BULLETIN DE L'ASSOCIATION MINERALOGIQUE DU CANADA

THE CANADIAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL ASSOCIATION OF CANADA

Volume 27 September 1989 Part 3

Canadian Mineralogist
Vol. 27, pp. 353-362 (1989)

THE NATURE OF "INVISIBLE" GOLD IN ARSENOPYRITE

LOUIS J. CABRI
Process Mineralogy Section, CANMET, 555 Booth Street, Ottawa, Ontario K1A 0G1

STEPHEN L. CHRYSSOULIS
Process Mineralogy Section, Surface Science Western, London, Ontario N6A 3K7

JOHAN P.R. DE VILLIERS*
Departments of Geology and Chemistry, Arizona State University, Tempe, Arizona 85287, U.S.A.

J.H. GILLES LAFLAMME
Process Mineralogy Section, CANMET, 555 Booth Street, Ottawa, Ontario K1A 0G1

PETER R. BUSECK
Departments of Geology and Chemistry, Arizona State University, Tempe, Arizona 85287, U.S.A.

ABSTRACT

Gold-bearing arsenopyrite from the Elmtree deposit, New Brunswick, and the Sheba mine, Transvaal has been characterized by a variety of techniques including optical microscopy, electron microprobe analysis, scanning electron microscopy, secondary ion mass spectrometry and high-resolution electron microscopy. The arsenopyrite from these two deposits of widely different ages contains structurally bound Au, thus making the mineral refractory to metallurgical treatment by cyanidation. Gold in solid solution in arsenopyrite was found to attain 912 ppm in the Elmtree sample and up to 0.44 wt.% in the Sheba sample.

Keywords: submicroscopic Au, invisible Au, structurally bound Au, arsenopyrite, refractory Au ores, Elmtree deposit, New Brunswick, Sheba mine, Transvaal.

SOMMAIRE

L'arsenopyrite aurifère provenant du gisement de Elmtree, au Nouveau-Brunswick, et de la mine Sheba, au Transvaal, a fait l'objet d'un étude approfondie par microscopie optique, analyse à la microsonde électronique, microscopie électronique à balayage, spectrométrie de masse des ions secondaires, et microscopie électronique par transmission à haute résolution. L'arsenopyrite des deux milieux, d'âge très disparate, contient de l'or dans sa structure, ce qui la rend réfractaire à un traitement métallurgique par cyanuration. L'arsenopyrite de Elmtree contient jusqu'à 912 ppm d'Au incorporé par un mécanisme de solution solide, tandis que celle de Sheba peut en contenir jusqu'à 0.44% par poids.

(Traduit par la Rédaction)

Mots-clés: Au submicroscopique, Au invisible, Au en solution solide, arsenopyrite, minerai aurifère réfractaire, gisement de Elmtree, Nouveau-Brunswick, mine de Sheba, Transvaal.

---

*Present address: MINTEK, Private Bag X3015, Randburg, 2125, South Africa.

INTRODUCTION

Concern about the nature of gold in sulfide minerals such as pyrite and arsenopyrite is not new; it arose when metallurgists discovered that certain gold ores are not directly amenable to cyanidation. Mineralogical studies of many so-called refractory gold ores have revealed that there are probably six mineralogical factors that can give rise to refractory behavior of a gold ore to cyanidation (Cabri 1988a). A similar list of mineralogical factors by Dry & Coetzee (1986), however, omits the one that is the subject of this paper: "invisible" gold.

Investigations into the problem of "invisible" gold began with Bürg's (1930) observations of pyrite from the Bradisor mine (Roumania) using optical microscopy and his heating experiments on pyrite (Bürg 1935). An excellent review and discussion of the literature on this subject are given by Boyle (1979, p. 30-32), who pointed out that two views on the nature of "invisible" gold predominate: "one that the gold is present in chemical combination in the pyrite and arsenopyrite, and the other that the gold is present in a finely divided (colloidal?), often submicroscopic state (<0.1 μm)." Boyle concluded that the former view appears more probable.

The nature of "invisible" or submicroscopic gold also was discussed by Haycock (1937), who concluded that "As regards actual milling practice, it may be of little significance whether sub-microscopic gold is merely very finely divided, colloidal, or in solid solution, because . . the lower limit of visible gold falls below the lower limit of the field of cyanidation . . .". Whereas this view may have been true in the past, when a lower price of gold required the milling of richer and more easily extractable gold ores, the trend today is toward treatment of leaner and refractory gold ores (Cabri 1987, 1988b).

Resolution of the problem of "invisible" gold continues to attract attention, and results from different approaches have been published recently. Mironov & Geletiy (1979) and Mironov *et al.* (1986) hydrothermally synthesized six sulfide minerals and magnetite in the presence of radioactive ^{195}Au, and then studied them by optical microscopy, electron and laser microprobes, and autoradiography. These authors concluded that gold enters the structure of some sulfides interstitially (pyrrhotite) and others by substitutional isomorphism (galena, chalcopyrite and greenockite). In other minerals (pyrite, magnetite and sphalerite), however, the conclusion was that gold is not structurally bound but occurs as microinclusions at the boundaries of crystals.

Kravtsova & Solomonova (1984) studied pyrite from Late Cretaceous gold–silver vein deposits in the north Okhot'ye volcanogenic area (Ohkotsk–Chutotka volcanogenic belt), Siberia. Their experimental approach was to dissolve pyrite (containing "invisible" gold) in HNO_3, and to dissolve the resulting residue in aqua regia. Though they recognized that the solubility of native gold in HNO_3 increases with a decrease in its grain size, they concluded that their results could be explained only by structurally incorporated gold in the pyrite.

From the relation between the arsenic and gold contents in beneficiation products of the Fairview mine, Barberton, Transvaal, a method was devised by Swash (1988) to determine the amount of refractory gold in these samples. Using his determinative graph, the amount of refractory gold present in the Fairview arsenopyrite could be deduced to be 600 g/t in a bulk sample. In individual grains, Swash has determined, by electron-microprobe analysis (EPMA), maximum levels of 2700 and 488 ppm in arsenopyrite and pyrite, respectively.

Chryssoulis *et al.* (1987) developed an *in situ* microanalytical technique using an ion microprobe or secondary ion mass spectrometer (SIMS) to quantitatively measure the gold content of sulfides. Calibration procedures accurate to 15% in the quantification of one ppm (g/t) are discussed by Chryssoulis *et al.* (1989). The in-depth profiling capability of the ion microprobe permits the identification of subsurface, submicrometer-scale inclusions. Depending on the operating conditions and the sulfide matrix, submicrometer-scale inclusions as small as about 100 Å (0.01 μm) can be detected by in-depth profiling, thus leading to more accurate determinations of the gold that is dispersed in the crystal structure of the sulfides. Chryssoulis (1989) reported the "invisible" gold content of a few sulfides to be: arsenopyrite (0.5 to 2500 ppm), pyrite (<0.3 to 108 ppm), pyrrhotite (<0.3 to 0.4 ppm), chalcopyrite (0.2 to 6.0 ppm), marcasite (<0.2 to 4.1 ppm), and galena (<0.2 to 0.4 ppm).

None of the studies cited above, however, provides direct evidence of structurally incorporated gold in sulfide minerals. Application of ^{197}Au Mössbauer spectroscopy to this problem by Wagner *et al.* (1986) has confirmed that such gold exists, even though its chemical state (Au^0, Au^{1+}, Au^{3+}) is not known. The Mössbauer spectrum (no quadrupole splitting and a large negative isomer shift) of a pyrite concentrate with visible native gold inclusions was found to differ from the more complex spectrum of an arsenopyrite–pyrite concentrate containing "invisible" gold. Roasting the arsenopyrite–pyrite concentrate resulted in a different spectrum, with a peak similar to that of the pyrite concentrate containing visible native gold, in addition to a smaller peak corresponding to that in the unroasted concentrate. These results were confirmed by leaching tests. Zhang *et al.* (1987) also concluded, using Electron Spin Resonance Spectrometry, that a certain amount of structurally bound gold is present in sulfide minerals such as arsenopyrite and pyrite.

Thus, research published to date has demonstrated that a certain amount of structurally bound gold can occur in sulfide minerals in some deposits. As a further contribution to resolution of this problem, we have sought to examine well-characterized individual crystals, in contrast to bulk-composition studies. The electron-microprobe results were used as a reference point to determine the gold content of the grains because of our confidence in the results obtained by that technique. However, this approach limited the samples available for study and required selection of minerals containing relatively high levels of gold, above a minimum detection level of about 200 ppm. There are very few reports in the literature of sulfides with greater than 200 ppm Au. In addition, the published electron-microprobe data contain very few analytical details* (Aubert *et al.* 1964, Swash 1988, Schouwstra & De Villiers 1988).

SAMPLE PREPARATION

We selected for study arsenopyrite samples from the Elmtree deposit, New Brunswick, and from the Sheba mine, Barberton, Transvaal. The Elmtree deposit occurs within and adjacent to the faulted unconformable contact between the Ordovician Elmtree Group and the Silurian Chaleurs Group. The mineralization consists of narrow, gold-bearing quartz veinlets with galena, arsenopyrite, stibnite, pyrite, sphalerite, some sulfosalts and two tin-bearing minerals (Watson 1988). Two ore-types occur: a partly oxidized ore in which submicroscopic gold is associated with Fe hydroxides, scorodite, arsenian pyrite and arsenopyrite, and a sulfide ore. Both contain minor visible native gold. The arsenopyrite from the Elmtree deposit was preconcentrated using heavy liquids. Polished sections from the sink fraction were prepared for electron- and ion-probe microanalysis.

The Sheba mine is located in an Archean greenstone belt in the Barberton Mountainland. The gold deposits in the area comprise quartz veins and lenses as well as pyritic ores and complex sulfide ores (Boyle 1979). Schouwstra & De Villiers (1988) reported that arsenopyrite is the most significant sulfide mineral in the Main Reef Complex at the Sheba mine because of its good correlation with high gold values. They reported gold grains to vary considerably in size (1 - 40 μm), to be mostly associated with arsenopyrite-rich samples, occurring along crystallographic planes, in microfractures or as fillings in skeletal arsenopyrite. Arsenopyrite with no visible inclusions contains submicroscopic gold concentrations up to 0.5 wt.% (by EPMA). Submicroscopic gold is one of five main mineralogical causes of refractoriness in ores from this area (Swash 1988). The samples from the Sheba mine are taken from arsenopyrite-rich zones on the 24th level of the MRC section of the mine. Arsenopyrite in one sample (RPS-353) was purified by leaching in HF according to the method described by Neuerburg (1975). The leached sample contains crystals of arsenopyrite with minor pyrite. After HF dissolution, the sample assayed 1190 ppm Au. Polished sections were prepared from both samples for the electron- and ion-probe studies.

ANALYTICAL METHODS

Electron-microprobe and SEM analyses

The analyses were performed on a JEOL 733 electron microprobe by wavelength-dispersion spectrometry. The measurements were done at 20 kV with a beam current (cup reading) of 25 nA, using the following X-ray lines and standards: Fe$K\alpha$ and S$K\alpha$ (natural pyrite), As$K\alpha$ (synthetic $CoAs_2$ or CoAsS), Sb$L\alpha$ and Au$L\alpha$ (metals). The trace-element analyses (Sb and Au) were done with a beam current of 50 nA, with counting periods of 100 seconds. Accurate measurements of background were done at the Au$L\alpha$ line position on pre-analyzed Au-"free" arsenopyrite from Sherbrooke, Nova Scotia. Quantitative corrections for atomic number, absorption, and fluorescence effects were performed with Tracor Northern's ZAF program (Version 12).

Ion-probe micro-analysis (SIMS)

A CAMECA IMS-3f ion microprobe was used to determine quantitatively the gold concentration of arsenopyrite. The measurements were done with a cesium primary beam of about 400 nA at 14.1 keV while monitoring negative ions. Molecular ions were eliminated by energy offset with partly closed energy slits. In addition to $^{197}Au^-$, two matrix ions, $^{33}S^-$ and $^{75}As^-$, were monitored to determine signal variations due to instrumental instability during the analysis. Calibration was done by external standardization using gold-implanted arsenopyrite (Chryssoulis *et al.* 1989).

High-resolution transmission electron microscopy (HRTEM)

Selected arsenopyrite crystals from the HF-leached sample (RPS-353) were crushed and mounted on carbon-coated grids. Other crystals were mounted in epoxy resin and sectioned (sample RPS-355). These were examined by optical microscopy and then analyzed by electron microprobe. Part of this section was removed for HRTEM studies. After grinding to a suitable thickness, the samples were ion milled and carbon coated. Many other grains from RPS-355, obtained by crushing single crystals, also

---

**Note added in proof*: except for the recent data of Marcoux *et al.* (1989).

TABLE 1. GOLD CONTENT OF ARSENOPYRITE FROM THE ELMTREE SAMPLE*

GRAIN #	Au, ppm	GRAIN #	Au, ppm
4	10.4	63	11.8
5	38.5	64	156.0
10	57.5	65	30.0
11	7.8	66	542.0
17	8.9	67	721.0
23	39.2	69	57.7
26	20.0	70	8.1
30	8.7	72	450.0
32	4.9	73	290.0
34	240.0	74	32.1
35	49.0	77	16.5
38	56.0	79	55.6
41	525.0	80	8.5
42	7.1	81	110.0
46	230.0	90	33.0
47	17.0	93	164.4
53	91.0	95	31.1
54	50.9	97	912.0
57	0.4	99	112.0
58	10.5	101	64.8
59	24.5	103	33.3
60	27.7	106	20.0
61	26.5		

*as determined by Secondary Ion Mass Spectrometry

TABLE 2. GOLD CONTENT OF ARSENOPYRITE FROM THE SHEBA MINE BY EPMA AND SIMS

GRAIN #	EPMA (wt.%)	SIMS (wt.%)
1	0.08, 0.12, n.d.*	0.090
2	0.44, 0.31, 0.06	0.190
3	0.06, n.d., 0.23, 0.25	0.092
4	n.d., 0.11, 0.26	0.150
5	n.d., 0.15, 0.29, 0.07	0.143
6	n.d., 0.10, 0.34, 0.06	0.160
7	0.32, n.d., n.d., n.d., 0.19	0.112
8	0.14, n.d., 0.24, 0.19	0.135
9	0.13, 0.09, n.d.	0.075
10	0.04, 0.04, 0.32, 0.32	0.112
11	n.d., 0.08, 0.24, 0.14	0.044
12	0.26, n.d., 0.12, 0.23	0.051
13	n.d., 0.09, 0.30	0.080
14	0.14, 0.08	0.090
15	n.d., n.d.	0.068
16	0.13, 0.09, 0.10	0.092
17	0.16, 0.27, 0.30	0.180
18	n.d., n.d., 0.20	0.100
19	0.13, 0.12	0.120
20	n.d., 0.06	0.054
21	n.d., n.d., 0.06	0.108
22	0.19, 0.07	0.108
23	0.33, 0.33, 0.33	0.063
24	0.04, 0.21	0.085
25	n.d., n.d., 0.18	0.112

*n.d. = not detected (3σ MDL = 0.035 wt%); Sample RPS-353. After SIMS analyses, the polished section was touched up with a vibratory polisher using 0.05 μm γ-alumina and ethylene glycol. It was then carbon-coated for EPMA.

were examined by HRTEM. These were not individually analyzed and were mounted on carbon-coated grids in the same manner as for crystals from sample RPS-353.

The samples were examined using a JEOL 200CX electron microscope operated at 200 keV with a LaB_6 filament and equipped with a 12° double-tilt, top-entry goniometer stage. The microscope has a spherical aberration coefficient (C_s) of 1.22 mm and a structure resolution of 2.6 Å. Beam damage was moderate, but magnifications up to 530,000 were possible with care. Diffraction patterns of the arsenopyrite were indexed on the basis of the monoclinic cell with *a* 5.740(2), *b* 5.6699(1), *c* 5.764(2) Å, *β* 111.6° ($P2_1/c$ setting).

Some samples were also examined in a Philips 400T analytical electron microscope, operated at 120 keV. Energy-dispersion spectra were collected with a beam size of approximately 400 Å with a Tracor Northern TN2000 analyzer. Unfortunately, the Au contents of all grains were found to be below the limit of detection of the instrument.

In order to determine whether certain features observable on the electron micrographs result from the presence of Au, these features were illuminated on the photographic negative with a collimated laser beam, and the diffraction pattern of the feature was generated optically. This optical diffraction pattern was then compared to that of the arsenopyrite. If the image of metallic Au occurs on the negative, then its diffraction pattern would be that of Au in a specific crystallographic orientation, and it will differ from that of arsenopyrite.

RESULTS

Ion-probe microanalysis (SIMS)

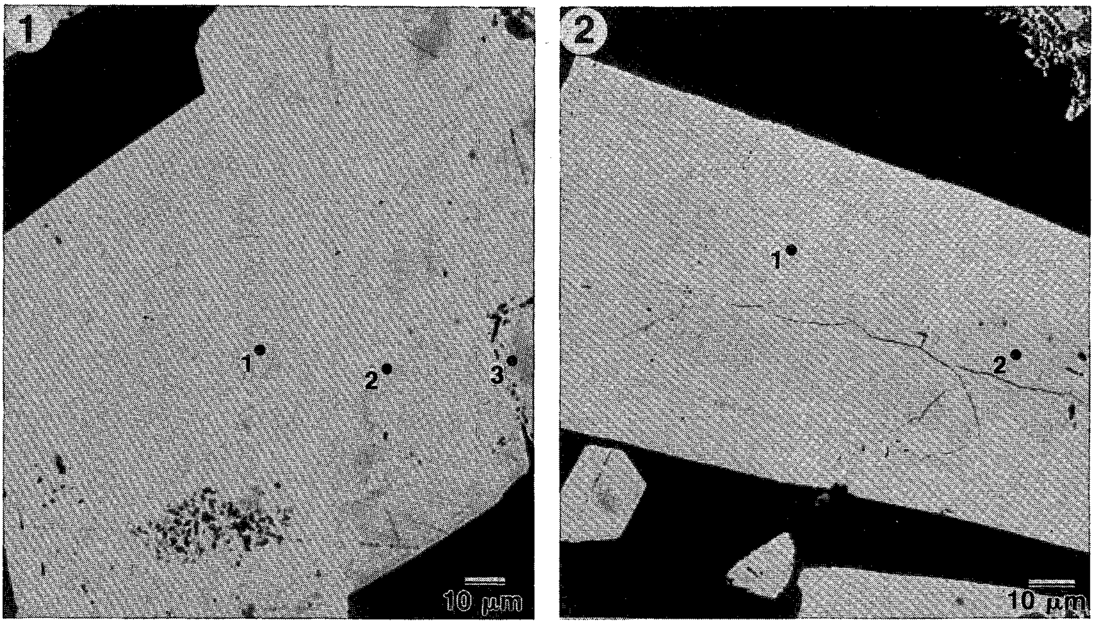
The Au content in 44 arsenopyrite particles from the Elmtree deposit ranges from 0.4 to 912 ppm, with a confidence interval of 61 ppm at a 95% significance level (Table 1). Arsenopyrite is one of the two principal "invisible" Au carrier-minerals in the Elmtree ore; the other is arsenian pyrite, which averages 26.2 ppm (Chryssoulis 1989). No other sulfides were analyzed.

The Au concentration determined in 25 arsenopyrite particles from the Sheba mine ranges from 440 to 1,900 ppm and averages 1,046 ppm with a confidence interval of 154 ppm (Table 2). No other sulfides were analyzed.

SEM and electron-microprobe data

Arsenopyrite grains from sample RPS-355 (Sheba mine) were examined by SEM after optical microscopy failed to reveal any visible gold. No gold inclusions were detected by SEM, but complicated As:S zoning is readily evident in back-scattered electron images (Figs. 1, 2).

Seven arsenopyrite grains with the highest Au content, as determined by SIMS, were analyzed by electron microprobe without altering the surface of the polished section, by selecting areas unaffected by the SIMS raster. Comparison of the electron-microprobe data to SIMS results is given in Table 3. Thirty-five grains of arsenopyrite from the Sheba mine were analyzed quantitatively; ten of these grains were from



FIGS. 1, 2. Backscattered electron image of large arsenopyrite grains (sample RPS–355) illustrating complex compositional-crystallographic zoning. Lighter areas are As-rich. (Fig. 1, grain #3; Fig. 2, grain #10 in Table 3). Filled circles represent sites of electron microprobe analysis (Table 3).

sample RPS–355, an arsenopyrite-rich ore sample (Table 4), and twenty-five grains were from sample RPS–353, an arsenopyrite concentrate, purified by leaching in HF (Table 2). As determined from 103 spot analyses, the Au content of the arsenopyrite is variable (<MDL to a maximum of 0.44 wt.%), even within a single grain, *e.g.*, grain 2 of the second series analyzed, where the Au content ranges from 0.06 to 0.44 wt.%. No correlation between the Au and As contents is apparent (Fig. 3), except that gold-bearing arsenopyrite seems to require a minimum of about 43.3 wt.% As to contain more than 0.035 wt.% Au. On the other hand, many arsenopyrite grains with less than 0.035 wt.% Au (*i.e.*, below the Minimum Detection Level by EPMA) can have As contents ranging up to 45.4 wt.%.

TABLE 3. COMPARISON OF SIMS AND EPMA RESULTS FOR GOLD ON SELECTED GRAINS FROM THE ELMTREE SAMPLE

GRAIN #	SIMS (wt.%)	EPMA (wt.%)
34	0.024	n.d., n.d., n.d.
41	0.0525	n.d., 0.04, 0.04
46	0.023	n.d., n.d., n.d.
66	0.0542	n.d., n.d., 0.03, n.d.
67	0.0721	0.05, 0.05, n.d.
72	0.045	0.04, 0.04, 0.04
73	0.029	n.d., n.d., n.d.

n.d. = not detected (3σ MDL = 0.03 wt.%)

TABLE 4. GOLD CONTENT OF ARSENOPYRITE FROM SHEBA MINE AS DETERMINED BY EPMA

GRAIN #	Au wt.%
1	n.d., n.d., 0.06
2	0.06, n.d.
3	0.21, 0.08, 0.22
4	n.d., 0.15, 0.21
5	n.d., n.d.
6	0.05, 0.20
7	0.14, 0.21
8	n.d., 0.23, 0.15
9	0.08, 0.30, 0.26
10	n.d., n.d.

n.d. = not detected (3σ MDL = 0.04 wt.%); Sample RPS–355.

High-resolution transmission electron microscopy

High-resolution transmission electron microscopy (HRTEM) images were obtained for numerous arsenopyrite grains in various crystallographic orientations. The typical domain structure of arsenopyrite is evident in Figure 4. The domains appear as regions of different contrast that cut across the fringe contrast that arises owing to increasing thickness. This domain structure probably results from the ubiquitous pseudomerohedral twinning in arsenopyrite. The *a* and *c* cell dimensions (5.740 and 5.764 Å, respectively), are sufficiently different to cause a slight misfit between adjacent (101) twin domains.

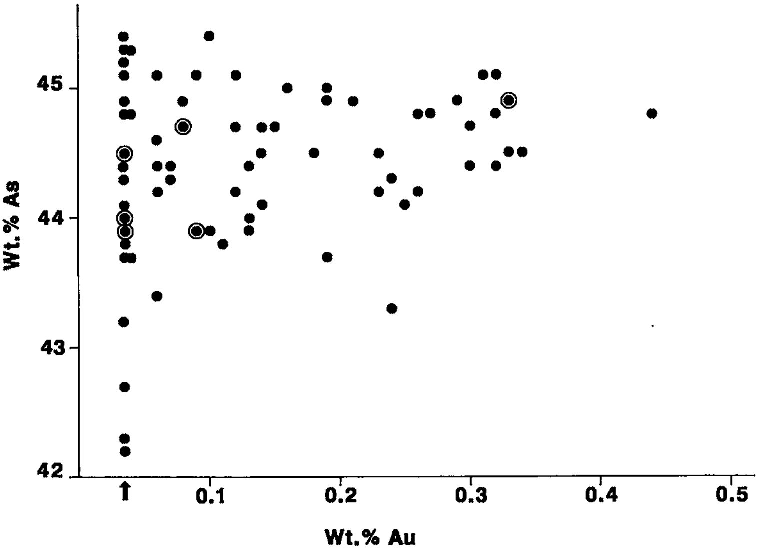


FIG. 3. Results of spot analyses for Au *versus* As (wt.%) in arsenopyrite obtained by electron microprobe, sample RPS–353. The arrow points to the MDL (0.035 wt.%). Two data points are off scale: n.d. with 41.3 wt.% As and 0.20 wt.% Au with 41.0 wt.% As.

This misfit shows up as the V-shaped zone of different contrast in the figure. The dark circular area in the top right corner of the figure is due to the presence of graphite deposited during carbon coating of the ion-milled sample. This coating was identified by the typical scrolling of graphite as well as by its diffraction pattern.

Irregular and linear features as marked in Figure 5 also are observed. These probably arise from crystal defects, causing differences in contrast.

Optical diffraction patterns of all the features in Figure 3 failed to confirm the presence of Au. All the different features examined by optical diffraction methods exhibit the diffraction pattern of arsenopyrite showing normal contrast (Fig. 6). This observation is true for all the grains examined. The presence of particulate Au in the gold-containing arsenopyrite grains could therefore not be established by high-resolution electron microscopy.

DISCUSSION AND CONCLUSIONS

The careful examination of a large number of arsenopyrite grains failed to reveal the presence of enclosed particulate Au. The presence of submicroscopic Au was determined by quantitative SIMS analyses. Where the Au content was high enough for analysis by the electron microprobe, the same grains were re-analyzed by EPMA with fairly good correlation, considering the difference in apparent inhomogeneous distribution of gold (Table 2) and the large differences in volumes analyzed by the two methods (Chryssoulis, in prep.).

In the case of the Sheba mine arsenopyrite (sample RPS–353), the average Au content as measured by SIMS (1,064 ± 154 ppm) compares closely with that of the HF-leached arsenopyrite concentrate (1,190 ppm). Pyrite is only a minor constituent, estimated to be about 5%, and probably also is gold-bearing.

Arsenopyrite from both deposits failed to reveal particulate Au down to about 100 Å by SIMS analyses and, in the case of Sheba mine arsenopyrite, down to almost the atomic level by HRTEM. We did not observe Au atoms by high-resolution imaging, although the TEM we used has a point-to-point resolution of 2.6 Å. It should have been possible to resolve individual Au atoms with that instrument under optimal conditions, but our measurements were not sufficiently constrained (mainly in regard to the TEM operating conditions and sample thickness) to permit the requisite calculations. Thus, we do not know the minimum number of Au atoms in a cluster that would be resolvable under our operating conditions; we would certainly have been able to recognize clusters containing relatively few Au atoms had they been present. The selected-area electron-diffraction patterns show only the arsenopyrite symmetry, and optical diffraction patterns of features showing variations in contrast are identical to the arsenopyrite host. It is conceivable, however, that crystals of arsenopyrite containing very

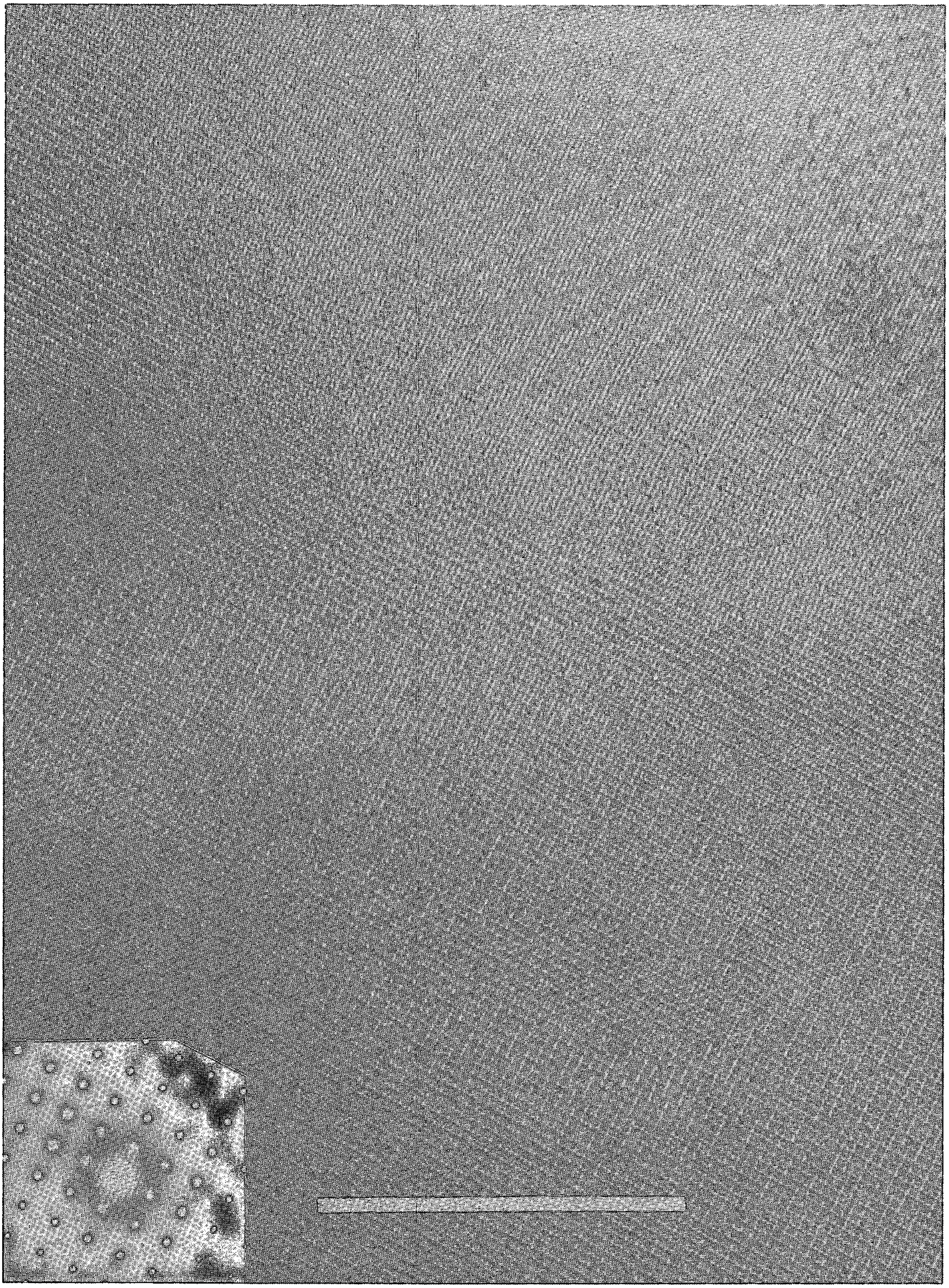


FIG. 4. Transmission electron microscope image of Au-containing arsenopyrite along the (100) zone-axis. The (010) and (001) spacings, 5.67 Å and 5.76 Å, respectively, are present. A V-shaped area showing a slight misfit between the lattice fringes causes variations in contrast. Magnification: 2.3 million. The bar scale represents 200 Å; grain 3, sample RPS–353.

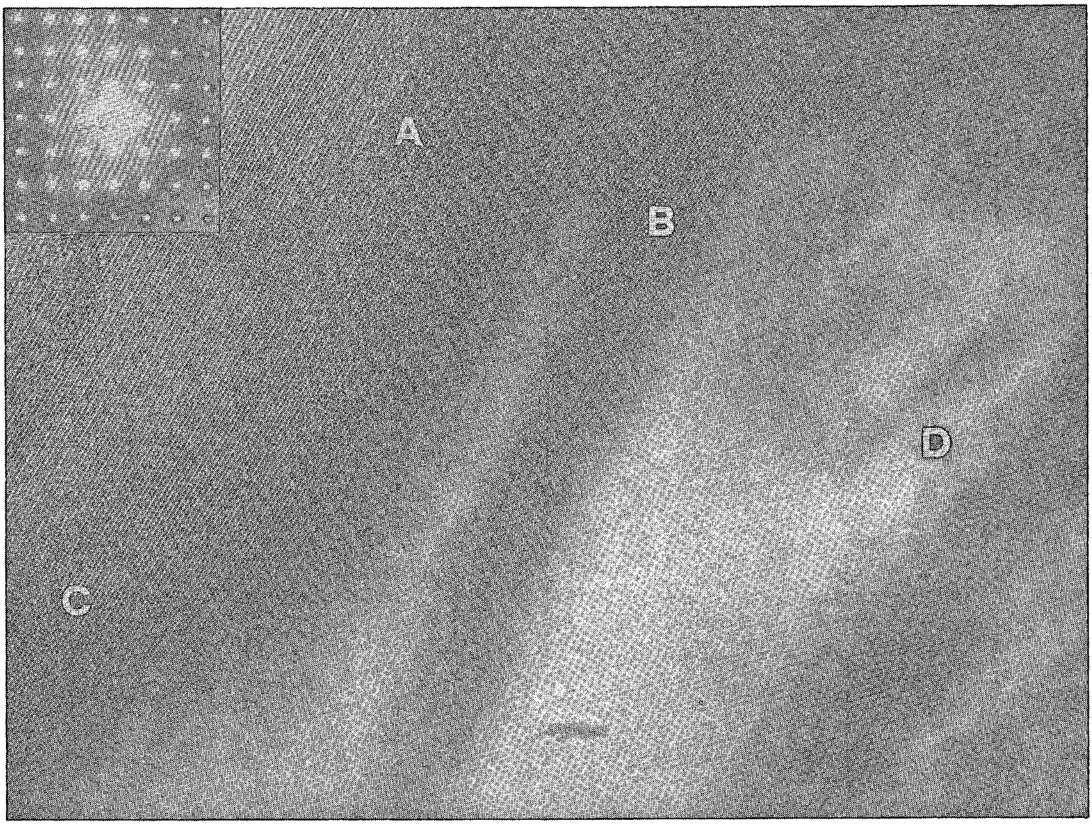


FIG. 5. Features in Au-containing arsenopyrite showing variations in contrast, also along the (100) zone axis. The marked features (A–D) have been examined using optical diffraction methods. Magnification: 810,000. The bar scale represents 200 Å; grain 3, sample RPS–353.

fine particulate Au may have had these hypothetical particles of Au preferentially ion-milled away, or, because of the high magnification of the TEM, that we simply did not chance upon areas containing Au atoms. This reasoning may explain Au concentrations obtained by electron microprobe with no evidence of particulate Au by HRTEM. This hypothesis is not considered likely in view of the many other grains from sample RPS–355 that were simply crushed single crystals deposited on the amorphous carbon grids. Complete elimination of particulate Au by ion milling also is unlikely because some of these should survive in thicker parts of the sample wedge.

No evidence could therefore be found for the occurrence of Au particles in the dispersed, so-called "colloidal" form, such as has been reported by Bakken *et al.* (1989) in several minerals from the Carlin sediment-hosted Au deposit. Bakken *et al.* (1989) located discrete particles of native Au 50–200 Å in diameter encapsulated in pyrite, cinnabar and, more rarely, quartz, as well as particles 200–1000 Å in diameter associated with 1*M* illite.

On the basis of the findings above, there is indirect evidence that the Au is randomly distributed in the arsenopyrite structure as a solid solution, possibly related to the As content of the host*. No evidence of ordering resulting from the presence of Au in arsenopyrite could be observed in the selected-area diffraction patterns. The random nature of the Au substitution in arsenopyrite would make it difficult for the individual Au atoms to be observed in HRTEM images.

One implication of structurally bound gold in

**Note added in proof*: Very recently, Johan *et al.* (1989) proposed that the strongly zoned gold-bearing arsenopyrite from the Châtelet and Villeranges deposits may be explained by the substitution 2As[Fe] $\rightleftharpoons$ (Au,Sb) + Fe.

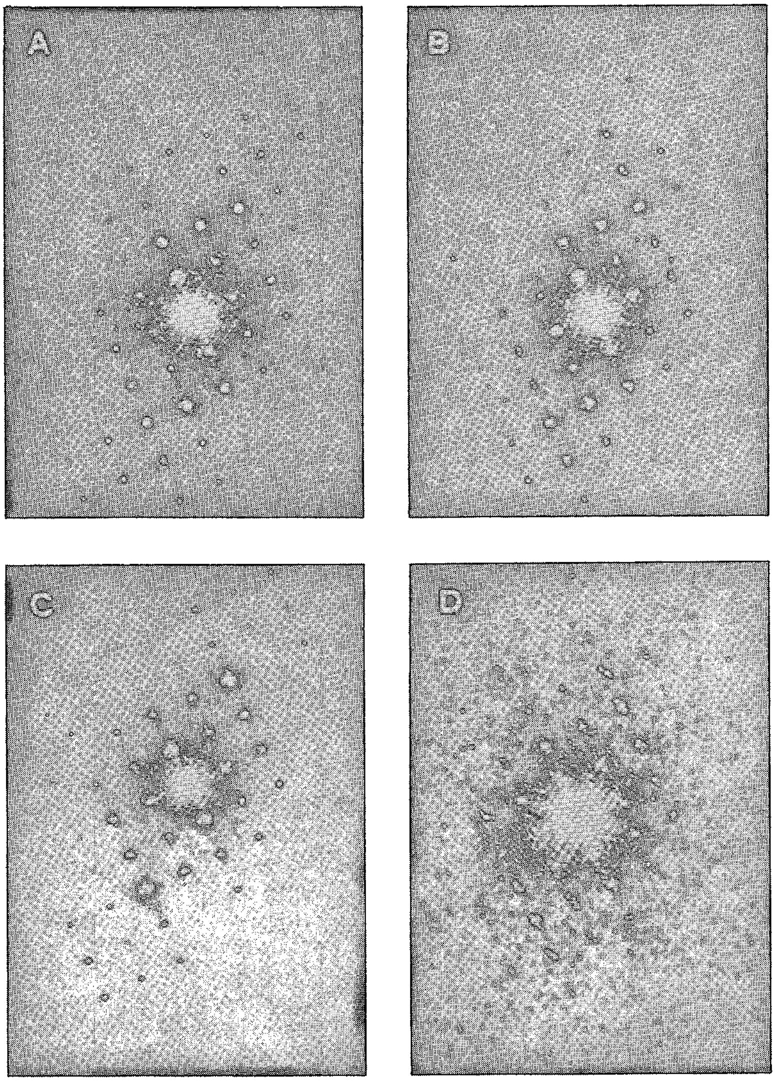


FIG. 6. Optical diffraction patterns of the features marked in Figure 3. All show the same symmetry.

"refractory" ores is that finer grinding will **not** improve the recovery of gold by cyanidation. Therefore, it is of paramount importance to provide the metallurgical engineer with a detailed mineralogical balance of gold **prior** to flowsheet developments.

ACKNOWLEDGEMENTS

Electron microscopy was done at the ASU Facility for High Resolution Electron Microscopy, which is supported by the NSF and ASU. We thank Ishmael Hassan, Carl Weiss, and John Wheatley of the ASU HREM Facility for instruction and help with the microscope study, and Chris Weisener and Garry Mount for their enthusiastic help with the SIMS analyses. Helpful comments by Robert F. Martin, Michael F. Hochella, Jr. and an anonymous referee are acknowledged. The work was supported in part by NSF Earth Sciences Division grant EAR8708529. The paper is published with the kind permission of Lacana Mining Corp.

REFERENCES

AUBERT, G., DUONG, P.K. & GEFFROY, J. (1964): Sur la localisation de l'or dans le minerai du Chatelet (Creuse). *Bull. Soc. fr. Minéral. Cristallogr.* **87**, 623-624.

BAKKEN, B.M., HOCHELLA, M.F., JR., MARSHALL, A.F. & TURNER, A.M. (1989): High resolution microscopy of gold in unoxidized ore from the Carlin mine, Nevada. *Econ. Geol.* **84**, 171-179.

BOYLE, R.W. (1979): The geochemistry of gold and its deposits (together with a chapter on geochemical prospecting for the element). *Geol. Surv. Can. Bull.* **280**.

BÜRG, G.H. (1930): Die Sichtbarmachung des feinverteilten Goldes in goldhöffigen Erzen und ihre wirtschaftliche Bedeutung. *Metall u. Erz* **27**, 333-338.

______ (1935): Natur des in den Pyriten nicht sichtbar enthaltenen Goldes. *Z. prakt. Geol.* **43**, 17-32.

CABRI, L.J. (1987): The mineralogy of precious metals: new developments and metallurgical implications. *Can. Mineral.* **25**, 1-7.

______ (1988a): The role of mineralogy in gold metallurgy. *CANMET, Rep. MSL* **88-51**.

______ (1988b): New developments in determination of the distribution of precious metals in ore deposits. *Proc. Seventh Quadrennial IAGOD Symp., E. Schweizerbart'sche Verslag, Stuttgart* (149-154).

CHRYSSOULIS, S.L. (1989): Ion probe microanalysis of gold in common sulphide minerals and implications for enhanced gold recovery from refractory gold ores. *Surface Science Western, Univ. Western Ontario, CANMET Contract Rep.* **79037-01-SS**, 380 p.

______, CABRI, L.J. & LENNARD, W. (1989): Calibration of the ion microprobe for quantitative trace precious metal analyses of ore minerals. *Econ. Geol.* **84**, (in press).

______, ______ & SALTER, R.S. (1987): Direct determination of invisible gold in refractory sulphide ores (R.S. Salter, D.M. Wyslouzil & G.W. McDonald, eds.). *Proc. Int. Symp. on Gold Metallurgy*, **1.** *Proc. Metall. Soc. of the Can. Inst. Min. Metall.*, 235-244.

DRY, M.J. & COETZEE, C.F.B. (1986): The recovery of gold from refractory ores. Refractory Gold. *In* Gold 100. Proc. Int. Conf. on Gold. 2. Extr. Metall. of Gold (259-274).

HAYCOCK, M.H. (1937): The role of the microscope in the study of gold ores. *Can. Inst. Min. Metall., Trans.* **40**, 405-414.

JOHAN, Z., MARCOUX, E. & BONNEMAISON, M. (1989): Arsénopyrite aurifère: mode de substitution de Au dans la structure de FeAsS. *C.R. Acad. Sci.* **308**, *Sér.* II, 185-191.

KRAVTSOVA, R.G. & SOLOMONOVA, L.A. (1984): Gold in pyrite from ores and metasomatites of the gold-silver deposits in the north Okhot'ye volcanogenic fields. *Geochem. Int.* **22(5)**, 9-14.

MARCOUX, E., BONNEMAISON, M., BRAUX, C. & JOHAN, Z. (1989): Distribution de Au, Sb, As, et Fe dans l'arsénopyrite aurifère du Châtelet et de Villeranges (Creuse, Massif Central français). *C.R. Acad. Sci.* **308**, *Sér.* II, 293-300.

MIRONOV, A.G. & GELETIY, V.F. (1979): Experimental study of gold distribution in sulfides. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **247**, 194-197.

______, ______, NESTEROVA, I.N. & TSEPIN, A.I. (1986): A radioisotope study of the traces of gold in sulfides and magnetite. *Geochem. Int.* **23(9)**, 117-128.

NEUERBURG, G.J. (1975): A procedure, using hydrofluoric acid, for quantitative mineral separations from silicate rocks. *J. Res. U.S. Geol. Surv.* **3**, 377-378.

SCHOUWSTRA, R.P. & DE VILLIERS, J.P.R. (1988): Gold mineralization and associated wallrock alteration in Main Reef Complex at Sheba mine, South Africa. *Trans. Inst. Min. Metall. (Sect. B)* **97**, 158-170.

SWASH, P.M. (1988): A mineralogical investigation of refractory gold ores and their beneficiation, with special reference to arsenical ores. *J.S. Afr. Inst. Min. Metall.* **88(5)**, 173-180.

WAGNER, F.E., MARION, P. & REGNARD, J.-R. (1986): Mössbauer study of the chemical state of gold in gold ores. *In* Gold 100. Proc. Int. Conf. on Gold. 2. Extr. Metall. of Gold (435-443).

WATSON, G.P. (1988): Geologic setting, mineralogy and alteration studies, Elmtree Au deposit, New Brunswick. *Geol. Assoc. Can. - Mineral. Assoc. Can., Program Abstr.* **13**, A132.

ZHANG, ZHENRU, YANG, SIXUE, & YI, WEN (1987): Studies of submicro-gold and lattice-gold in some minerals. *J. Cent. - South Inst. Min. Metall.* **18(4)**, 355-361.

Received November 23, 1988, revised manuscript accepted March 22, 1989.