

Gold-bearing arsenopyrite and pyrite in refractory ores: analytical refinements and new understanding of gold mineralogy

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ABSTRACT

A multidisciplinary approach has been used to study Au occurrences within pyrite and arsenopyrite in four refractory Au ores from Colombia, France (Le Châtelet and Villeranges) and Portugal (Neves Norte). The Au was characterized by optical and scanning electron microscopy and analysed using electron and ion microprobes to determine Au distribution, with particular attention to spectral interferences in electron and ion microprobes, background measurements in electron probes, and quantitative analysis using external standardization in ion probes. The ionic emission rate is proven to be dependent on the Au status; combined Au has a greater ion emission than metallic Au. Invisible Au occurrences are closely linked to As distribution. Gold bonding in arsenopyrite, examined by transmission electron microscopy, is shown to be dispersed within the FeAsS crystal structure. Typical growth patterns and As-Au diffusion zoning in pyrite and arsenopyrite may account for the very irregular distribution of Au in these minerals.

KEYWORDS: gold, arsenic, arsenopyrite, pyrite, refractory ores, growth zoning, electron microprobe analysis, secondary ion mass spectrometry, transmission electron microscopy.

Introduction

GOLD is generally recovered by hydrometallurgical dissolution and cyanide complexation. When found in the native form, leaching of Au is usually easy after sufficient ore milling. In other cases, often described as refractory ores, the Au cannot be dissolved economically by cyanide. In these cases the Au is contained within sulphide crystals, commonly pyrite (FeS₂) and arsenopyrite (FeAsS). Refractory Au has also been classified as

'invisible' Au but this definition includes native Au found as micro-inclusions in the sulphide crystals undetectable by conventional microscope techniques (Fig. 1). Liberation of 'invisible' Au is difficult by mechanical means, requiring a preliminary oxidation treatment using roasting, and chemical oxidation under high pressure or bioleaching to convert the Au to a more accessible metallic state (Wagner *et al.*, 1989; Monroy, 1993; Monroy *et al.*, 1993). Figure 2 illustrates porous hematite grains containing very small Au particles after roasting refractory Au-bearing arsenopyrite. Harris (1990), Chrysosoulis and Cabri (1990), Cook and Chrysosoulis (1990) and Chen *et al.* (2002) discussed mineralogy and recovery of 'invisible' Au. Cabri *et al.* (2000)

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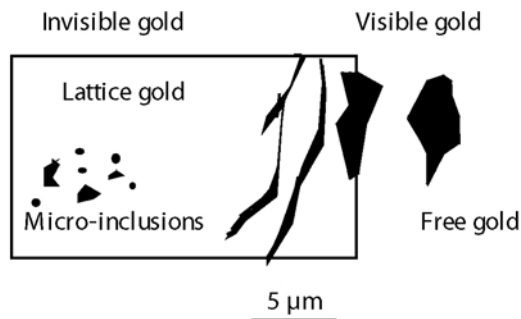


FIG. 1. Schematic illustration of the different types of Au associated with sulphides.

published a comprehensive literature review on the chemical bonding of Au in arsenopyrite. Current views for establishing the nature of Au in sulphides may be summarized as follows:

Direct evidence of Au segregation: This is studied by optical or scanning electron microscopy (SEM) (Marion, 1988; Marion *et al.*, 1991a) or scanning transmission electron microscopy (STEM) (Bakken *et al.*, 1989; Cabri *et al.*, 1989; Yang *et al.*, 1998). Observations are limited by instrument resolution and quantification. Yang *et al.* (1998) succeeded, using TEM measurements coupled with EDS, to reveal submicrometre Au occurring mainly as 0.07 to 0.15 µm spheres on growth surfaces of pyrite and in micro-fissures in stibnite. Recovery prediction by grain-counting

and image analysis is difficult, but possible, for 'visible' Au.

Element analysis: This is initially performed by wet chemical analysis on bulk separated grains. Modern developments of electron microprobe analysis (EMPA), using SEM backscattered electron images (e.g. Bonnemaïson, 1987; Marion, 1988; Fleet *et al.*, 1989; Kojonen and Johanson, 1995; Remond *et al.*, 1996), secondary ion mass spectrometry (SIMS) or ion microprobe (Chrysosoulis *et al.*, 1987; Chrysosoulis and Cabri, 1990; Marion *et al.*, 1991a, Yvon *et al.*, 1991; Boiron *et al.*, 1994; Cabri and McMahon, 1995; Larocque *et al.*, 1995; Benzazoua, 1996), synchrotron X-ray fluorescence (SXRF) and proton induced X-ray emission spectrometry (PIXE) (Cabri, 1988; Ashley *et al.*, 2000) allow local probe analysis with submicron lateral resolution and digital Au mapping and detection of 'invisible' Au distribution within crystals. The first mineralogical explanations for refractory Au ores were by Johan *et al.* (1989) as well as by Wu and Delbove (1989), for natural and synthetic Au-bearing arsenopyrite. Quantification depends on detection limits of the apparatus and the availability of precise standards for SIMS analysis. However, no knowledge of the chemical bonding of Au is obtained.

Characterization of solid chemical state of Au by wet chemical dissolution: Refractory behaviour is observed by laboratory experiments

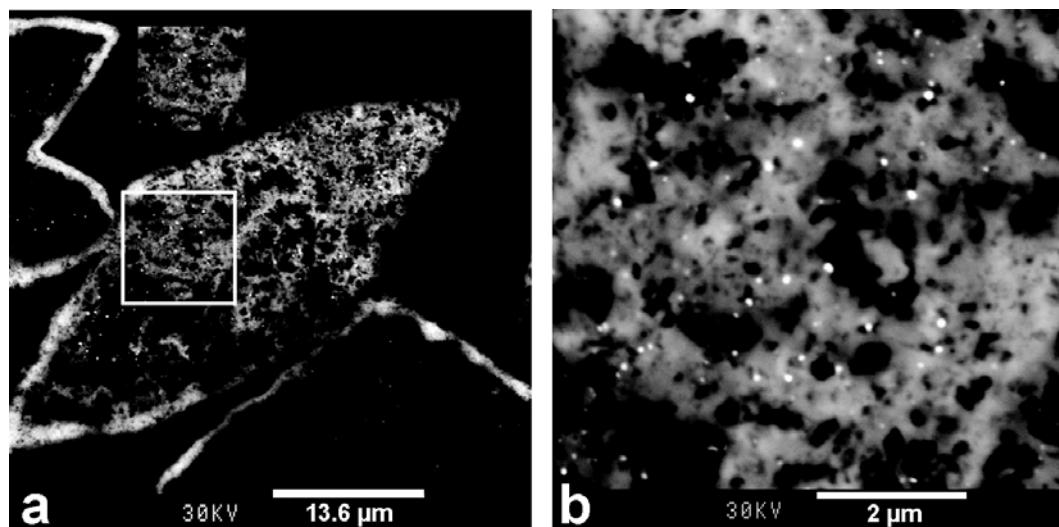


FIG. 2. (a) SEM BSE image of hematite grains (small white grains) within a roasted arsenopyrite concentrate from the Le Châtelet mine and (b) corresponding zoom image of the white square.

(Korobushkin, 1970) and hydrometallurgical plant outputs.

Gold chemical bonding determination: Various spectroscopies, such as ^{197}Au Mössbauer spectroscopy, or resonance absorption of nuclear gamma rays, can enable surface or near-surface bonding to be determined (Marion *et al.*, 1986; Wagner *et al.*, 1986, 1988; Marion, 1988; Friedl, 1989; Friedl *et al.*, 1992, 1995; Yang *et al.*, 1998; McCoy *et al.*, 2002), X-ray photoelectron spectroscopy (XPS) (Li *et al.*, 1995), X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) (Wong and Rao, 1983; Simon *et al.*, 1999a; Cabri *et al.*, 2000), electron paramagnetic resonance (EPR) (Voitsekhovskii *et al.*, 1975; Zhang *et al.*, 1987).

Crystallographic studies on Au-bearing minerals (pyrite and arsenopyrite) and synthesis of Au-bearing sulphides: X-ray diffraction (XRD) (Kurantu, 1941), TEM and electron diffraction (Backen *et al.*, 1989; Cabri *et al.*, 1998) are used to correlate lattice parameters with the presence of inserted Au atoms.

A major finding is that lattice Au exists in both arsenopyrite and pyrite, probably as a covalent bond to Au^+ , substituting Fe atoms. This type of Au frequently co-exists with particles of metallic Au in the same host mineral. Also, the distribution of Au within natural arsenopyrite or pyrite grains is mostly non-uniform. Mapping frequently reveals zoning, and a common feature is Au-As overlap of zonings and positive correlation of local contents. Only a multidisciplinary approach can lead to a major advance in the understanding of the crystal-chemistry of Au in sulphides. Genkin *et al.* (1998), Cabri *et al.* (2000) and Ashley *et al.* (2000) give recent examples. This current paper shows some of the results on pyrite and arsenopyrite collected from different ore-bodies and processing plants. It contains some analytical refinements that contribute to a multidisciplinary approach for better understanding of the complex state of the Au.

Samples

The samples used in this study were selected on the basis of availability and diversity: (1) Le Châtelet (Creuse, Massif Central, France): Sample from shear-zone mineralization. The Au ore is characterized by high As and refractory Au. Amalgamation processing yields poor results, and thus the ore is treated by flotation, roasting and cyanidation (Aubert *et al.*, 1964;

Bonnemaison, 1987). The sampled vein (Filon Marthe) contains quartz, phyllosilicates, arsenopyrite and minor pyrite. The Au-containing phases were concentrated by CHBr_3 heavy-medium separation, giving 1800 $\mu\text{g/g}$ Au content in the concentrate. Arsenopyrite is the major phase, with pyrite (~10%) and rare quartz. No 'visible' Au is present. (2) Villeranges (Creuse, Massif Central, France): The sample comes from an underground exploration drift, in a probable shear-zone environment. It contains mainly quartz, phyllosilicates, arsenopyrite and pyrite (Boiron, 1987). Arsenopyrite is the major phase, with some coarse grains of pyrite embedded in quartz and no 'visible' Au. (3) Neves Norte (Alentejo, Portugal): The samples are from a newly mined area of the volcanogenic massive sulphide (VMS) Cu-Sn Neves Corvo deposit (Pinto *et al.*, 1997, 1998; Ferreira *et al.*, 1997; Cabri *et al.*, 1998; Gaspar, 2002). They contain pyrite and arsenopyrite, chalcopyrite, bornite and other minor minerals (Pinto, 1999). Two samples were selected and assayed at 32.8 $\mu\text{g/g}$ (sample I) and 25.4 $\mu\text{g/g}$ (sample II). Pyrite is the major phase, with arsenopyrite (~40%) and minor chalcopyrite, galena, stannite, tetrahedrite and quartz, with no native Au. (4) Colombia (South America): The sample is of sandy mine tailings (unknown location). After coarse grinding, the ore was cyanidized for Au extraction producing a residue that had significant Au and Ag contents. The studied sample is derived from a flotation concentration of the cyanidation residue and contains 92 $\mu\text{g/g}$ Au. Pyrite is the major phase (90%) with no visible arsenopyrite and rare quartz. Native Au is visible as small inclusions within the pyrite. Initial descriptions and analyses were published by Marion (1988) and Marion *et al.* (1991a,b).

Analytical methods and associated refinements

Figure 3 describes the characterization pathway after appropriate sulphide concentrates were prepared.

Scanning electron microscopy

The electron microscope was used in back-scattered electron imaging mode to identify fine Au inclusions in the sulphides and to map the chemical zoning within pyrite and arsenopyrite. These results were important to guide later EMPA

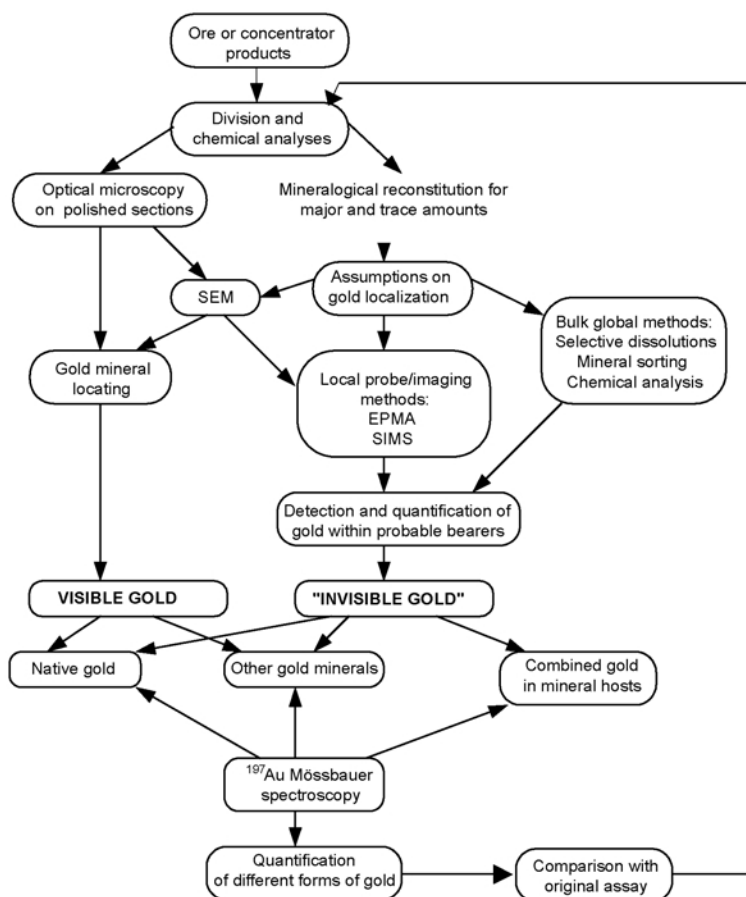


FIG. 3. Mineralogical characterization protocol of gold associations.

or SIMS Au analysis. Measurements were performed at the SCM (Service Commun de Microanalyse, Laboratoire de Chimie Minérale, University Henri Poincaré, Nancy, France) on a Hitachi S-2500 microscope.

Electron microprobe analysis

Measurements were performed at the SCM and CMTC (Consortium des Moyens Technologiques Communs, Institut National Polytechnique de Grenoble) using a Cameca SX50. An accelerating voltage of 25 kV and a beam current of 10 or 20 nA were used for major elements (Fe, As and S) and 60 nA for Au at the same resolution/beam size (see Table 1). For the reasons given below, Au-free sulphide standards were used.

Graham *et al.* (1989) improved the Au detection limit to 10 ppm by measuring the

Au- $L\alpha$ line under extreme conditions (40 kV and 500 nA). In the present study, different choices were made because: (1) a constant accelerating voltage of 25 kV is suitable for simultaneous analysis of trace and major elements, minimizing beam shift; (2) a relatively small probe obtained good lateral resolution; and (3) potential element migration under the beam was limited.

Figure 4 shows the WDS spectra centred on the Au- $L\alpha$ line and obtained on pure pyrite and an As-Au-bearing pyrite grain from the Colombian concentrate. Au- $L\alpha$ line height intensity measurement is particularly difficult due to the 'hole' in the spectrum background (Self *et al.*, 1990; Remond *et al.*, 1996). Figure 4 shows the Au- $L\alpha$ peak position (1.277 Å or $2\theta = 36.98^\circ$ on a LiF (200) monochromator) located in the 'hole'. Background intensity was measured at +1000 (in abscissa coordinate $\sin\theta$) from the Au- $L\alpha$ line to

TABLE 1. EMPA analytical conditions.

Element	Standard	Line	Peak time (s)	Background time (s)	Confidence interval at 95% detection limit
Fe	FeS ₂ or FeAsS	<i>Kα</i>	10	5	±0.5 wt.%
S	FeS ₂ or FeAsS	<i>Kα</i>	10	5	±0.6 wt.%
As	FeAsS	<i>Lα</i>	10	5	±0.2 wt.%, 1900 ppm
Au	Au ⁰	<i>Lα</i>	120	120	±200 ppm wt., 480 ppm

minimize the hole effect. Background intensity under the Au-*Lα* line is defined by equation 1, with slope determined by the pure pyrite scan shown in Fig. 4.

$$I_{Bg(Au-L\alpha)} = I_{Bg(+1000)} * \text{slope} \quad (1)$$

X-ray mapping conditions were the same as for spot analyses, except for voltage and beam, at 30 kV and 200 nA, respectively. Scan field size was 62 × 62 μm, image resolution was 128 × 128 pixels (*x* and *y* steps ~0.5 μm) and counting time was 1 s/pixel, i.e. an X-ray image acquisition required 4.5 h. The X-ray maps in Fig. 5 were made at peak positions with background offset. Background measurement was required for trace Au qualitative analysis, the background being more intense for Au-rich than pure pyrite zones, since the presence of Au and As increases the mineral mean atomic number. This is evident in Fig. 5*b,c*. Thus, bright pixels in the Au-*Lα* peak image with small Au contents could be due to background effect alone. Considering the slope to determine background intensity, (Pk–Bg), the

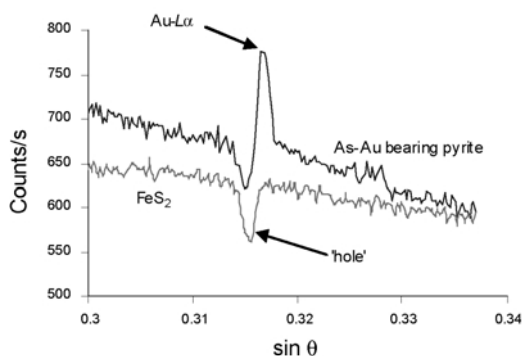


FIG. 4. EMPA wavelength scans centred on the Au-*Lα* line for a pyrite without As or Au and a Au-As-bearing pyrite. Spectra were acquired at 30 kV with a beam current of 200 nA and a counting time of 20 s per point.

Au-*Lα* signal reached ~200 counts/s for the richest zones shown in Fig. 5*c*. Further quantitative X-ray mapping would require higher magnification to avoid spectrometer defocusing and reduce the counting rate for major elements (possibly by using *Kβ* lines to maintain a 200 nA beam current for minor element analysis).

Secondary ion mass spectrometry

Ion microprobe analysis provides low detection limits for trace element analysis and mapping, improved by at least two orders of magnitude compared to EMPA, but a drawback is standardization, requiring matrixes similar to the analysed sample. We used two instruments at the LAM (Laboratoire d'Analyse Minérale, University of Luxembourg): a Cameca IMS-5f and a Cameca prototype especially designed for LAM purposes. A positive Cs ion source gave the primary beam (10 kV with 50 nA for depth profiling and 0.5 nA for scanning mode), and we monitored negative secondary ions. Figure 6 shows the mass spectra of auriferous pyrite and arsenopyrite near 197 a.m.u. Because Au has only one natural isotope and exhibits no mass change under analysis, a high mass-resolution of approximately $M/\Delta M = 6000$ was selected to avoid main interference at 197 a.m.u. between Au and polyatomic ions FeAsS₂ and CsS₂. Comparison of ¹⁹⁷Au[–] and ¹⁹⁵FeAsS₂[–] images (see also Fig. 20) demonstrates no residual interference. Another option is filtering polyatomic ions by applying a voltage offset to the secondary ion beam although this significantly reduces the Au signal.

Two modes were used to quantify Au concentrations: (1) integration of ion count intensities from the large window ion images; and (2) scan a 150 μm × 150 μm zone and analyse a central 60 μm diameter circle with a

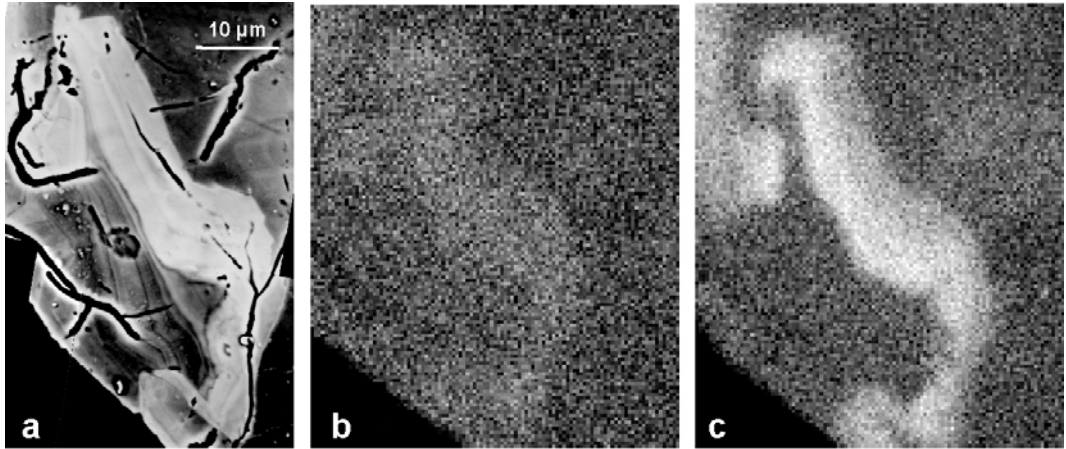


FIG. 5. EMPA X-ray mapping within a pyrite grain shown in Fig. 12 (zone 1). (a) BSE image; (b) background Au-L α ; (c) peak Au-L α

depth profile. Steady-state depth profiles were used to offset the surface effect described below (in the sub-section: *Growth zoning and late diffusion in arsenopyrite and pyrite* below).

However, both modes are difficult to validate for accuracy.

Standardization

An external standardization using Au⁺-implanted sulphides at 2 MeV with a dose of $1.09 \times 10^{15} \pm 5\%$ at./cm² was used. Implant matrixes were natural automorphous crystals of pyrite (Logrono, Spain) and arsenopyrite (Panasquera, Portugal), selected for their mineralogical purity and size. Figure 7 presents SIMS depth profiles for pyrite and arsenopyrite implanted standards. Depth was determined with a profilometer that measures crater depth caused by ion firing. Observed profile disturbance in the first micrometres corresponds to an artefact due to ion firing. Relative sensitivity factor (RSF) values of Au relative to matrix ions ¹⁰⁷As⁻ and ⁸⁹Fe⁻ are calculated from depth profiles. Results are summarized in Table 2.

Relative sensitivity factor calculation allows quantification of the analysed elements with equations 2 and 3:

$$\text{Conc. (at./cm}^3\text{)} = \text{RSF} \times \text{trace ion emission/matrix ion emission} \quad (2)$$

$$\text{Atomic conc. of trace (at./at.)} = \frac{\text{Conc. (at./cm}^3\text{)}}{\text{No. atoms in host (at./cm}^3\text{)}} \quad (3)$$

Pyrite and arsenopyrite contain 7.5×10^{22} and 6.7×10^{22} Au at./cm³, respectively. Atomic concentration was converted into mass concentration by multiplying by 4.93 for pyrite and 3.63 for

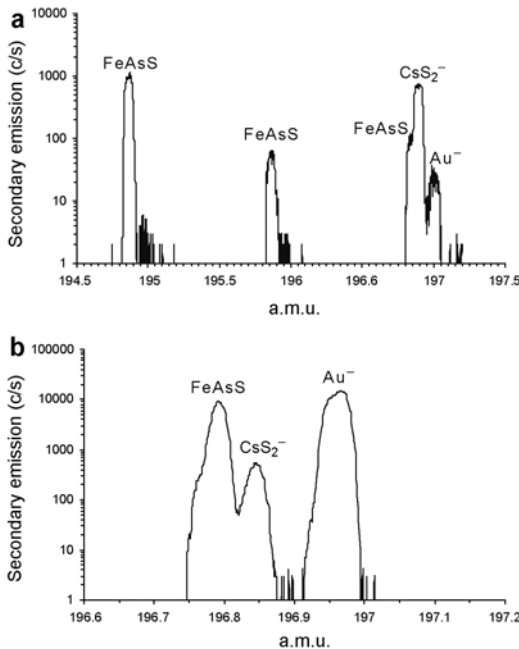


FIG. 6. SIMS mass spectrum between 195 and 197.5 a.m.u. of Au-As-bearing pyrite, mass resolution $M/\Delta M \sim 4000$ (a) and SIMS mass spectrum near 197 a.m.u. of Au-bearing arsenopyrite, mass resolution $M/\Delta M \sim 6000$ (b).

TABLE 2. Relative sensitivity factors in pyrite and arsenopyrite.

	RSF $^{197}\text{Au}/^{107}\text{AsS}$ (atoms/cm ⁻³)	RSF $^{197}\text{Au}/^{89}\text{FeS}$ (atoms/cm ⁻³)
Arsenopyrite	1.205×10^{20}	1.06×10^{20}
Pyrite	2.081×10^{20}	—

arsenopyrite (see Benzaazoua, 1996 for more details). The detection limit, derived from implant depth profile plateaux, is 0.03 µg/g for arsenopyrite and 0.16 µg/g for pyrite. Analytical conditions are similar to Cabri *et al.* (1998).

Effect of Au status on ion emission rate

The SIMS depth profiles of pyrite and arsenopyrite Au-bearing grains (Fig. 7) show that the first mineral layers enhance Au emission during the Au SIMS analysis: steady state is reached only after penetrating 50–100 nm into the sample. The surface state effect on SIMS emission is explained by the crystal-chemical disturbance of the first layers due to polishing and superficial oxidation. Differences between secondary emissions corresponding to different known bonding Au states were investigated by blending powdered arsenopyrite with two different chemical Au states in

known contents: (1) combined Au samples produced with Au-bearing arsenopyrite concentrate (Le Châtelet); and (2) pure metallic Au added by a cathode evaporator to powdered Au-free arsenopyrite (Panasqueira). Thus, different Au concentrations mixed with arsenopyrite were produced by successive dilutions of Au source powders with Au-free arsenopyrite powder. Mixtures were homogenized by intense grinding then compressed into thin platelets (15×10^3 kg/cm²) prior to SIMS analysis. Results were normalized in relation to ions from the matrix (^{90}FeS or $^{195}\text{FeAsS}$). Results (Fig. 8) show different secondary emissions, with combined Au greater than metallic Au. Gold quantification using implanted standards with unknown Au status therefore becomes hypothetical. Quantification is obtained using implanted standards.

Comparison with EMPA analyses

Figure 9 shows grade profiles obtained by SIMS and EMPA analysis, superimposed for comparison. The EMPA and SIMS Au values differ. Very different pyrite volumes involved during the analysis can explain this, since SIMS sputters into the superficial layers (a few Å) while the electron beam excites a pear-shaped volume of several cubic microns. Another explanation is differing emission yields between implanted Au standards and combined Au within pyrite, as demonstrated above for Au in arsenopyrite.

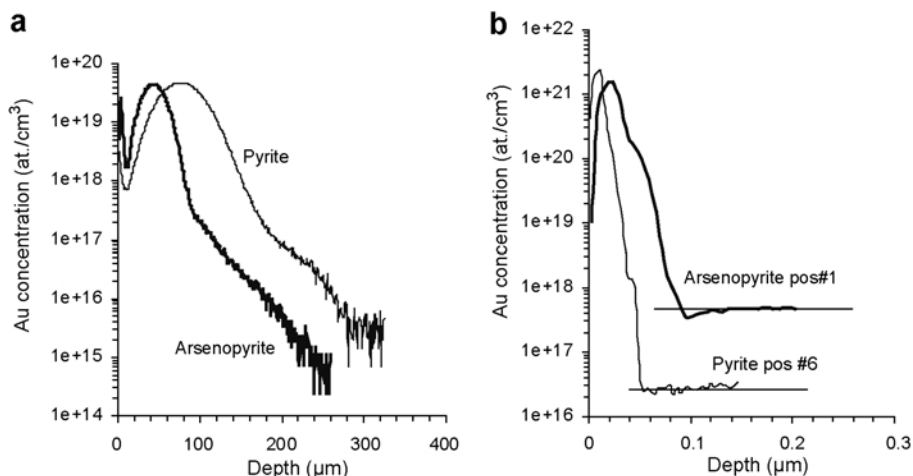


FIG. 7. (a) SIMS Au concentration depth profile in Au-implanted pyrite and arsenopyrite (2 MeV, 10^{15} at./cm²), and (b) Local SIMS $^{197}\text{Au}^-$ depth profile within natural Au-bearing pyrite and arsenopyrite (Neves Norte ore sample II). The analysed zones correspond to positions 1 (arsenopyrite) and 6 (pyrite) of Table 4.

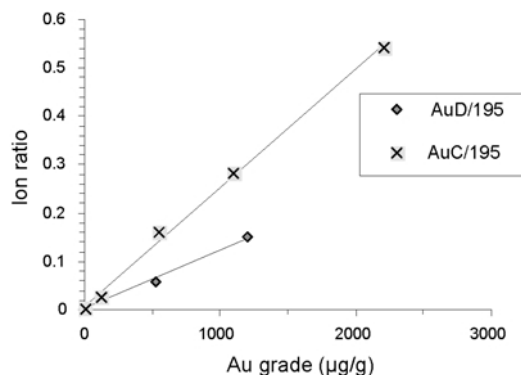


FIG. 8. SIMS $^{197}\text{Au}^-$ secondary emission of two types of Au-bearing products. AuD: artificially Au-enriched powdered arsenopyrite; AuC: Blend of natural Au-bearing and combined-Au bearing arsenopyrite. Ion intensities were normalized with respect to $^{195}\text{FeAsS}^-$.

However, results using both methods remain similar enough to assess the reliability of quantitative SIMS calibration and measurement.

Transmission electron microscopy

The goal here is to study the Au content of enriched zones within Au-bearing pyrite and arsenopyrite with local lattice characteristics. However, there are two challenges: (1) preparing samples and finding sufficiently thin zones in grains for TEM (Benzazoua, 1996); and (2) it is impossible to verify Au content by other methods

(SEM, MSE) before TEM and energy dispersive elemental analysis. Thin-sample preparation was limited to milling the samples sufficiently and using only fine fractions separated by alcohol sedimentation. Ultra-thin grains ($<1\ \mu\text{m}$) were mounted on carbide or Formvar film. As sulphide edges are transparent to electrons less than $\sim 10\ \text{nm}$, images were taken on only very limited zones at particle edges. Irregular sample thickness made it difficult to obtain appropriate contrasts due to composition variations and crystalline structures. Measurements were made at the SCM on a Philips STEM CM20 microscope. Transmission imaging (bright/dark fields) and electron micro-diffraction at high voltage (200 kV max.) and high magnification (up to $\times 750,000$) revealed Au micro-inclusions or micro-precipitates in the sulphide matrix. EDS X-ray microanalysis was performed on an EDAX system with a Si-Li detector, allowing large surface and nanoprobe mode. Electron acceleration voltage was 80 kV and spot size was $\sim 7\ \text{nm}$. Detection limit was $\sim 1000\ \mu\text{g/g}$ for Au (Au- $L\alpha$ line at 9.71 kV) with 100 s acquisition time. The Au- $M\alpha$ line (2.12 kV) is more intense but suffers interference by the S- $K\alpha$ line.

Results and discussions

Structurally bound Au in arsenopyrite

The Le Châtelet and Villeranges arsenopyrites show strong chemical zoning in BSE SEM imaging (Figs 10 and 17). This is largely due to

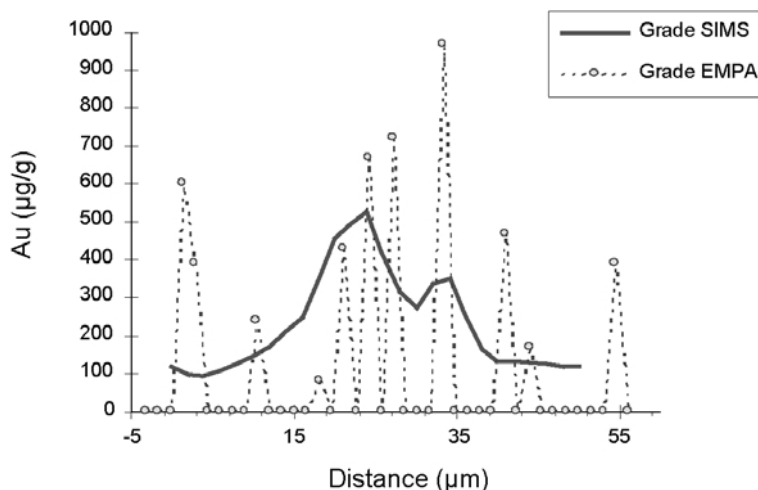


FIG. 9. Comparison between SIMS and EMPA analyses along a line crossing a pyrite grain from the Le Châtelet mine (line drawn in Fig. 19).

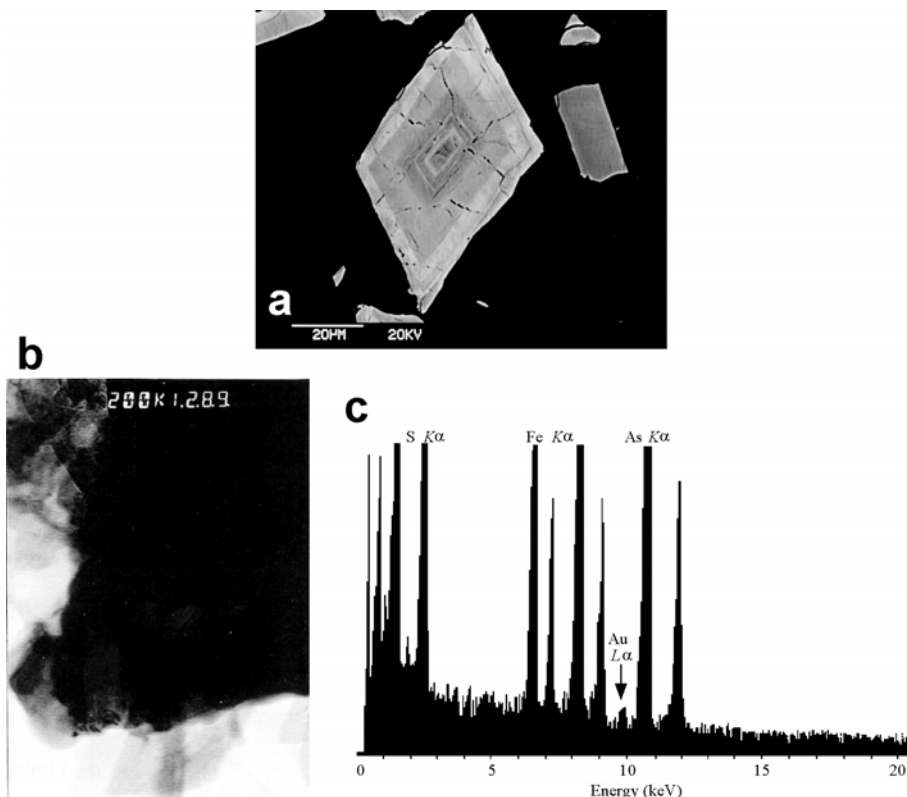


FIG. 10. SEM BSE image (a), TEM image at 200,000 magnification (b), and TEM coupled EDS spectrum (c) on arsenopyrite grains from the Le Châtelet mine.

variable As content as well as the presence of Au concentrations well correlated with As. Mössbauer spectrometry found only chemically bound 'invisible gold' in arsenopyrite concentrate from the Le Châtelet ore (Marion, 1988; Cathelineau *et al.*, 1989). EDS X-ray microanalysis coupled with TEM also shows the presence of Au in the thin edges of fine arsenopyrite grains (Fig. 10). The Au- $L\alpha$ line is visible on the spectrum (Fig. 10), and quantification reveals Au-rich areas ($>10,000 \mu\text{g/g}$) with no evidence of micro-precipitates even at high magnification ($\times 750,000$) in scanning and diffraction modes. This suggests that Au is incorporated into the arsenopyrite structure (Benzaazoua, 1996).

In Fig. 11, the Le Châtelet arsenopyrite EMPA analyses are compared to arsenopyrite compositions from other mines: (Villeranges (France), Hillgrove (New South Wales, Australia, Ashley *et al.*, 2000), Barbrook (South Africa), and Fairview

(South Africa)). Marion (1988), Friedl (1989), Wagner *et al.* (1989) and Friedl *et al.* (1992) characterized these using EMPA, SIMS and Mössbauer spectrometry. All showed a predominance of combined Au. Compared to the Le Châtelet arsenopyrite, with its excess As, the other arsenopyrites are As-deficient. The Le Châtelet data show clear correlations between As and Au content, vs. more dispersed data for the other samples. However, the Villeranges and Hillgrove samples also show increased Au with As. The maximum Au content hosted by arsenopyrite appears directly related to mean As content.

Crystal-chemical state of Au hosted by pyrite

The status of pyrite-hosted Au appears more complicated than Au in arsenopyrite. Lower Au content, frequent mixtures with Au-bearing arsenopyrite and the very frequent presence of

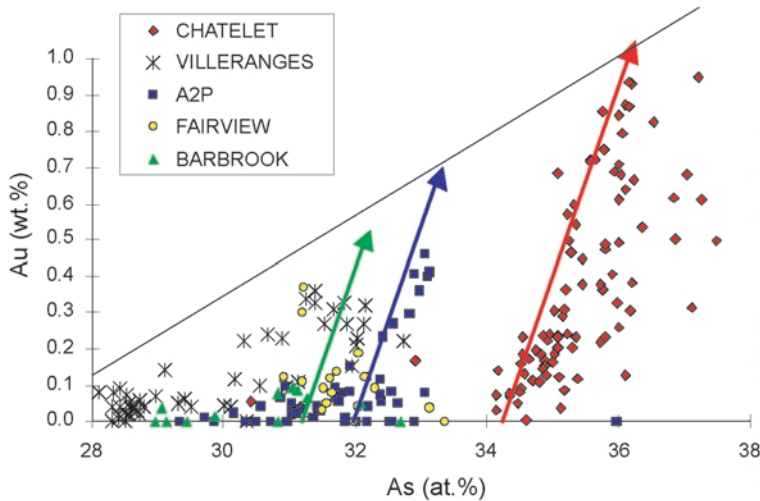


FIG. 11. Relationship between Au (wt.%) and As (at.%) for EMPA analyses for arsenopyrite grains from different origins. Oblique lines: inferred correlations for Le Châtelet, Villeranges and Hillgrove. Dotted line: upper limit of experimental data from this study.

native Au impair accurate characterization. Backscattered electron SEM imaging of pyrite in the Colombian ore shows strong zoning (Fig. 12a). Zoning in arsenopyrite is strongly correlated with the As content, producing a locally higher average atomic number. Some pyrite grains also contain electrum. SIMS images on both grains are presented in Figs 13 and 15, confirming the strong correlation between As and Au locations. The line-scan profile in Fig. 14 corresponds to the ion image in Fig. 13. Peak Au content at 45 μm is calculated at

1420 $\mu\text{g/g}$, in good agreement with EMPA data, at up to 2150 $\mu\text{g/g}$ (for 4.6 at.% As, see Fig. 16, zone 1).

Figure 16 presents the electron microprobe analyses of the Colombian pyrite (see also Fig. 12), with data on Au-bearing pyrite from other sources (Le Châtelet: Marion, 1988; Villeranges: Marion *et al.*, 1991a,b; Benzaazoua, 1996; USA, Nevada, Twin Creeks: Simon *et al.*, 1999b; USA, Nevada, Carlin and Cortez: Wells and Mullens, 1973; South Africa, Barberton, Agnes: Claassen, 1991; and Fairview: Fleet *et*

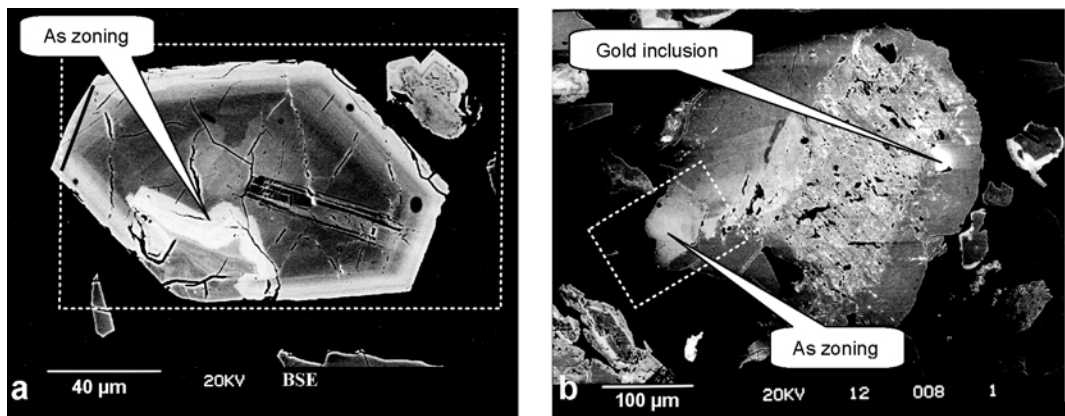


FIG. 12. SEM BSE images of two pyrite grains from the Colombian mine. (a) zone 1; (b) zone 2. Brightest areas in b are native Au grains. Frames correspond to ion images in Figs 13 and 15.

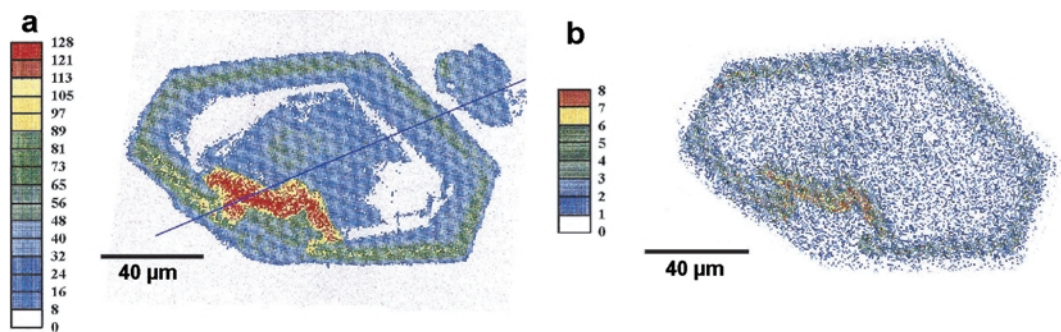


FIG. 13. SIMS image of $^{107}\text{AsS}^-$ (a) and $^{197}\text{Au}^-$ (b) within the pyrite grain in Fig. 12a (a: zone 1). 180 s acquisition time. The line drawn on the AsS image corresponds to the line scan in Fig. 14.

al., 1993, described by Swash and Ellis, 1986). Colombian pyrite shows two distinct data sets corresponding to contrasting compositions: relatively little Au (≤ 0.2 wt.%) and large, anomalous, As (almost 6 at.%), and much Au (> 0.5 wt.%) with relatively small As (≤ 2 at.%) contents. The Nevada and South Africa pyrite contain intermediate amounts of Au and As. Linear relationships between As and Au contents are seen for certain data sets, e.g. Colombia, zone 2, Villeranges and possibly Fairview (black arrow in Fig. 16), suggesting Au contained within the pyrite lattice.

The presence of chemically-bound Au is confirmed by Mössbauer spectroscopy in the Colombian concentrate (Marion, 1988; Friedl, 1989; Friedl *et al.*, 1992; Marion *et al.*, 1991a,b;

Yvon *et al.*, 1991), the Agnes concentrates (129 $\mu\text{g/g}$ Au, $\sim 95\%$ pyrite and no visible arsenopyrite by optical microscopy, Marion, 1988; Wagner *et al.*, 1988, Friedl, 1989) and in the Villeranges ore (200 $\mu\text{g/g}$ Au, nearly 100% pyrite and no arsenopyrite visible by optical microscopy, Marion, 1988; Friedl, 1989; Friedl *et al.*, 1992). Native Au is also found in the Mössbauer spectra of the Colombian and Agnes concentrates, consistent with optical microscope observations. The chemically-bound Au, which is identified within the Colombian concentrate, absorbs gamma rays at distinctly lower velocities compared to the lattice Au within all the studied arsenopyrites. In contrast, Villeranges and Agnes concentrates show combined arsenopyrite-type Au, implying Au insertion into the pyrite structure

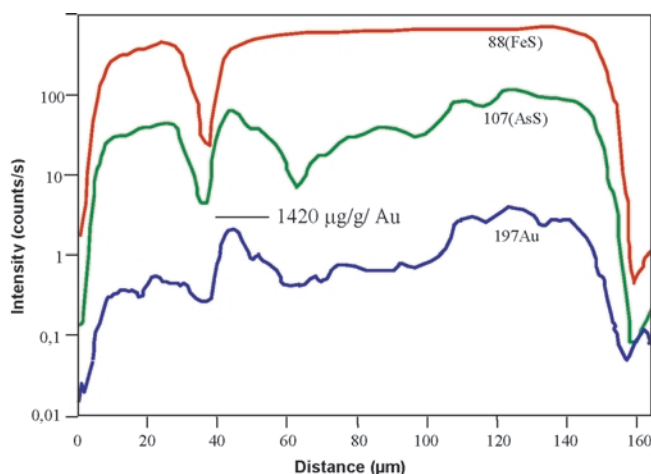


FIG. 14. SIMS line-scan of the different ion emissions in the pyrite grain in Fig. 12. The beginning of the scan corresponds to the upper right end of the line drawn in Fig. 13. At a distance of 45 μm , the calculated Au grade is 1420 $\mu\text{g/g}$.

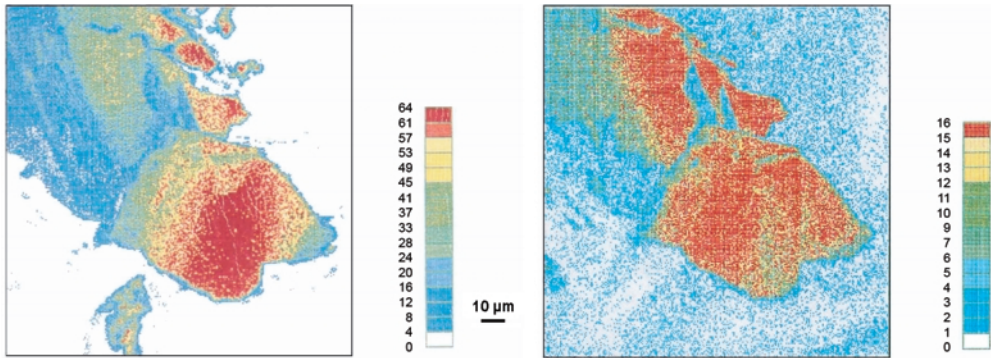


FIG. 15. SIMS image of $^{107}\text{AsS}^-$ (a) and $^{197}\text{Au}^-$ (b) within a pyrite grain from Colombia, Fig. 12b (zone 2). 180 s acquisition time.

in the Colombian concentrate, whereas the presence of Au-bearing arsenopyrite micro-precipitates could explain the Villeranges and Agnes concentrates. This does not exclude the contribution of chemically-bound Au of the Colombian pyrite type, albeit a minor species, although EMPA analysis shows Au associated with As within pyrite.

The Colombian pyrite displays anomalous As contents with complicated internal structures, compact cores and porous, As-enriched edges (Marion *et al.*, 1991c; Monroy *et al.*, 1993). Many similarities exist between the Colombian concentrate pyrite and Au-bearing arsenian pyrite in the strata-bound ores described by Fleet *et al.* (1989, 1993). Simon *et al.* (1999a), using XANES and STEM, concluded that Twin Creeks pyrite

(Carlin Trend, Nevada) include Au^0 as submicro-metric inclusions of native gold and Au^+ , possibly concentrated in 'randomly distributed layers within a marcasite or arsenopyrite structure'. Fleet and Mumin (1997) suggested that 'invisible' Au in pyrite, marcasite and arsenopyrite of sediment-hosted deposits is chemisorbed from hydrothermal fluids at As-rich sites and incorporated into a metastable solid solution. Yet, from the STEM characterization of the Le Châtelet arsenopyrite, and attempts to find Au in arsenian pyrite by thin-edge examination using STEM-EDS failed.

Growth zoning and late diffusion in arsenopyrite and pyrite

Figure 17 shows a BSE image of the Villeranges arsenopyrite with at least two crosscutting

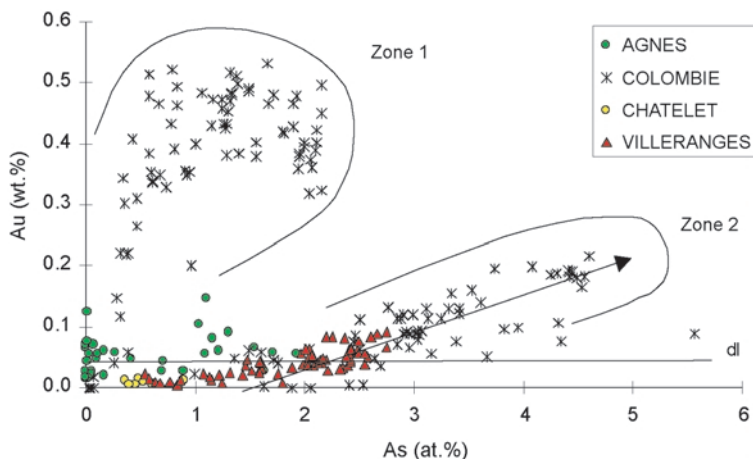


FIG. 16. Relationship between Au (wt%) and As (at.%) for EMPA analyses for pyrite grains from different origins. Horizontal line: detection limit for Au in the present work. Oblique line: inferred correlation for lattice Au.

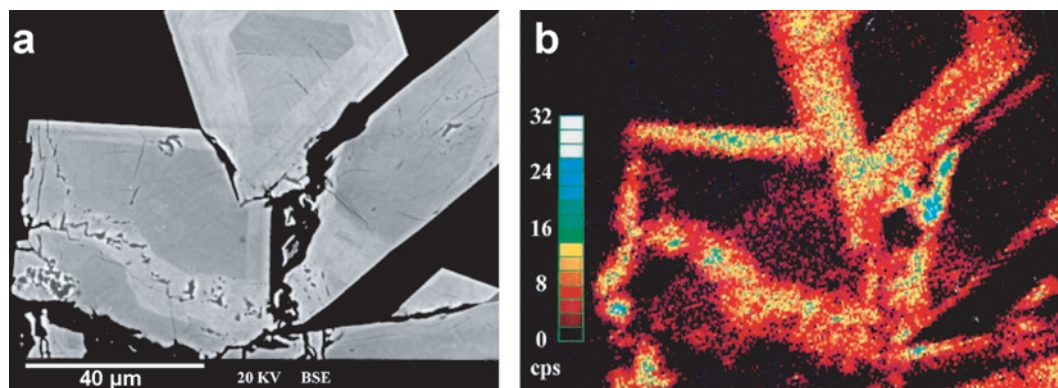


FIG. 17. BSE SEM image of arsenopyrites from the Villeranges orebody displaying at least two cross-cutting chemical zonings due to growth and later diffusion along a fracture (a), and corresponding $^{197}\text{Au}^-$ SIMS image (b).

chemical zonings related to As concentration. Similar Au-enrichment is proven by SIMS imaging (Fig. 17). The same phenomenon might occur in an arsenopyrite crystal from the Hillgrove mine (Ashley *et al.*, 2000), but remains unexplained. Imaging by BSE of automorphous pyrite shows paragenetic features similar to the Villeranges arsenopyrite sample, which also displays superimposed zonings (Marion *et al.*, 1991a,b). The first-formed is a growth oscillatory zoning, consequently cross-cut by a secondary diffusion zoning (Fig. 18). Again, Au follows As, as shown by SIMS imaging, and major Au mineralizing is the last diffusion event. The Le Châtelet pyrite further indicates thin bands due to variations in the within-grain As/S ratio, unrelated to crystal growth, and caused by diffusion into the crystals around voids and along cracks (Fig. 19). White areas (in cracks, voids or isolated) in Fig. 19 are Au-bearing arsenopyrite grains. SIMS images (Fig. 19) show complex patterns of As and Au diffusion: Au is always accompanied by As but not *vice-versa*. Unfortunately, no current method provides reliable information on the chemical state of Au and As incorporated in these small bands in pyrite. Bulk analysis, such as Mössbauer spectroscopy, is hindered by diluted potential responses in the major signal of arsenopyrite-structurally bound Au.

These observations lead to the following conclusions: (1) the chemical state of Au in pyrite is difficult to determine using single-method data. For example, EMPA data in Fig. 16 indicate Au-As correlation, possibly due to inserted Au-As complexes, but also Au-rich zones, possibly due to discrete phases of native

Au and/or Au-bearing arsenopyrite; (2) observed co-diffusional Au and As processes support the assertions and literature review of Simon *et al.* (1999b) that Au forms complexes with As in hydrothermal solutions. The better-known Au bisulphide complexes (Feet and Mumin, 1997; Simon *et al.*, 1999a) do not produce such patterns, with Au closely related to As, as revealed by SIMS imaging; (3) during or after Au-As complex diffusion, Au-bearing arsenopyrite may crystallize as the pyrite structure becomes over-saturated with Au and As (Fig. 19).

Overgrowth of late Au-bearing arsenopyrite

As 'visible' native Au is absent in the Neves Norte deposit, arsenopyrite probably accounts for a significant part of the Au assay. From the BSE imaging, arsenopyrite is frequently highly As-zoned. Gold EMPA analysis of arsenopyrite gave only three positive points among 38 (621 $\mu\text{g/g}$ in sample I, 1710 and 520 $\mu\text{g/g}$ in sample II) (Tables 3 and 4). Arsenic and Au bulk chemical data of the rock sample implies that arsenopyrite contains a maximum average of 72.5 $\mu\text{g/g}$ of Au in sample I and 62.2 in sample II, assuming arsenopyrite as the only Au host. These low average contents fully justify the use of SIMS analysis. Differences in average Au contents of arsenopyrite between samples I and II defy interpretation due to: (1) analytical conditions (large integration windows in ion images for sample I and 60 μm diameter depth profiles for sample II), with possible analytical bias of surface Au emission enhancement (see *Effect of Au status on ion emission rate* above); and (2) Au and As

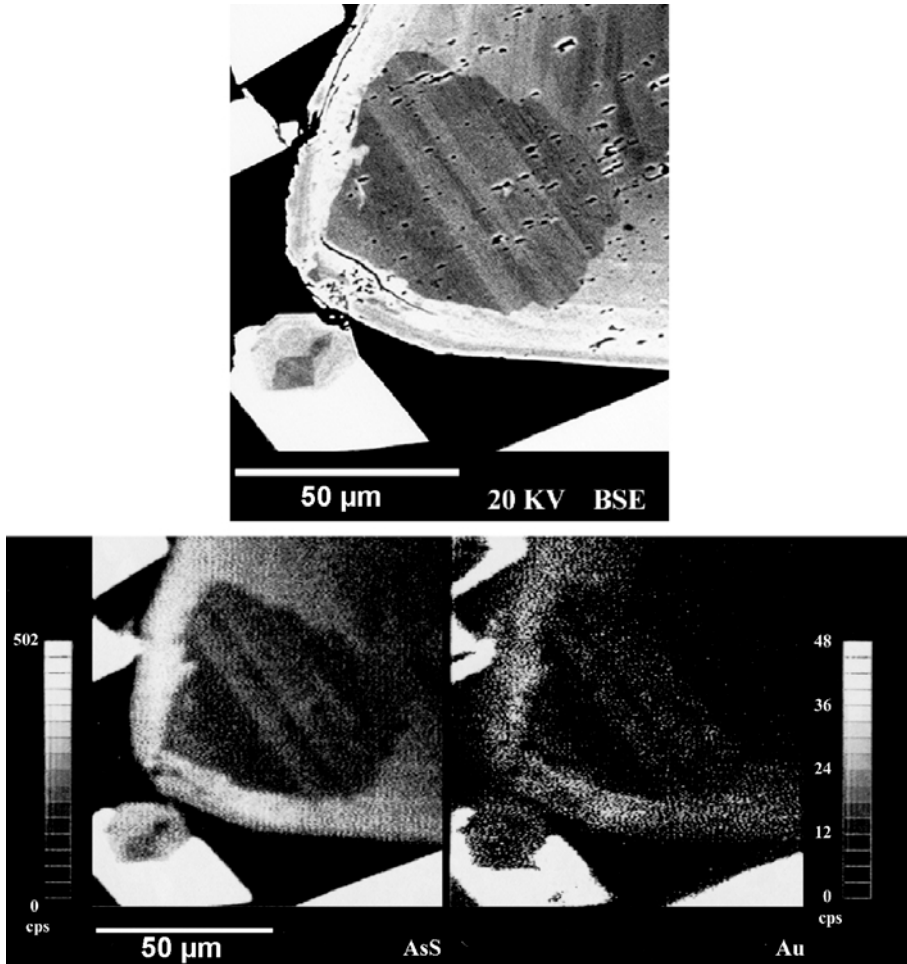


FIG. 18. SEM BSE image of a pyrite grain from the Villeranges orebody displaying two cross-cutting generations of chemical zoning due to growth and later diffusion (upper), and corresponding $^{197}\text{Au}^-$ and $^{107}\text{As}^-$ SIMS image (bottom).

TABLE 3. Average Au concentrations in arsenopyrite grains from the Neves Norte ore sample I, (see ion images and integrating windows for zones 1 and 2 in Fig. 20).

Analysis window	Total (counts/s) $^{197}\text{Au}^-$	Total (counts/s) $^{107}\text{As}^-$	$^{197}\text{Au}/^{107}\text{AsS}$	$^{197}\text{Au}/^{107}\text{AsS} \cdot \text{RSF}$ $\text{at.}_{\text{Au}}/\text{cm}^3_{\text{FeAsS}}$	Concentration (ppm)
Zone 1	52,405	836,012	0.0627	7.55348×10^{18}	400
Zone 2	7,143	782, 527	0.0091	1.09994×10^{18}	58
Zone 3	670,134	4,193,794	0.1598	1.92549×10^{19}	1021
Zone 4	39,901	3,624,881	0.0110	1.32641×10^{18}	70
Zone 5	168,211	3,813,944	0.0441	5.31456×10^{18}	282

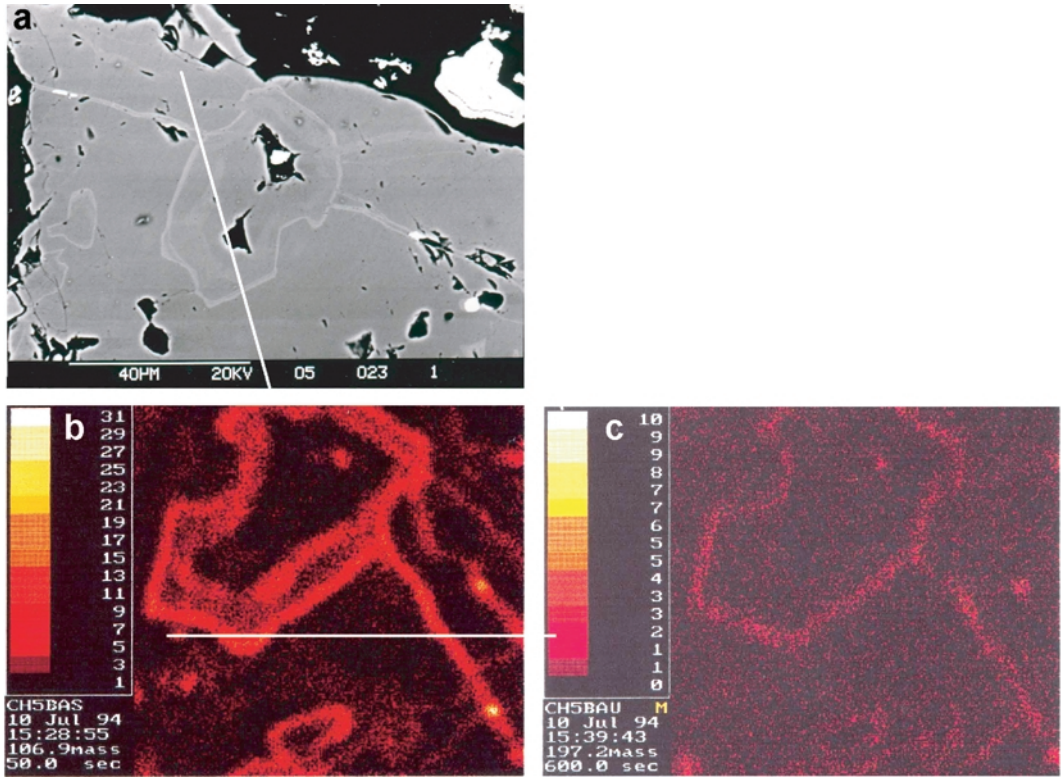


FIG. 19. SEM BSE images of a pyrite grain from the Le Châtelet mine displaying As zoning (a), and corresponding SIMS images of $^{107}\text{AsS}^-$ (b) and $^{197}\text{Au}^-$ (c) distribution at 600 s acquisition time for Au, 50 s for As.

arsenopyrite zoning, which may distort the sampling process, especially for sample II. The wide Au grade range in sample I could be explained by the zoning in some arsenopyrite crystals, and several mineralization stages. Figure 20 shows late Au-rich arsenopyrite in small crystals (400 $\mu\text{g/g}$ on average, zone 1 of

Table 3, upper integration window in Au image in Fig. 20), grown on a pre-existing Au-poor arsenopyrite nucleus (58 $\mu\text{g/g}$ on average, zone 2 in Table 3, lower integration window in Au image in Fig. 20). Furthermore, Table 4 and the ion images in Fig. 20 show Au-free pyrite in the low-As samples (<0.2 wt.%).

TABLE 4. Gold concentrations in arsenopyrite and pyrite grains from the Neves-Norte ore sample II, (see Fig. 7 for local 60 μm diameter SIMS $^{197}\text{Au}^-$ depth profiles from which data were obtained).

Position	Mineral	$^{197}\text{Au}/^{89}\text{FeS}^*\text{RSF}$ at. $\text{Au}/\text{cm}^3 \text{FeAsS}$	Concentration (ppm)
1	Arsenopyrite	4.7×10^{17}	25
2	Arsenopyrite	3.0×10^{17}	16
3	Arsenopyrite	3.5×10^{17}	19
4	Arsenopyrite	3.0×10^{17}	16
5	Arsenopyrite	6.6×10^{17}	35
6	Pyrite	2.6×10^{16}	1.7

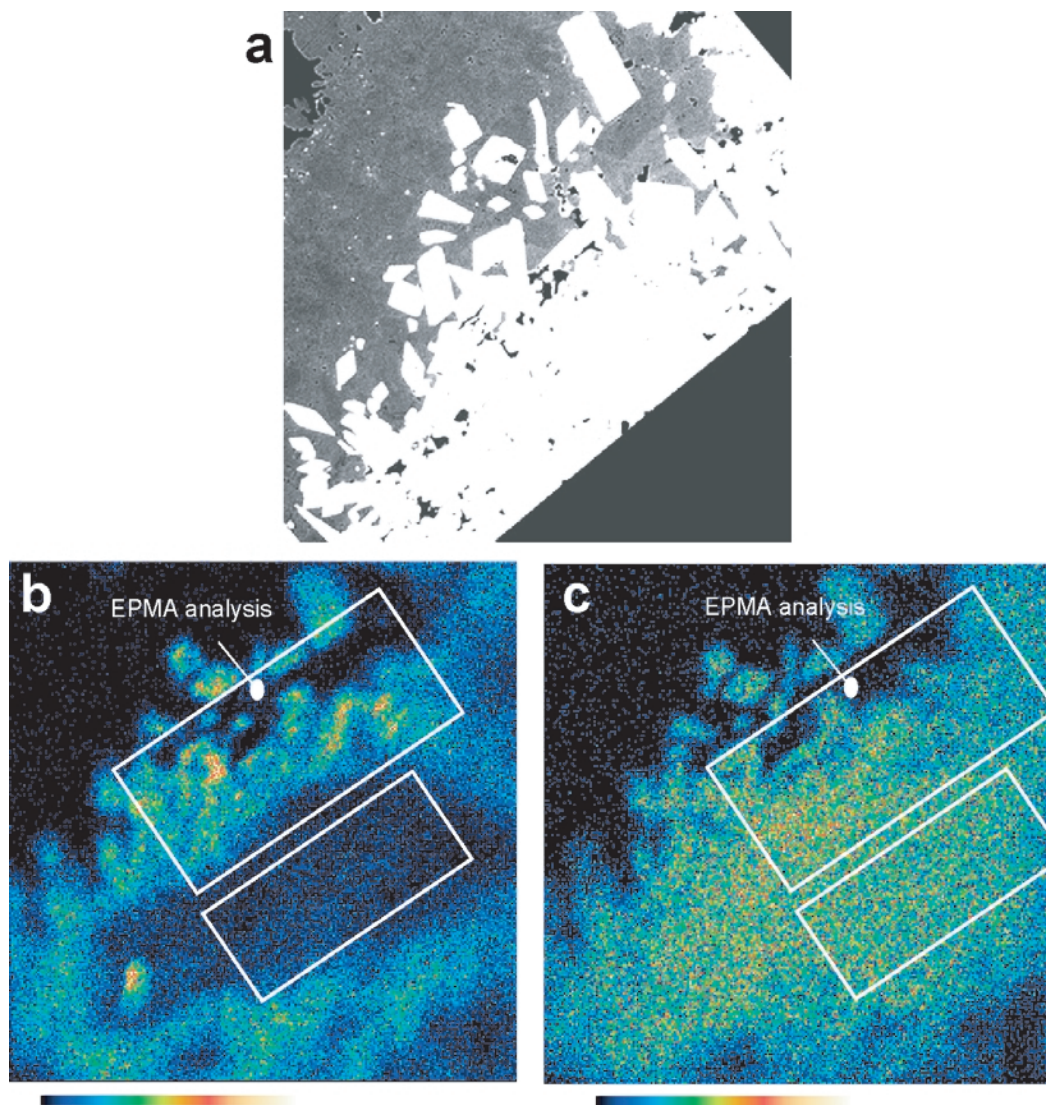


FIG. 20. SIMS ion distribution image within a pyrite-arsenopyrite association of the Neves Norte orebody. Imaged field: $200\ \mu\text{m} \times 200\ \mu\text{m}$. (a) 16 kV BSE image (bright arsenopyrite in dark pyrite), (b) $^{197}\text{Au}^-$, $5 \times 60\ \text{s}$ acquisition time; (c) $^{195}\text{FeAsS}_2^-$, $5 \times 2\ \text{s}$ acquisition time. The large and small rectangles are zones 1 and 2, respectively, of Table 3 for count integration. White circle: location of an EMPA analysis ($620\ \mu\text{g/g Au}$).

Conclusions

A multianalytical approach is needed to establish fully the nature of Au in sulphide ores. It consists of direct observation when Au is well expressed (visible), element analysis using electron, ion or proton probes to measure small Au contents, characterizing the chemical state of Au by wet chemical dissolution, determining the Au chemical

bonding by various spectrometry techniques (Mössbauer, XPS, XANES, EXAFS, EPR, etc.), or by a crystallographic investigation followed by the use of XRD or TEM coupled with electron diffraction. This paper shows the results from some of these techniques on Au in pyrite and arsenopyrite collected from ore-bodies and processing plants where Au presents complex occurrences.

The Au within these ores frequently co-exists with particles of metallic Au in the same host mineral. The Au distribution within the pyrite and arsenopyrite is mainly non-uniform. Backscattered electron images and X-ray mapping can reveal zoning and a common feature is Au-As overlap of zonings and positive correlation of local contents. Gold quantification by EMPA must take into account a background hole around the Au-L α line that can lead to an underestimation of the amount present. SIMS is useful for mapping and quantifying the occurrences of very small amounts of Au.

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