates of chalcopyrite, pentlandite and pyrrhotite from Sudbury. The Pt and Pd contents of these concentrates, shown in Table 1, assay in the ppm range, which should just be detectable by proton microprobe, if present as solid solution in the main phase. Cabri *et al.* (1984) were unable to detect any PGE in the individual grains of these Sudbury concentrates, and deduced that Pd and Rh could not exceed 1.2 to 3 ppm, whereas Pt must be less than 50 to 60 ppm. The general conclusion was that the PGE are not dissolved at economically viable levels in these samples of chalcopyrite, pentlandite and pyrrhotite.

Secondary Ion Mass Spectrometry (SIMS), in the form of the ion microprobe, also has been used to tackle the problem of establishing the background levels of PGE in these sulfide phases. Chryssoulis *et al.* (1989) reported that the detection limit of the method on spots about 10 μm in diameter is at or above the levels of PGE in these phases, namely around the ppm level. The SIMS method suffers from a background of noise due to molecular overlaps, particularly in the high mass region, where atoms of many lighter elements may combine to give a molecule of almost identical mass to the element of interest. These effects may be reduced at the expense of sensitivity by voltage offset and high mass-resolution (Cabri & Chryssoulis 1990). Further, the dark current of the ion detector, which operates in the keV range, results in a count rate of about 0.05 per second, even where there is no signal, and this effectively establishes a very practical limit of detection. More recently, Chryssoulis & Cabri (1991) have determined the minimum detection limits (MDL) for Pt, Pd, Rh and Ir on a number of sulfide and oxide minerals using the ion microprobe on an area 60 μm in diameter. Summarizing their results, the MDL fall in the 10 to 100 ppb range, as based on the 3σ of the level of detector noise. The standards on which these MDL were determined range from 0.5 to 200 ppm. Whereas this latest MDL obtained with SIMS is considerably lower than the PIXE limit, no results of *in situ* analyses of PGE in minerals by low-energy SIMS at the ppb range have been reported, except in the recent oral presentation by Chryssoulis *et al.* (1991).

Accelerator Mass Spectrometry (AMS) may present a solution to this problem. This method is a variant on SIMS, but it uses a tandem accelerator to raise the energy of the extracted ions into the MeV range, where molecules may be eliminated and the particle counters do not suffer from the background noise seen in their low-energy counterparts. Thus we are able to count, and identify with great reliability, individual atoms extracted from a solid sample, though the efficiency may be as low as 1 atom detected per 10,000 extracted. The method has been described in some detail elsewhere (Rucklidge *et al.* 1982, 1990). AMS is most commonly used for measuring concentrations of rare long-lived radioisotopes such as ^{14}C or ^{129}I, which occur naturally at levels of about 1 part in 10^{12} of the stable major isotope, ^{12}C or ^{127}I. In terms of concentrations of trace elements, these measurements translate to levels of parts per trillion (ppt), and hence it is natural to think that AMS might be applied to the *in situ* analysis of individual mineral grains for trace elements. In principle, this is possible, but because the main use of these instruments is to generate as much signal from a homogeneous solid sample as possible, the primary beam that probes the sample surface is inevitably intense and relatively large. Typically, the beam current is 100 μA, and the beam diameter, 0.5 mm. Collimating the beam to micro-dimensions and lowering the current to safe levels would reduce the analytical performance considerably. It is likely that developments in this direction will take place (McDaniel *et al.* 1990), but no AMS instruments exist at the present time that are capable of performing micrometer-scale analyses.

Nevertheless, although the probing beam is far too large to be focused on individual grains of a sulfide concentrate, the amount of material required for analysis is extremely small. With normal AMS ion-source conditions, we have measured the rate of consumption of material in a pressed concentrate of pyrrhotite to be about 10^4 μm^3 per second or 0.05 μg per second; 5 μg or 10^6 μm^3 would be burned up in the course of a typical 100-second analysis. In a mineral concentrate where the average grain-size might be equivalent to a cube with an edge of 20 μm, the equivalent of 125 grains would be consumed; with a coarser grain-size, which is quite likely, fewer grains would be used. If platinum-group minerals (PGM), *i.e.*, phases with major concentrations of the PGE, were to occur in grains of similar size at the rate of one grain of PGM in a million of host sulfide, as indicated above, then it is highly unlikely (one chance in 8,000) that such a grain will be encountered during the analysis. AMS can thus produce what is effectively a bulk trace-element analysis, but the "bulk" is extremely small. In analyzing a mineral concentrate, the signal obtained should usually be representative of the level of the trace element in the major phase; if an enriched grain is encountered, it will be immediately apparent because the ion count-rate will increase suddenly and enormously, and an anomalous reading will be noted.

This argument should perhaps be qualified by noting that PGM, if present, would almost certainly have grain sizes much smaller than the typical 20 μm cube taken for the model. A PGM grain size of 2 μm along the cube edge, being 1000 times smaller, would result in a probability 1000 times greater of encountering a PGM during a 100-second analysis, *i.e.*, one chance in eight, which, though still unlikely, is almost certain to be encountered in a series of measurements when a few tens of readings are taken. Subsequent experiments have confirmed that this is a realistic scenario.

For comparison, a micro-PIXE analysis on an 11 × 22 μm spot in pyrite would sample approximately 5000 μm^3 continuously, and a spot 60 μm in diameter with SIMS would sample approximately 2400 μm^3 in the course of a 6- to 8-minute analysis (Cabri *et al.* 1991). When applied to untreated mineral grains, this use of PIXE or SIMS yields "point" analyses that are not comparable with the "bulk" concept derived above. Of course, probe methods also may yield "bulk" analyses if the trace elements are homogenized, as is done when fire-assay-preconcentrated specimens are analyzed by PIXE or SIMS. In this type of approach, a PIXE MDL for Pt, Pd and Au is 5 ppb (Sie *et al.* 1989); the other PGE are lost in the cupellation process.

Returning to the discussion of the AMS analysis of a sulfide concentrate, one can say that the 5 μg of pyrrhotite consumed during the 100-second analysis contains 7×10^{16} atoms; an element present at a concentration in the 1 ppb range will yield about 10^8 atoms, of which 10^4 might be detected. This is a sufficiently large signal to make the determination unambiguous. Unfortunately, there are factors, particularly ionization probabilities and isotope abundances, that lower the efficiency for certain elements and limit the detection levels that may be attained. However, ppb levels of detection are realistic for all the PGE to be sought in the major phases of the concentrates.

The arguments outlined above suggest that the extraordinary sensitivity of the AMS method may be used to establish the true level of trace elements in the major phase of a mineral concentrate. Accordingly, we decided to test this idea on the same Sudbury concentrates that were used by Cabri *et al.* (1984).

EXPERIMENTAL

The chalcopyrite, pentlandite and pyrrhotite concentrates were prepared from the –100 +200 mesh fractions of the mill products from the Copper Cliff secondary mill, and are typical of the ore processed in 1981 by Inco Metals Company. About 5 mg of each concentrate was fed through a pipette tip into the 1.5-mm-diameter bore of a 6.35-mm-diameter stainless steel cylinder. The powder was pressed by a weight of 86 kg applied to a piston behind the charge; it was thus packed tightly against a clean stainless steel surface (foil), thus making a solid surface flush with the face of the stainless steel cylinder, which could be inserted into the ion source of the IsoTrace Accelerator Mass Spectrometer. The same die and press are used for the preparation of AgI samples for analysis of ^{129}I by AMS at IsoTrace. Details of the equipment used for sample preparation are shown in Figure 1.

The pressed sample surfaces were examined by optical and scanning electron microscopy both before

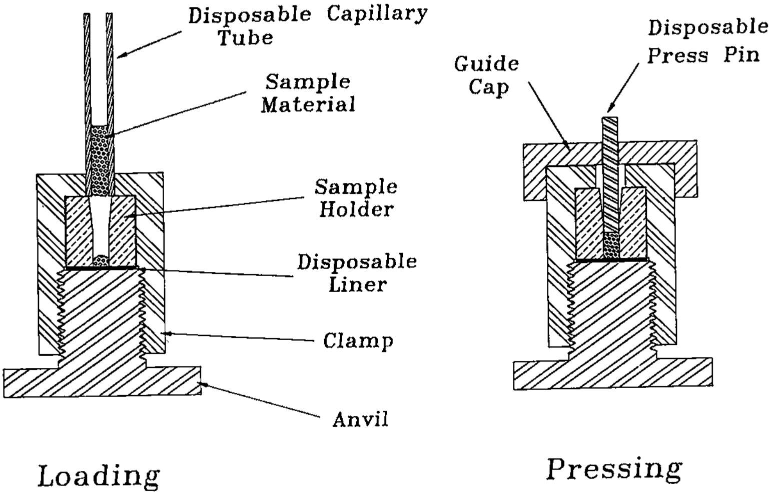

FIG. 1. Preparation of powders or granular materials for analysis by AMS. Grains are loaded into the 1.5-mm-diameter bore of a stainless steel cylindrical sample holder. The grains are then compacted with a disposable press pin against a disposable stainless steel liner.

and after analysis. In this way the volume removed by the ion beam could be measured, and the erosion rate estimated.

Quantitative estimates of the concentrations of the different elements in the concentrate were made by linear comparison with the intensities measured on the standard SARM 7. This well-known reference material has been prepared in the form of a nickel sulfide bead, parts of which are then inserted into the ion-source of the accelerator mass spectrometer, which produces sputtered negative ions. The description of this standard, its preparation and the analytical procedure are contained in Wilson *et al.* (1991). Normally, this standard has been used in the form of a single polished slab; however, for this work, because the materials being analyzed are grains of sulfide concentrates, the SARM 7 also was used in a granular form.

Altogether, three sets of samples were prepared and analyzed over a period of two months. Data were collected for the six PGE (Pt, Ir, Os, Pd, Rh, Ru), Au and Ag. The specific isotopes selected for analysis, along with their abundances, are shown in Figure 2. Where possible, the most abundant isotope was selected for analysis, but a more important consideration was that the mass should be a number not divisible by 6, 3 and, if possible, 2. This criterion arises because the selected ions are analyzed in the 6+ charge-state, and other ions with one half, one third or one sixth the mass, at charge-states 3+, 2+ and 1+, respectively, will have identical values for *E/q* (electric rigidity) and ME/q^2 (magnetic rigidity). This means they will be transmitted along identical trajectories in the accelerator mass spectrometer. For this reason, ^{101}Ru, whose mass is a prime number, is chosen in preference to the more abundant isotope ^{102}Ru. Another example arises when measuring $^{195}Pt^{6+}$, because conditions are right for the passage of $^{65}Cu^{2+}$ if the trimer molecule $^{65}Cu_3^-$ is being created in the ion source. The ubiquitous occurrence of Cu along with Pt arises because of the nature of the major sulfides, especially chalcopyrite. Such a pairing does in fact produce a convenient pilot beam for alignment of the complex ion optics. The energies of these potentially interfering species are of course different and can be resolved by energy discrimination in the final detector, but in the event that the lighter ion were abundant relative to the heavy, then separation becomes a problem. This in fact prevents $^{195}Pt^{6+}$ being used in the analysis for Pt in the presence of Cu, but the selection of $^{196}Pt^{6+}$ reduces this interference to a manageable level (see Fig. 3). An alternate charge-state, say 5+ or 7+, might be considered, but practical factors may rule this out. The yield of the higher charge-states in the stripping canal falls off rapidly, so that sensitivity suffers. The lower charge-states may be more abundant, but because of their higher magnetic rigidity, they are difficult to bend in the analyzing magnet, and may be excluded on this count. There is thus only a narrow range of charge-states that can be used in practice. The subject of charge-ratio mass spectrometry, which is peculiar to AMS, has been treated by Kilius *et al.* (1984).

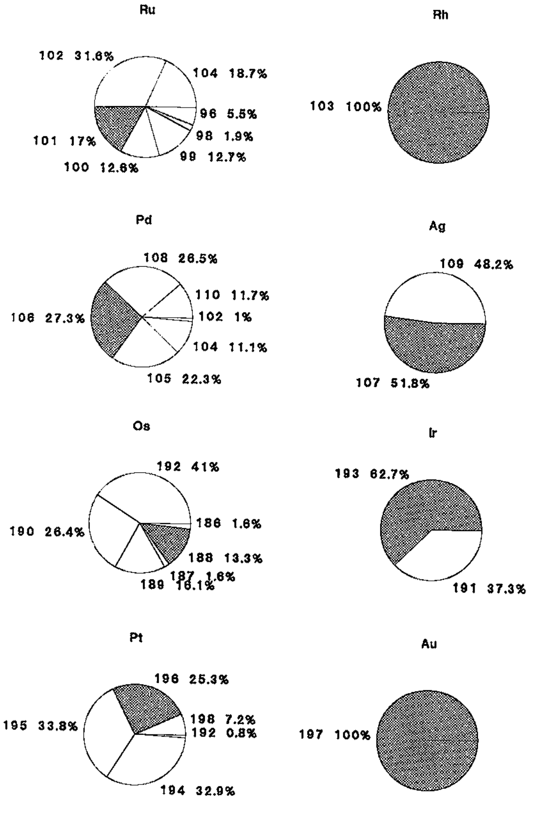

FIG. 2. Isotopic compositions of Ru, Rh, Pd, Ag, Os, Ir, Pt and Au. The isotopes selected for analysis are shaded.

Another consideration for selecting the isotope for analysis is that there should not be another isotope of identical mass, belonging to another element. Such a situation would preclude the unambiguous identification of the element in question. For example, both Os and Pt have isotopes at mass 192 and, for this reason alone, mass 192 should be avoided. The fact that this mass number is also divisible by 6 makes it doubly unfavored, so that the less abundant isotope ^{188}Os is chosen in preference to ^{192}Os.

The analytical setup for the accelerator mass spectrometer was: primary bombardment by approximately 150 µA of Cs$^+$ at 30 kV; secondary extraction of negative ions at 20 kV; 45° electrostatic analysis; 90° magnetic analysis; acceleration to 2 MeV; charge change in Ar stripping canal to 6+; further acceleration to 14 MeV; 15° electric sector to remove fragmented molecules; 90° high-energy magnetic analysis; 45° electrostatic analysis; particle counting and energy determination in a final

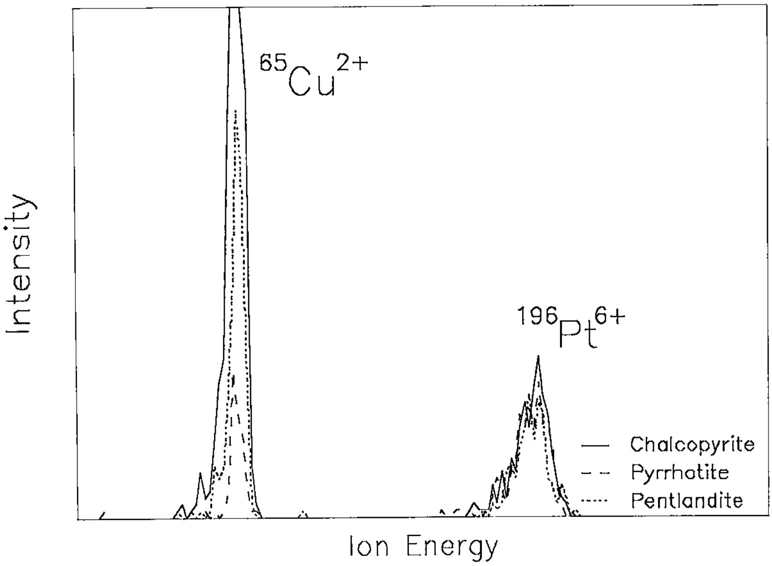

FIG. 3. Energy spectra from the final detector when the accelerator mass spectrometer is tuned to $^{196}Pt^{6+}$ on chalcopyrite, pentlandite and pyrrhotite. Note the peak of $^{65}Cu^{2+}$, which arises from the trimer molecule $^{65}Cu_3^-$ in the low-energy part of the system, and which yields $^{65}Cu^{2+}$ in the accelerator. Cu is a major component of the sulfide phases, especially chalcopyrite. The tail of this intense beam is transmitted along with the $^{196}Pt^{6+}$ but is readily resolved by the detector.

gas detector (Kilius *et al.* 1990). A typical energy spectrum from the final detector is shown in Figure 3, where peaks for Pt and Cu are seen to be well separated. Despite the multiple filters in the ion-beam line, conditions exist, as mentioned above, whereby ions of different mass and charge may pass through to the detector, and may only be distinguished by their energy.

Points for analysis were selected on the standard and at least three unknowns, and the positions of these points were recorded in the computer. The sample stage could then be moved between these points reproducibly.

The data-collection strategy was to tune the instrument to the selected isotope using the SARM 7 standard. As mentioned above, the initial tuning of the heavy PGE was greatly facilitated by using the $^{65}Cu_3$ trimer molecule as a pilot beam to locate the position of ^{195}Pt. From mass 195 to the selected mass in the range 188 to 197 (Os to Au), the settings could be calculated and fine-tuned on the standard. The light-PGE group was located using the $^{56}Fe_2$ dimer molecule, which pins down mass 112, from which the masses 101 to 107 (Ru to Ag) may be found. Identification of peaks in AMS is nontrivial because of the myriad of ions and charge-states that emerge from the accelerator. Data were collected in 100-second units at each point, and repeated up to five times to ensure reproducibility. The isotopes were measured sequentially; all samples and standards were measured for one isotope, and then the instrument was retuned. Isotopes measured first in the sequence started with a pristine surface on the sample; those done later worked on the crater produced by the earlier measurements. As will be noted later, a number of factors contribute to render the results semiquantitative, of which cratering is among the less important.

TABLE 2. RANGE OF LIGHT PGE AND Ag (PPB) MEASURED IN CONCENTRATES BY AMS

	Ru	Rh	Pd	Ag
Chalcopyrite	3 - 30	0.3 - 4	30 - 400	2000 - 8000
Pentlandite	30 - 300	10 - 900	6 - 4000	600 - 4000
Pyrrhotite	10 - 600	40 - 400	20 - 400	20 - 3000

TABLE 3. RANGE OF HEAVY PGE AND Au (PPB) MEASURED IN CONCENTRATES BY AMS

	Os	Ir	Pt	Au
Chalcopyrite	2 - 2000	0.2 - 20	0.8 - 400	10 - 200
Pentlandite	4 - 10	4 - 20	1 - 100	6 - 400
Pyrrhotite	20 - 30	20 - 30	2 - 100	5 - 300

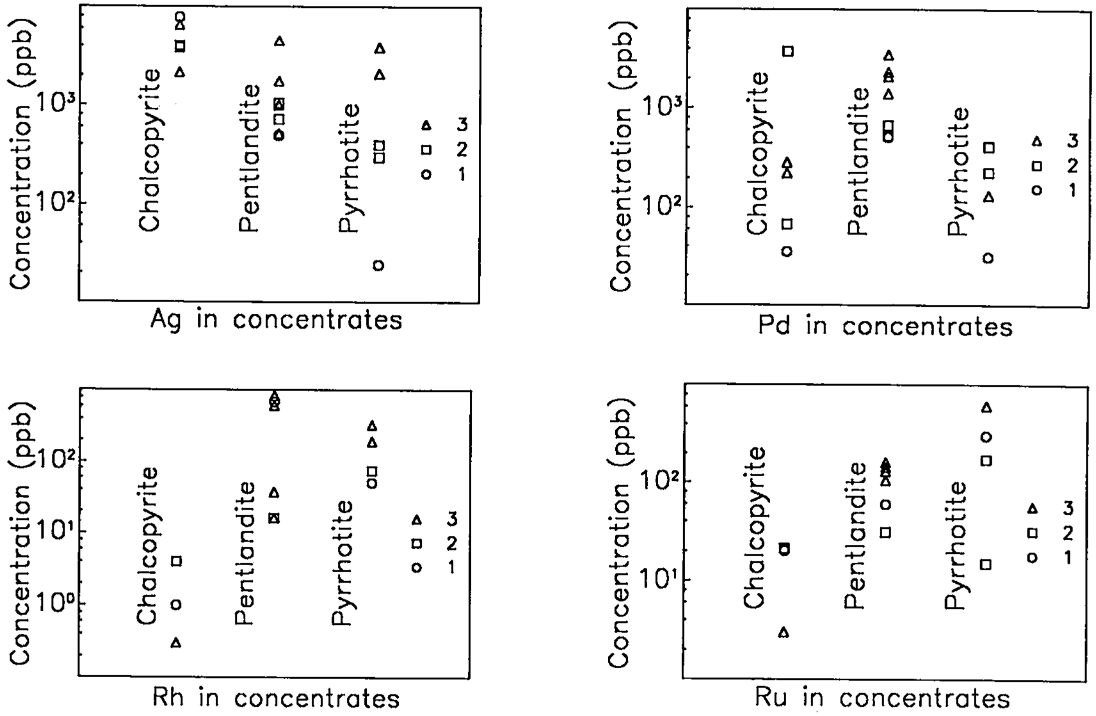

FIG. 4. Concentrations of the light PGE and Ag plotted to show the relative concentrations in chalcopyrite, pentlandite and pyrrhotite. The different symbols identified in the right of each diagram refer to different runs, *i.e.*, measurements made on different samples at different times.

RESULTS

Signals above background were detected for all the elements on all the samples. The data were found to be extremely variable, ranging over two orders of magnitude. This contrasts with the behavior of solid (*i.e.*, nongranular) samples. The results for the light PGE and Ag are summarized in Table 2, and the heavy PGE and Au in Table 3. The same data are shown in Figures 4 to 6, where the ranges measured in individual runs can be seen. Concentrations were recorded as low as 0.2 ppb Ir in chalcopyrite, and as high as several ppm Ag in all three minerals.

The integrated time spent on each sample varied from 3000 to 4200 seconds. This time is much longer than the 100-second analysis time mentioned in the preamble to this paper, because the samples have to be analyzed sequentially for the eight different elements; repeat measurements have to be made, and there is a certain amount of unproductive time when the beam falls on the samples between measurements. This exposure resulted in the excavation of craters approximately 0.5 mm in diameter and 0.2 mm deep. Examination of the samples after analysis revealed rather different effects in each of the three minerals. These are illustrated in Figure 7. Redistribution of material was apparent in the case of chalcopyrite, where a "cactus-like" feature developed on one side of the crater. Erosion rates were determined to be about 0.05 μg/s.

The signals from a single sample varied with time, with varying time constants. High-intensity bursts of counts, lasting for a few seconds, were noted quite frequently, and these were interpreted as due to grains of highly enriched material suddenly exposed to the beam. A grain or large inclusion of a platinum-group mineral (PGM) would produce such behavior, and of course such a reading would be rendered useless in determinations of the trace levels in the major phase. Such readings were discarded.

Slower variations with smaller excursions in intensity also occurred, perhaps arising from very small inclusions of PGM. These probably account for the wide range in the values recorded. Clearly these data too are not particularly useful when making statements about the PGE content of the chalcopyrite, pentlandite and pyrrhotite. Only *minimum* concentrations may have some value in this respect. If a reading of 0.2 ppb Ir is recorded on one sample of chalcopyrite, then one can

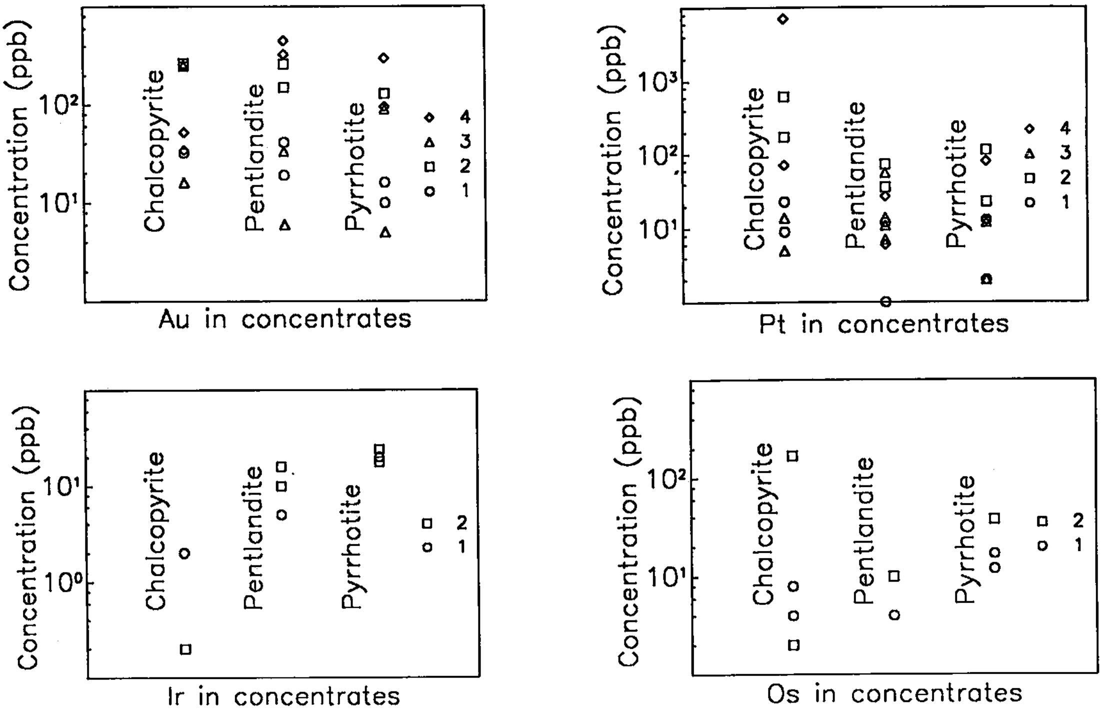

FIG. 5. Concentrations of the heavy PGE and Au plotted to show the relative concentrations in chalcopyrite, pentlandite and pyrrhotite.

state that many grains have a value as low (perhaps lower), and that higher readings arise from impurities.

DISCUSSION

The extreme variability of the results prevent one from assigning average values of trace elements to the concentrates of chalcopyrite, pentlandite and pyrrhotite. However, the sensitivity of the method is such that signals indicating the presence of the trace elements *at some level* are always present. The material, being mineral separates prepared from a mill concentrate, had purities ranging from 92.8% to 98.1%, so that at any time in the analysis, a number of heterogeneous grains could be emitting ions at different rates, depending on the trace-element content of an individual grain. As the grains are consumed by the primary ion-beam, so the signal would be expected to change, and this was in fact observed. If we take the minimum values measured for each of the phases, these can be taken to establish reasonable levels of the background.

In a comparison of these values with the levels reported by Cabri *et al.* (1984), we see that there is no conflict. Table 4 shows the range of levels for Pd and Rh in the three minerals of the Sudbury concentrates determined by AMS and the minimum detection-limit of the PIXE method. The AMS values extend two to three orders of magnitude lower than could possibly be measured by PIXE, and even the maximum values rarely reach the PIXE cutoff, except those probably due to impurities in chalcopyrite and pentlandite. The difference is that the PIXE determination can be made on single grains, whereas the AMS measurements incorporate hundreds of grains.

The AMS data show that none of the minerals concentrate the PGE to the levels recorded by the assay results (Table 1). There are, however, measurable concentrations in all of the phases, and these indicate partitioning among the phases. This can most easily be seen in Figures 4 and 5, where the concentrations of each element in the three phases are plotted. Li *et al.* (1993) have reported very similar AMS measurements of levels of the PGE on single crystals of sulfides from the Strathcona mine, Sudbury.

Ag, present in the ppm range, is most enriched in chalcopyrite, and is 100 times less so in pyrrhotite. Pentlandite is intermediate. Pd approaches ppm levels in pentlandite, but chalcopyrite and pyrrhotite have 10

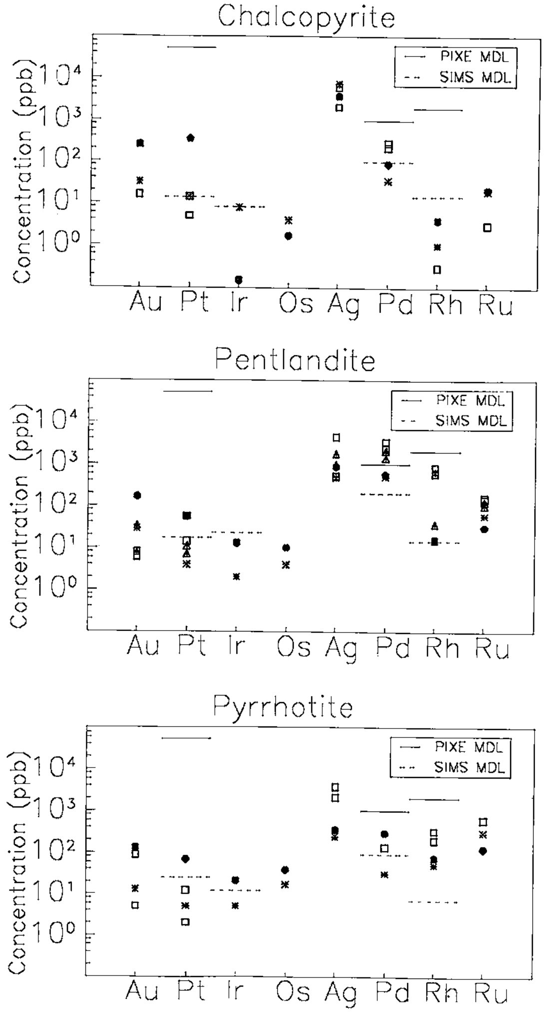

FIG. 6. Concentrations of all the PGE, Au and Ag plotted in the three ore minerals, arbitrarily in order of decreasing atomic number. The minimum detection limits obtained by PIXE (PIXE MDL) for Pt, Pd and Rh, after Cabri *et al.* (1984), and the SIMS MDL for Pt, Ir, Pd and Rh, after Chryssoulis & Cabri (1991), are shown for comparison.

times less. Rh and Ru show similar patterns, being most depleted in chalcopyrite (<1 ppb), whereas pentlandite has 10 times more. Pyrrhotite is intermediate. Au is present at the 10 ppb level in all three phases. Pt is present in the range 1 to 10 ppb in all phases, with pentlandite showing the most depletion. Ir is strongly depleted in chalcopyrite at the sub-ppb level, and is clearly enriched in pyrrhotite, with more than 10 ppb. Pentlandite is intermediate. Os is present at the 1 – 10 ppb level in all phases, possibly with slight relative enrichment in the order chalcopyrite, pentlandite, pyrrhotite, but in view of the rather poor counting statistics on Os, this observation may not be reliable.

The differences in behavior of the various minerals in the ion source lead one to question the validity of quantifying these results, as we have done. The different crystal structures and compositions undoubtedly imply quite variable matrix corrections, which should be applied to the simple model of linear calibration that we have used. However, the variability of the data over several orders of magnitude far exceeds the error introduced by the neglect of the matrix effect. We believe that these data should be treated as being semiquantitative, but they indicate the correct order of magnitude. The yield of negative ions from a mineral in the ion source depends on, among other factors, the temperature of the emitting surface. If it becomes very hot (several hundred degrees Celsius), then the yield of negative ions may fall off. This happens because Cs from the primary beam does not adhere to the surface at high temperatures, and the work function of a Cs-free surface is much higher than when it is coated with a thin layer of Cs. The temperature of the grains in the pressed concentrate targets may vary widely depending on the degree of contact with their neighbors, through which heat may be dissipated by conduction. Hence, one would expect that the results from samples prepared in the way described here could very well exhibit considerable variation on the basis of thermal considerations alone. The fact that sublimation effects ("cactus growth") were observed on the sample surfaces indicates that severe thermal conditions did exist, which through surface irregularities could lead to distortions in the electric field and hence variable yields of ions. This is yet another reason for implying only semiquantitative significance to the data. Careful monitoring of a major species of ions at the ion source is necessary to ensure that the sample is emitting satisfactorily.

CONCLUSIONS

These experiments on the analysis of sulfide concentrates for the PGE, Au and Ag by acceleration mass spectrometry have shown that all the elements can be detected unambiguously, even at sub-ppb levels. The quantity of material on which an individual 100-second analysis is performed is about 5 μg. It differs from a bulk analysis in that, though it samples several grains at once, the number of grains is too small to be truly representative of the bulk. It therefore falls between the individual grain microanalysis and the bulk analysis. Statistically, in a reasonably pure concentrate one might expect the average volume analyzed to contain only grains typical of the major phase. Any impurities may modify the analytical data by raising the detected levels in the event that the impurity contains high levels of the measured element; otherwise, it will have little effect. The range of values measured are therefore probably meaningful in that they approach the background levels at the lower end of the range. Repeated measurements

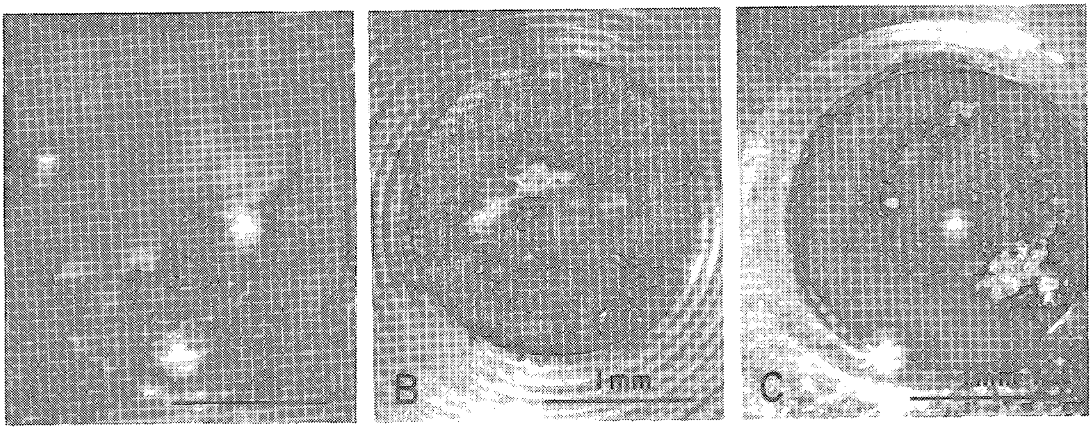

FIG. 7. Photomicrographs of the surfaces of chalcopyrite (A), pentlandite (B) and pyrrhotite (C) pressed concentrates after analysis by AMS. The out-of-focus part of the chalcopyrite picture is a "cactus-like" excrescence that has grown above the surface. The pentlandite shows regions that appear to have fused into tiny beads. The pyrrhotite appears to have congealed without fusion. Before Cs bombardment, all three surfaces were similar. These effects are thought to be due to the thermal conditions created by the interaction of the Cs beam and the surface of the pressed concentrate. On "normal samples", *i.e.*, solid polished surfaces, cratering is the principal result.

on different samples may be necessary to determine this lower limit.

The measurements have confirmed, with a reasonable degree of quantification, what was already known about the distribution of PGE in the common sulfides from Sudbury. Namely, the economical extraction of PGE from these ores has to be done from separate PGM or inclusions of PGM. The concentrations in solution in the chalcopyrite, pentlandite and pyrrhotite do not constitute economically recoverable levels, except that the traces of Rh and Ru in pyrrhotite actually represent an enormous quantity that is lost (Cabri & Laflamme 1984). In contrast, many other PGE-bearing deposits contain significant amounts of PGE in sulfide solid-solution, such as Pd, Rh and Ru in pentlandite in the Stillwater complex (Cabri *et al.* 1984).

Considering the expenses in running an AMS machine, and the difficulties of reproducible preparation of samples, we do not consider this a viable method of analyzing sulfide concentrates for trace elements. However, with an ion microprobe source on an AMS instrument, analysis of polished surfaces of minerals should be able to yield trace-element data in a range of concentrations well below those presently attainable by PIXE.

TABLE 4. PIXE LOWER LIMITS AND AMS RANGES FOR Pd AND Rh IN SUDBURY CONCENTRATES (PPB)

	Pd PIXE	Pd AMS	Rh PIXE	Rh AMS
Chalcopyrite	2100	30 - 4000	1900	0.3 - 4
Pentlandite	1800	6 - 4000	1600	10 - 900
Pyrrhotite	1200	20 - 400	3000	40 - 400

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