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# COMPARATIVE ANALYSIS OF SULFIDES FOR GOLD USING SXRF AND SIMS

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## ABSTRACT

Sulfides may be analyzed for gold using Secondary Ion Mass Spectrometry (SIMS) and Synchrotron X-Ray Fluorescence (SXRF); we have compared the two methods with respect to instrumental requirements, time, analysis volume, and detection limits. A limitation in this comparison is the inhomogeneous distribution of Au within arsenopyrite, as demonstrated using SIMS imaging for samples from the São Bento deposit, Brazil. Analysis of the same grains of arsenopyrite produces good agreement between the two techniques; discrepancies are attributable to slight shifts in analysis locations between the two techniques or the different volumes being analyzed. Whereas SIMS has imaging capability and sub-ppm detection limits, quantitation is difficult. SXRF spectra are relatively simple, and quantitative analysis is not as matrix-dependent as with SIMS. The detection level for Au in arsenopyrite by SXRF is limited by the background from As$K\alpha$ to about 50 ppm, but will be reduced to about 15 ppm using more intense synchrotron sources.

*Keywords*: gold, sulfides, secondary-ion mass spectrometry (SIMS), synchrotron X-ray fluorescence, São Bento deposit, Brazil.

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## SOMMAIRE

On peut analyser les sulfures pour l'or en utilisant la spectrométrie de masse des ions secondaires (SIMS) et la fluorescence X sur synchrotron; nous avons comparé les deux méthodes par rapport aux exigeances instrumentales, à la durée des analyses, au volume analysé et au seuil de détection. La comparaison est limitée par la distribution hétérogène de l'or dans l'arsénopyrite, comme le démontre les images des échantillons choisis, du gisement de São Bento, au Brésil, obtenues par la méthode SIMS. Une analyse des mêmes grains d'arsénopyrite mène à une bonne concordance entre les résultats des deux techniques; les divergences seraient dues aux légers décalages dans les sites choisis pour les analyses d'une méthode à l'autre, ou bien aux différents volumes analysés. Quoique la technique SIMS possède comme atouts une capacité de produire des images et un seuil de détection inférieur au ppm, la quantification s'avère difficile. Par contre, les spectres SXRF sont relativement simples à obtenir, et une analyse quantitative dépend moins des effets de matrice qu'avec la technique SIMS. Le seuil de détection de l'or dans l'arsénopyrite par SXRF est limité à environ 50 ppm à cause du bruit de fond provenant du pic As*K*α, mais on s'attend à une réduction jusqu'à environ 15 ppm avec l'utilisation de sources synchrotron plus intenses.

(Traduit par la Rédaction)

*Mots-clés*: or, sulfures, spectrométrie de masse des ions secondaires (SIMS), fluorescence X avec synchrotron, gisement de São Bento, Brésil.

## INTRODUCTION

Analytical methods for trace metals, such as gold in sulfides, are of both economic and geological interest. Analyses provide data on concentrations, homogeneity, and distribution among phases that are important in evaluating methods of concentration and extraction. From a scientific viewpoint, we wish to use these measurements to understand how a trace element is distributed, how it is partitioned, and how it may have migrated under certain geological conditions. These basic data may then allow predictions regarding other occurrences. There are many microbeam techniques available, such as electron-microprobe analysis (EPMA), secondary-ion mass spectrometry (SIMS), proton-induced X-ray excitation (PIXE), and laser-ablation microprobe – inductively coupled plasma – mass spectrometry (LAM–ICP–MS). In the present study, we report new data on the levels and distribution of gold in sulfide minerals using both synchrotron X-ray fluorescence and secondary-ion mass spectrometry. These data allow an evaluation of the relative benefits and limitations of these two techniques.

## BACKGROUND FOR THE PRESENT STUDY

Bulk analyses for trace elements are useful for relatively large-scale spatial variations, but here we address analytical techniques that allow quantitative *in situ* analysis on a ~20 μm scale. By *in situ*, we specifically mean analysis of grains in polished sections of samples for which the most common method is electron-probe microanalysis (EPMA). However, analysis techniques appropriate for precious metals, which may have both a restricted spatial resolution and a sub-ppm level of detection, are limited. SIMS has been established as a suitable technique for analysis [*e.g.,* Cabri & McMahon (1995) and references therein]. Synchrotron-based X-ray fluorescence (SXRF) should provide similar results, but as yet its capabilities have not been described with respect to quantitative analysis of sulfides. In addition, there are limited published data on comparative studies for trace precious metals using different techniques [*e.g.*, Cabri *et al*. (1984) for Pd by EPMA *versus* PIXE; Cabri *et al*. (1991) for Au by PIXE *versus* SIMS; McMahon & Cabri (1998) for Au by EPMA *versus* SIMS).

Sulfide minerals are currently one of the most important sources of gold. The gold concentration in sulfides is low and variable (<1 to several thousand ppm), but it may be economical to mine and extract gold from sulfides with concentrations as low as a few ppm by low-cost heap-leaching methods (Hausen *et al*. 1997, and references therein). Critical questions during exploration and mining operations are the concentration of gold in sulfides and how it is distributed among different sulfides. Gold is commonly distributed inhomogeneously within a single phase, and it is important to determine this variability, both in terms of absolute concentration and of spatial distribution (*e.g.,* Genkin *et al.* 1998). Gold can also be located within a sulfide substituting within the structure ("chemically bound gold"), concentrated as inclusions of any size ranging upward from ~2 nm ("invisible gold") to microscopic segregations, or occurring in zones that are in some cases, but not invariably, related to crystallography. The exact location of the gold is most important to optimize the method used to extract gold, a critical question from an economic and environmental point of view.

Using a suite of gold-bearing sulfides from the Minas Gerais region, Brazil, we first characterize the capabilities of the SXRF technique of analysis for low levels of gold in sulfides, and then compare these data with results of SIMS analyses for some of the same grains. We report the relative advantages and disadvantages of each technique so that the interested reader might better interpret results of similar studies.

## The São Bento Mine and Gold Ore

For purposes of illustration, we have chosen sulfide samples from an operating gold mine in Brazil. The São Bento deposit (Santa Bárbara, Minas Gerais) occurs in the middle portion of the Quadrilátero Ferrífero (*sensu lato*) (Ladeira 1988), which is hosted by the São Bento iron formation. This banded iron-formation (BIF) is composed of fine layers of oxide, carbonate, silicate, and sulfide facies (Abreu *et al.* 1988). The sulfides usually form veins of variable size cross-cutting the BIF layering at a very small angle to form the Pinta Bem horizon.

The most important minerals in the deposit are arsenopyrite, pyrrhotite, chalcopyrite, sphalerite, galena, electrum, magnetite, ilmenite, siderite, ankerite, calcite, quartz, chlorite, stilpnomelane, and muscovite (Marquez 1995). Arsenopyrite ($Fe_{1.10}As_{0.99}S_{1.00}$ to $Fe_{1.00}As_{0.82}S_{1.18}$) occurs mainly as rhombohedra that are zoned, with a petrographically clearly defined core. This core shows a variable As:S ratio, decreasing from center to rim, typical of As-rich environments (Kretschmar & Scott 1976). In arsenopyrite grains, the rim also exhibits rhythmic variations in the As:S ratio, increasing and tending to stoichiometry from the core to rim. The latter is typical of environments with high activity of S (Kretschmar & Scott 1976) and represents a second generation of arsenopyrite. Pyrrhotite ($Fe_{0.91}S_{1.09}$ to $Fe_{0.96}S_{1.04}$) is clearly remobilized, occurring as anhedral aggregates of crystals, in some cases elongate and oriented. Both monoclinic and hexagonal pyrrhotite occur, with the hexagonal variant ranging from 50 to 100%, as determined by X-ray diffraction. Two generations of pyrite occur: As-rich pyrite included in arsenopyrite and As-poor pyrite occurring as euhedral to subhedral crystals, with many inclusions of arsenopyrite, pyrrhotite, sphalerite, *etc*.

Gold and electrum (20 to 50 atom % Ag) occur in many different forms: 1) as small inclusions in arsenopyrite and pyrite, in some cases associated with pyrrhotite and gangue minerals, 2) as large inclusions in pyrrhotite, usually in contact with arsenopyrite, 3) less commonly, in mineral interfaces or in fractures associated with sulfides, and 4) rarely included within sphalerite or gangue minerals, or as a cavity filling in arsenopyrite associated with galena, sphalerite, chalcopyrite, and pyrrhotite. The São Bento refractory gold ores were first treated using the Sherritt Gordon pressure oxidation process in late 1986 (Berezowsky *et al.* 1988), whereas the current operation uses bacterial sulfide oxidation as a complementary method to the autoclave for the oxidation pre-treatment.

Results of electron-probe microanalyses of sulfides (arsenopyrite, pyrrhotite, chalcopyrite, sphalerite) indicated the presence of invisible gold, mostly in arsenopyrite (Marquez 1995). Different samples of arsenopyrite from the Pinta Bem horizon contain the highest gold content (ranging from 700 ppm, which is the detection limit, to 1,600 ppm Au), whereas arsenopyrite from the São Bento horizon contains the lowest level of gold. Thus arsenopyrite grains from the former horizon were chosen for this study.

## Analytical Methods

The analytical techniques that allow both ppm levels of detection and micrometer-sized analysis volumes include EPMA, SIMS, PIXE, LAM–ICP–MS and the technique illustrated here, SXRF. The electron microprobe is a well-developed instrumental technique and the most common instrument for analysis of micrometer-sized volumes in a polished section. The limitation for trace-element analysis is the production of *bremsstrahlung* background, which gives a statistical limit to the detection of any element. Heavy elements, like gold, have a low efficiency for the generation of X-rays. Analysis of samples at ppm levels is thus only possible using high incident electron currents, high accelerating voltage, and long counting times. Special attention must be given to the complex background profile in the neighborhood of the analytical peak, such as illustrated by Self *et al.* (1990). At present, the high keV requirements tax the limit of commercial instruments. This technique has been described with applications for gold analysis (Graham *et al*. 1989), and recent developments and applications in ore mineralogy are reviewed by Robinson *et al.* (1998).

SIMS has a very low background, but is a relatively destructive technique because the analysis region is sputtered during depth profiling or imaging. The generation of Au secondary ions is, among other parameters, a function of the matrix composition. It is difficult to compare a Au ion signal for one phase with that for another. Matrix corrections, which are often poorly known and must be experimentally derived, can be applied (Cabri & McMahon 1995). Thin-film ion-implant standards have been used, and the application of this technique has been described by Leta & Morrison (1980) and applied to analysis of sulfides for Au by Chryssoulis *et al*. (1989) and Marion *et al.* (1991). This technique was used in a survey of gold abundances in sulfides (Cook & Chryssoulis 1990) and in the determination of mineralogical balances of gold (Chryssoulis & Cabri 1990). SIMS instruments are not as common as electron microprobes, the light optics are inferior to those of the electron microprobe, and operation generally requires considerably more expertise. Analysis time depends on the particular problem, but routine depth-profiles for gold in arsenopyrite take 100 to 120 seconds per analysis after local calibration.

Applications of micro-PIXE in mineralogical and metallurgical samples have been given by Cabri (1988) and were more recently reviewed by Cabri & Campbell (1998). This technique has a lower background relative to EPMA, and analysis times vary, once again, depending on the problem and the mineral, but usually from about 3 to 10 minutes at a charge of 2.5 μC (Cabri & Campbell 1998). Detection levels in common sulfide minerals for precious metals such as Ru, Rh, Pd and Ag are of the order of 4 to 8 ppm, depending on the mineral (Oberthür *et al*. 1997). The quality of light optics is variable, depending on the laboratory. For example, a few laboratories that routinely perform mineralogical analysis (*e.g*., Guelph) have viewing and automated control of the stage comparable to modern electron microprobes. However, such instruments are not common. The most serious disadvantage for analysis by micro-PIXE is that all "mineralogical" PIXE facilities currently use only energy- dispersion detectors, with relatively high levels of detection for the Au*L*α peak. Analysis becomes impossible for arsenic-rich minerals such as arsenopyrite because of severe overlap of Au*L*α and As*K*α emission peaks. All three of these techniques require that the sample be in moderate to high vacuum systems.

LAM–ICP–MS facilities are becoming more common with the advent of commercial instruments. The technique has been demonstrated to be useful for quantification of many petrogenetically important trace elements (Fryer *et al.* 1995). However, as these authors pointed out, a number of elements, including Au, fractionate during analysis of silicate minerals, with errors on the order of ±50% (S.E. Jackson, pers. commun., 1999). Use of a directed jet reduces the fractionation by a factor of ~2, but this is not available on commercial instruments (S.E. Jackson, pers. commun., 1999). Analysis of sulfide minerals for Au by LAM–ICP–MS should be possible by using a chalcophile element with a fractionation index close to that of Au; unfortunately, development of this approach has not yet been done. Relative to both SIMS and SXRF, LAM–ICP–MS is destructive, and evidence of inhomogeneity may be lost during analysis.

The recent development of the synchrotron microprobe has progressed to a point where it may be competitive with the above techniques with respect to sensitivity, accuracy, spatial resolution and speed of analysis. Initial results are reported below based on one day of data collection at a bending magnet beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, New York, in 1996. Although no technique is ideal, the results presented below suggest that SXRF may equal or surpass other analytical techniques. Synchrotron radiation facilities equipped with insertion devices to provide a much higher flux of X-rays, up to some 60 keV, are available at several locations. These include the European Synchrotron Radiation Facility (ESRF) in France, SPring-8 in Japan, and the Advanced Photon Source (APS) in the United States. All of these facilities have SXRF beamlines that are available with varying procedures for access. At the APS, focusing optics for the primary beam allow analysis of smaller areas down to several micrometers without significant loss of incident flux. Combined energy- and wavelength-dispersion analysis, with analyzing crystals capable of analyzing 25 keV X-rays, and improved viewing optics and sample stage relative to those of the present study, also are available.

## EXPERIMENTAL

### *Synchrotron-based X-ray-fluorescence analysis*

Beamline X–26A at NSLS is a bending magnet with beam size and position selected by movable tantalum apertures. These were set at 50 × 50 μm, which becomes 50 × 70 μm on the sample due to the 45° orientation of the beam relative to the sample surface. The beam size is adjustable, but was maintained at the selected size for the duration of the data collection to allow simple comparison of intensities. If adjusted, data must be normalized to the open area of the movable apertures, which is proportional to the measured value of current produced by the incident X-ray beam as it passes through an ion chamber. Alternatively, the beam size can also be defined by pinhole apertures or focusing mirrors to about 6 or 12 μm diameter, respectively. Because the collection efficiency of a wavelength-dispersion detector is optimized at a point and decreases away from that point, it is important that the same "beam size" be used to allow comparison of different areas of analysis. We analyzed thick polished sections containing various sulfides, mainly arsenopyrite and pyrite in a silicate matrix from two locations currently mined for gold in Finland (Suurikuusikko deposit, Pekka *et al*. 1992) and Brazil (São Bento deposit, Marquez 1995). The samples from Brazil represent unknown samples, whereas those from Finland had previously been analyzed using SIMS and served in part as "standards", as approximate levels of Au were known. These samples had previously been examined using an electron microprobe to confirm sulfide identification and to document areas with photographs for analysis by SXRF.

In the five Brazilian samples selected for analysis, viewed in reflected light, the sulfides are easy to recognize by the difference in their reflectivity, which may be enhanced by carbon coating. A x–y–z stage allows movement and focusing of the sample over 2.5 × 2.5 cm with micrometer precision. The beam position is verified using a luminescent sample at optical focus, which is reproducible within about ±20 μm. An energy-dispersion (EDS) detector is mounted to accept only secondary X-rays near the plane of the synchrotron to optimize the peak-to-background ratio. Major-element X-ray lines including Fe*K*α (E = 6.4 keV) and As*K*α (E = 10.5 keV) are prominent, whereas S*K*α (E = 2.3 keV) is highly absorbed by the air path between sample and detector. Low-energy X-rays also are attenuated by X-ray filters purposely placed over the detector to reduce contributions of major-element X-rays to the recorded spectrum. The EDS display is the most useful in the present application as it allows confirmation of sample identification and beam location. Attempts to analyze for gold using the EDS detector were unsuccessful owing to the intense interference of the As$K\alpha$ peak (even in pyrite) with the Au$L\alpha_1$ peak at 9.71 keV.

To provide sufficient spectral resolution, a fully focusing wavelength-dispersion spectrometer with a LiF (200) analyzing crystal was aligned with the plane of sample, optical focus, position of incident beam, and Rowland circle of spectrometer coincident. The take-off angle is set at 40° with the sample in air, but spectrometer evacuated. Using a pure gold foil in the sample position, the spectrum shown in Figure 1 was obtained, confirming the expected resolution of the spectrometer and verifying the position of the Au peaks. Spectra (*e.g.*, Fig. 1 and later figures) were obtained by slowly scanning the spectrometer (10 minutes/spectrum) to allow excellent definition of the background profile due to both *bremsstrahlung* and to any spectral interferences, especially from As.

A major problem is the quantitative analysis of sulfide samples for gold where the matrix is complex. For the most accurate calculation of the gold content, it is desirable to have a standard with a similar matrix and a known amount of gold with a homogeneous distribution. Alternatively, theoretical corrections can be applied to correct for matrix effects. For the present study, we used previously analyzed sulfides (Pekka *et al*. 1992), which served both as examples of sulfides containing gold and as approximate standards, although it is known that gold is not homogeneously distributed within any one sample. Figure 2 illustrates the X-ray spectrum of pyrite in sample #434, with gold in the range 1–400 ppm based on results from four SIMS analyses (Pekka *et al*. 1992). Clearly shown in this spectrum is the Au$L\alpha_1$ peak superimposed on the smooth tail of the intense As$K\alpha$ peak. The critical information is that the background is smooth and can be approximated by a straight line in the vicinity of the Au peak to obtain a background-corrected intensity. Whereas the counting statistics do not appear to be very good, it must be remembered that most of the 10 minutes was spent obtaining unused information, and considerable time could be spent measuring two background positions on either side of the peak (to determine slope) and a peak position.

Knowing the peak position and shape, a number of 10-minute scans were made on arsenopyrite from this same sample. For these grains, only the region about the Au$L\alpha$ peak was scanned (Fig. 3). From SIMS data for four grains (Pekka *et al*. 1992), it is known that the gold distribution is inhomogeneous and varies from about 900 to 4000 ppm among the four published analytical data-sets. Figure 3 indeed shows that for the five grains analyzed by SXRF, the gold varies by a factor of about five. Though minerals such as pyrite and arsenopyrite appear to be very poor standards, they do serve to illustrate that Au can easily be detected and quantitative background-corrected intensities obtained.

### *Secondary-ion mass spectrometry*

Quantitative SIMS analyses and direct ion images were made at CANMET (Ottawa) on selected grains previously analyzed by SXRF. Analysis procedures were as described in Cabri & McMahon (1995) and in McMahon & Cabri (1998). Specific analytical conditions used in this study are listed in Table 1.

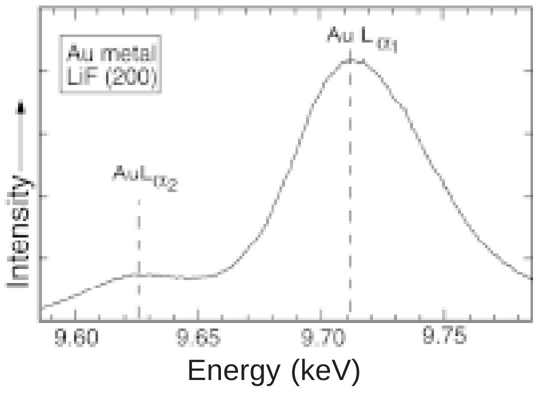

FIG. 1. SXRF spectrometer scan using LiF (200) crystal demonstrating the Au$L\alpha$ spectra from Au metal foil. Peaks show expected positions and relative intensities.

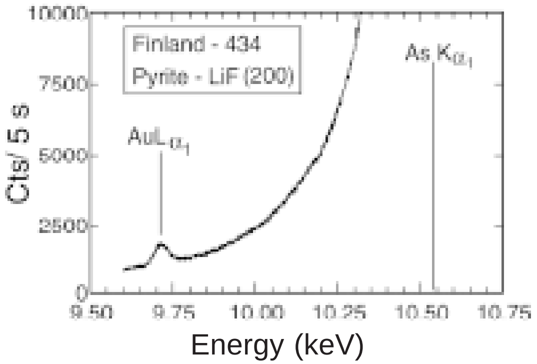

FIG. 2. SXRF spectrometer scan illustrating the severe interference between minor arsenic in pyrite and the trace $L\alpha_1$ peak of gold. The background in the region of the gold peak is smooth, allowing a background correction with either a simple linear fit of the background or a more complex nonlinear fit.

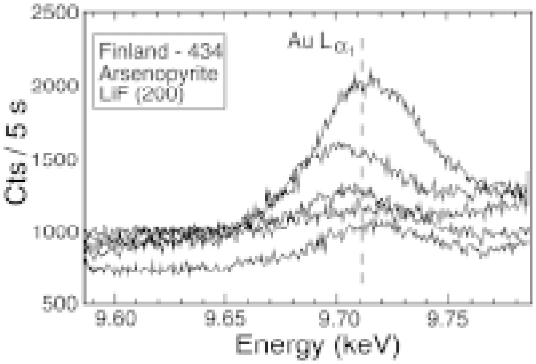

FIG. 3. SXRF spectrometer scans about the Au$L\alpha_1$ peak in five grains of arsenopyrite known to have between about 900 and 4,000 ppm gold, on the basis of ion-probe measurements (Pekka *et al.* 1992). Whereas the grains are not the same in the two studies, the range of intensities for SXRF is similar to the range of ion-probe-established concentrations. The slight shift in apparent positions of the peaks results from slight changes in focus position of the sample.

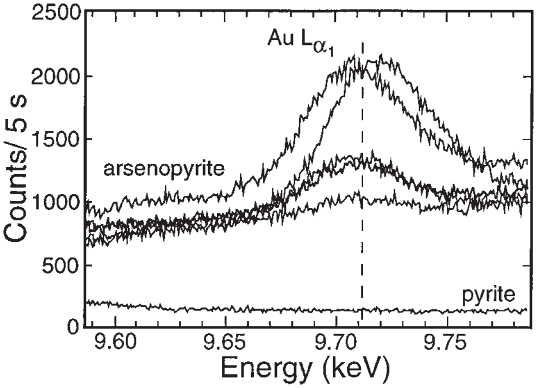

FIG. 4. Similar SXRF scans to those shown in Figure 3, but for five grains of arsenopyrite and one of pyrite from the São Bento deposit of Brazil. Clearly shown is a wide range of concentrations within arsenopyrite, as well as the absence of gold in pyrite.

TABLE 1. SIMS EXPERIMENTAL PARAMETERS

| | |
|---|---|
| Primary ion beam and polarity | Cs$^{+}$ |
| Secondary Ion polarity | Negative |
| Matrix masses measured | $^{56}$Fe, $^{57}$Fe$_2$ + $^{32}$S |
| Primary beam current | 320–395 nA |
| Primary beam accelerating voltage | 10 keV |
| Impact energy | 14.5 keV |
| Field-aperture diameter | 750 $\mu$m |
| Contrast-diaphragm diameter | 400 $\mu$m |
| Raster | 250 $\mu$m |
| Image field | 150 $\mu$m |
| Diameter of analysis area | 62.5 $\mu$m |
| Implant standards | arsenopyrite, pyrite, pyrrhotite |
| Implantation fluence, species | 2.5 ×10$^{13}$ ions$^{197}$Au/cm$^2$ |
| Counting time per mass per cycle | 1 second |
| Mass resolution | 2,000 m/Δm |
| Energy offset | none |
| Minimum detection-limits: arsenopyrite | 28–50 ppbw Au |
| pyrite | 89, 243 ppbw Au |
| pyrrhotite | 66, 69 ppbw Au |
| Depth of analyzed profiles | 0.3–2.0 $\mu$m |

## RESULTS AND DISCUSSION

As an illustration of an unknown sample, Figure 4 illustrates scans similar to those of Figure 3 but for samples from the São Bento deposit in Minas Gerais, Brazil. Of the six scans shown, the upper five are from arsenopyrite grains. Each clearly shows the presence of gold, albeit in different concentrations. The lower spectrum is from pyrite and suggests that gold is below detection. In total, sulfide samples from five locations in this mine were analyzed in a blind study, and the sample shown in Figure 4 to contain the most gold is known to be the richest of the five in gold. Although there are considerable uncertainties in the actual gold content in the reference standards used to produce Figures 2 and 3, calculated detection-limits for gold in arsenopyrite and pyrite are approximately 50 and 25 ppm, respectively, for counting times of 5 minutes based on counting statistics. The higher detection-limit for arsenopyrite is due to the distinctly higher background generated by the arsenic $K\alpha$ peak. These detection limits are mainly limited by count rates; these count rates will be significantly higher in third-generation synchrotrons, which operate at higher energy, have insertion devices to increase the intensity of the primary beam, and allow focusing of the primary beam in contrast to simple apertures. With a conservative estimate of a ten-fold increase in intensity of the primary beam, the detection limits will be decreased by approximately a factor of three.

A major problem in the comparison of results between the two analytical techniques is the uncertainty in homogeneity. SIMS images of Au distributions demonstrate that gold is not homogeneous in the São Bento samples. Three types of inhomogeneity are illustrated in Figures 5, 6 and 7. Figure 5 shows concentrations of Au that reflect the growth zoning in a small rhombohedron of arsenopyrite, with a gold-free core and gold-containing rim. Figure 6 shows fine-scale variations of gold parallel to growth zoning along one side of a much larger (700 μm) rhombohedron of arsenopyrite and a narrow (~10 μm) gold-free zone in arsenopyrite at the contact with pyrrhotite. Figure 7 shows a very inhomogeneous distribution of gold coarser than that of Figure 6 for an even larger (2 mm) grain of arsenopyrite. These

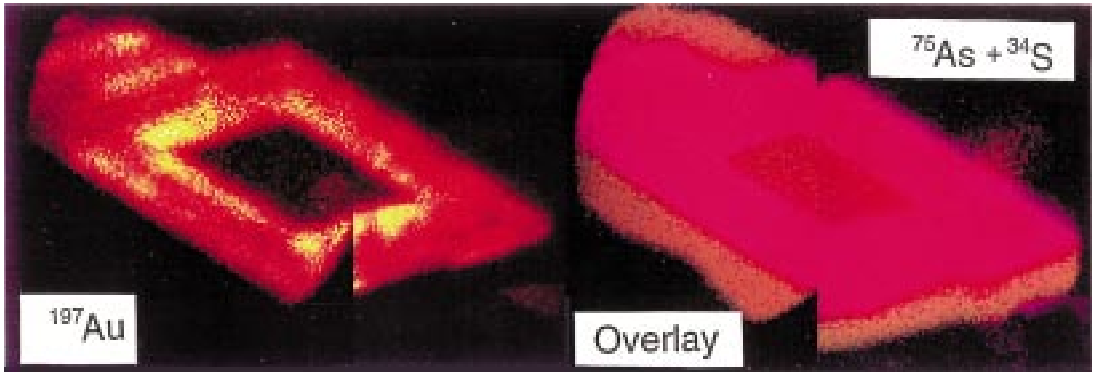

FIG. 5. Direct ion image for $^{197}$Au for a small rhombohedron of arsenopyrite (left) and a composite image where gold distribution is superimposed on image of $^{75}$As + $^{34}$S. These images clearly show that both the core and the rim are gold-free. Sample SPB–06, diameter of composite image field is 125 μm.

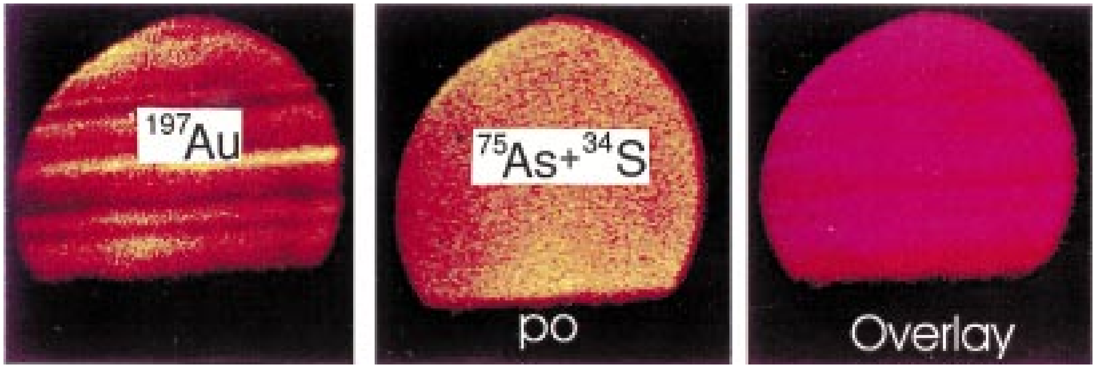

FIG. 6. Direct ion images at the edge of a large rhombohedron of arsenopyrite in contact with pyrrhotite for $^{197}$Au (left), ($^{75}$As + $^{34}$S) (center) and a composite image where these two images are overlain (right). The pyrrhotite and a ~10 μm zone in arsenopyrite in contact with pyrrhotite contain no detectable gold. Sample SPB–06, diameter of image field 62.5 μm.

FIG. 7. Direct ion images of $^{197}$Au, ($^{56}$Fe + $^{54}$Fe + $^{32}$S) and ($^{75}$As + $^{34}$S) at the edge of a large rhombohedron of arsenopyrite with a thin layer of silicate separating it from pyrrhotite. The pyrrhotite contains no detectable gold. A gold-rich area at the upper left was found to contain 360 ppm gold. Sample SPB–06, diameter of image field 62.5 μm.

inhomogeneous distributions are characteristic of sulfides, and no homogeneous distribution of gold has yet been documented by SIMS.

TABLE 2. COMPARISON OF Au CONCENTRATIONS FOR ARSENOPYRITE FROM BRAZIL BY SXRF AND SIMS

| No. | Area | SXRF | SIMS | No. | Area | SXRF | SIMS |
|---|---|---|---|---|---|---|---|
| 2 | 78 | 130 | 167 | 5 | 45 | 128 | 242 |
| 2 | 83 | 5 | 5.7 | 5 | 46 | 36 | 20 |
| 6 | 3 | 25 | 7.6 | 5 | 48 | 35 | 45 |
| 6 | 7 | 134 | 74 | 5 | 52 | 102 | 77 |
| | | | | 5 | 53 | 258 | 152 |

Data plotted in Figure 8. Area expressed in $\mu$m$^2$, concentrations, in ppmw.

The results of the blind study are given in Table 2 and Figure 8. The wide scatter from the ideal straight line passing through the origin suggests only slight agreement between the two techniques of analysis. However, there also appears no obvious bias for either technique, and the results must be interpreted in light of the images shown in Figures 5–7. In particular, four aspects must be considered in evaluating the results: (1) inhomogeneity of the gold distribution, (2) different analytical volumes, (3) error involved in accurately locating the same spot for analysis in the two techniques, and (4) systematic error due to uncertainty in the composition of reference standards. The inhomogeneous distribution of gold in arsenopyrite is well known; in this study, SIMS direct ion images of gold show different types of zoning, commonly on a micrometer scale. SXRF cannot match the imaging capability of SIMS; the latter is possibly the only technique that can demonstrate the distribution of an element on a micrometer scale. The SIMS analyses were all made with a 62.5 $\mu$m analysis area, so that the volume analyzed depends upon the duration of the analysis and sputter rate (average = 41 Å/s). For this study, typical volumes analyzed ranged from 2,225 to 3,432 $\mu$m$^3$, but most were ~3,000 $\mu$m$^3$. In the case of the SXRF analyses, the circular area analyzed by SIMS is only approximately matched by the 50 × 70 $\mu$m rectangular area of SXRF. In addition, the secondary X-rays that are analyzed originate from a depth that extends from the surface to about 4 $\mu$m, which represents the level for which Au$L\alpha$ X-rays can escape from the Fe,As,S matrix without significant absorption. This depth is significantly greater and gives an analytical volume near 1.4 × $10^4$ $\mu$m$^3$, approximately five times greater than that of SIMS. The relocation of the analyzed area is critical and depends in our study on the photographic documentation of each sample at the appropriate scales. Because these photographs were the only communication between the two analysts, the correspondence is possibly in error by tens of micrometers with considerable and unknown variation.

The combination of the above four factors precludes a rigorous test of the accuracy of analysis, at least from

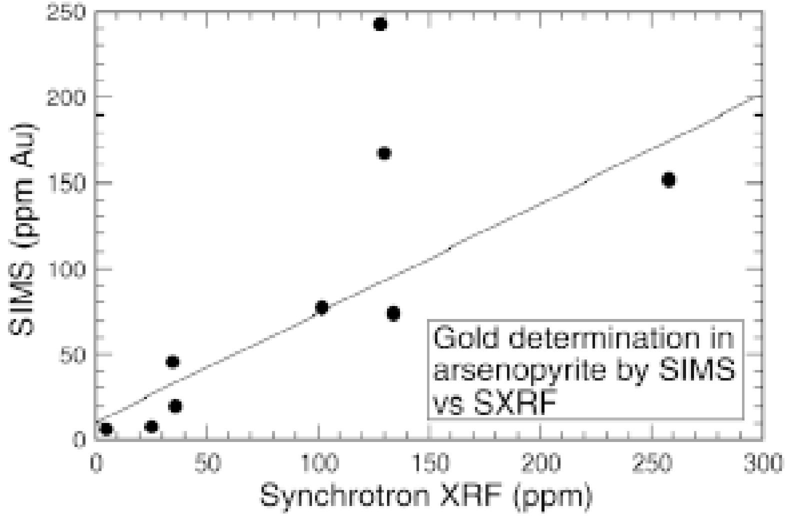

FIG. 8. Plot of results of SXRF analyses *versus* SIMS data for gold (ppm) in nine grains of arsenopyrite. Points were located as close as possible between the two techniques on the basis of photographic documentation, but the inhomogeneous distribution illustrated in Figures 5–7 clearly limits the correlation. The line shown represents a best fit to the data, but excludes the point with the highest SIMS value.

samples from the São Bento deposit. These results should serve as a warning for both the comparison of analytical techniques and the interpretation of results from a single analytical technique. Whereas a poor correspondence was shown in Figure 8, it must be realized that multiple techniques exist for Au determinations, each with specific advantages and disadvantages. The SIMS technique has the unparalleled imaging capability with high sensitivity, but with a rather stringent vacuum requirement and calibration for high accuracy. The SXRF technique as described here has a poorer detection-limit, but has the advantages of no vacuum requirement and a quantitative capability based on well-established X-ray-fluorescence correction procedures. We anticipate that third-generation synchrotron facilities, with higher primary beam flux and energy with simultaneous primary beam focusing, will lead to improvements of the detection limits to approximately 15 ppm.

## CONCLUSIONS

The comparison of SIMS and SXRF techniques using samples from the São Bento gold deposit in Brazil is limited by the inhomogeneous distribution of Au in arsenopyrite on the micrometer scale. This type of distribution seems to be characteristic of sulfides and must be addressed by any technique of analysis. The present results do show that detection limits for both techniques are satisfactory for a confirmation of the levels of gold in sulfide phases in potentially economic deposits. In particular, for the São Bento deposit, gold is concentrated in arsenopyrite, but not in the so-called type-I arsenopyrite, which corresponds to the core of many crystals. Pyrite and pyrrhotite both show no detectable gold using SXRF. Clearly, for any of these phases, multiple analyses must be made to confirm the range of inhomogeneity of the gold. Multiple analyses on many grains must be made in order to arrive at an "average" concentration for an inhomogeneous distribution.

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