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CONCENTRATIONS OF "INVISIBLE GOLD" IN THE COMMON SULFIDES

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ABSTRACT

Gold contained in the structure of the common sulfide minerals and that present as discrete inclusions smaller than 1000 Å are collectively termed "invisible gold", not detectable by optical and scanning electron microscopy. Concentrations of invisible gold range from less than 0.5 ppm to greater than 1000 ppm in sulfide grains from 12 ore deposits, as determined by ion-probe microanalysis (Secondary Ion Mass Spectrometry). Concentrations vary considerably from deposit to deposit, and between discrete ore facies within a single deposit. Minerals that most readily act as hosts are arsenopyrite and arsenic-rich varieties of pyrite. There is a positive correlation between the concentrations of arsenic and gold in pyrite, suggesting that substitution of gold into that structure is facilitated by the presence of arsenic. Where two or more distinct populations of arsenopyrite coexist, abundances of "invisible gold" are greater in the finer-grained type. Pyrrhotite, chalcopyrite, bornite, galena and tetrahedrite generally contain minor concentrations of "invisible gold".

Keywords: refractory gold, pyrite, arsenopyrite, ion microprobe, "invisible gold".

SOMMAIRE

On appelle "or invisible" l'or qui se trouve dans la structure des sulfures courants ou en inclusions distinctes d'une taille inférieure à 1000 Å, c'est-à-dire non décelables par microscopie optique ou par microscopie électronique à balayage. Les concentrations d'or invisible, qui ont été déterminées par microsonde ionique (spectrométrie de masse des ions secondaires), varient de moins de 0.5 ppm jusqu'à plus de 1000 ppm dans des grains de sulfures provenant de douze gisements. Les concentrations varient beaucoup d'un gisement à l'autre, et d'un facies à l'autre dans un seul gisement. Les sulfures les plus propices pour l'or invisible sont l'arsenopyrite et la pyrite arsenifère. Nous trouvons une corrélation positive entre concentrations d'arsenic et d'or dans la pyrite, ce qui fait penser que la présence d'arsenic favorise l'incorporation de l'or dans la structure. Dans les milieux où deux générations d'arsenopyrite coexistent, la teneur en or invisible est plus élevée dans la variété à grain fin. Pyrrhotite, chalcopyrite, bornite, galène et tétraédrite en contiennent de faibles concentrations, en général.

(Traduit par la Rédaction)

Mots-clés: or réfractaire, pyrite, arsenopyrite, microsonde ionique, "or invisible".

INTRODUCTION

The incorporation of gold into sulfide minerals has long been inferred by several investigators (Boyle 1979). However, Gasparrini (1983) and others noted that the analytical techniques used to detect gold are bulk in nature and fail to determine conclusively whether the gold is in solid solution or present as discrete inclusions of submicroscopic size. Boyle (1979) has extensively reviewed the evidence for both structurally bound and submicroscopic gold, and concluded that both types can exist. A more recent review has been given by Harris (1989). The term "invisible gold", used to denote gold in solid solution and of colloidal size, was introduced by Bürg (1930).

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Spectrographic techniques have recently been developed that prove that in some cases, gold is chemically combined within sulfide minerals rather than as discrete mineral inclusions. In studies of gold ores using Mössbauer spectroscopy, Wagner *et al.* (1986) and Marion *et al.* (in press) have shown conclusively that gold present in concentrates of pyrite and arsenopyrite may either be metallic (*i.e.*, present as inclusions) or structurally bound. Zhang *et al.* (1987) found several hundred ppm gold in solid solution in arsenopyrite from the Wuxi deposit, Hunan province, China by electron paramagnetic resonance spectroscopy. Recent studies with the electron microprobe (minimum detection limit 200 ppm) confirm that arsenopyrite may contain gold in appreciable concentrations (Cathelineau *et al.* 1988, Johan *et al.* 1989, Marcoux *et al.* 1989). The argument for structurally bound gold in arsenopyrite was tested by electron- and ion-probe microanalysis, coupled with high-resolution transmission electron microscopy (Cabri *et al.* 1989). Visible segregations of gold, a few Ångstroms in diameter, were not observed in grains containing up to 2000 ppm gold. However, the existence of colloidal gold (less than 200 Å in diameter) also has recently been confirmed in Carlin-type ores (Bakken *et al.* 1989). Oxidation of a gold-rich sulfide ore in which most of the gold is structurally bound results in the formation of metallic gold particles (*e.g.*, Graham *et al.* 1989). Enhanced gold extractions obtained by the cyanide leaching of roasted *versus* unroasted ores confirms this interpretation (*e.g.*, Avraamides *et al.* 1988).

Most common sulfide minerals, however, appear to contain gold in solid solution at rather lower concentrations than the special cases cited above. Only recently have analytical techniques been pioneered that allow the accurate and precise quantitative determination of gold abundance at less than one ppm in solid solution within a sulfide matrix. Of the available techniques, the ion microprobe, used in the

TABLE 1. LIST OF THE SULFIDE-RICH ORES STUDIED

DEPOSIT, LOCATION	AGE	SETTING, TYPE OF DEPOSIT	METAL PRODUCTION	MINERALOGY	SAMPLE TYPE
Golden Pond Quebec	Archean	Canadian Shield Superior Province, volcanic-sedimentary sequence	Au	Py-Apy-Ccp-Sp	Composite ore
Estrades Quebec	Archean	"	Au,Ag,Zn,Cu (planned)	Py-Sp-Mar-Ccp-(Apy)	Mill feed
Mobrun Quebec	Archean	"	Cu,Zn,Au,Ag	Py-Ccp-Sp	Rock chips Tailings
Trout Lake Manitoba	Archean	"	Cu,Zn,Au,Ag	Py-Sp-Ccp-(Apy)	Tailings
Ketza River Yukon	Cambrian	Stratiform limestone-hosted sulfide deposit	Au	Po-Apy-(Py)-(Ccp)	Composite ore
HW B.C.	Triassic	Coastal Insular belt volcanic-sedimentary hosted massive sulfide	Cu,Zn,Pb,Au Ag	Py-Ccp-Sp-Tt-(Bn)-(Gn)-(Cc)	Cu Concentrate rock chips mill feed
Lara B.C.	Triassic	"	Au,Ag,Zn,Pb,Cu (potential)	Py-Sp-Ccp-Gn-Tt	rock chips
Windy Craggy B.C.	Triassic	Mafic volcano-sedimentary massive sulfide	Cu,Co-Au-Ag (potential)	Py-Ccp-Po-Sp	rock chips
Congress B.C.	Triassic	Vein and replacement type hosted by sedimentary & volcanic rocks	Au,Ag,Sb (potential)	Py-Apy-(Stib)	composite ore
Elmtree N.B.	Ordovician	Quartz veinlets hosted within greenstone sequence	Au,Ag (potential)	Py-Apy-(Sp)-(Ccp)	composite ore
Olympias Greece	U.Jurassic /L.Cretaceous	Tethys greenstone belt polymetallic deposit	Pb,Zn,Au,Ag, Cu	Py-Apy-Gn-Sp-Ccp	composite ore
Sheba South Africa	Archean	Barberton greenstone belt Vein-type deposit	Au	Apy-Py	rock chips

Py: pyrite, Apy: arsenopyrite, Ccp: chalcopyrite, Sp: sphalerite, Mar: marcasite, Tt: tetrahedrite-tennantite, Bn: bornite, Gn: galena, Cc: chalcocite, Stib: stibnite.

Further details of sample type and location are given in Chryssoulis (1989).

present study, is the most suitable *in situ* microanalytical tool. With it, one can analyze individual sulfide grains of 50 to 100 μm in diameter for "invisible gold" above a minimum detection-limit of approximately 250 ppb for most sulfide phases (Chryssoulis *et al.* 1989).

The realization that solid-solution gold in sulfide minerals may reach considerable concentrations, and even attain minor element status in some specific cases, is of considerable interest to the economic geologist, exploration geochemist, applied mineralogist and mineral processor. Moreover, the complexing of gold with specific sulfide minerals has justified the selection of specific pathfinder elements in the geochemical exploration for gold, *e.g.*, arsenic. In many sulfide-bearing refractory gold ores, "invisible gold" may account for the majority of the gold present in the ore. The successful processing of these difficult ores can, therefore, clearly only be achieved by a better understanding of the mineralogy of the "invisible gold" and its distribution within and among coexisting common sulfide minerals. At present, there is a paucity of microprobe data in the literature concerning the distribution of "invisible gold" in single mineral phases.

Methodology and Sampling

Detailed *in situ* analyses for gold by ion microprobe have been recently carried out by Chryssoulis (1989) on pyrite, pyrrhotite, arsenopyrite, chalcopyrite, bornite, galena and tetrahedrite from twelve sulfide-rich deposits (Table 1).

The base and precious-metal volcanogenic massive sulfide deposits of the Superior Province are represented by four deposits: Mobrun (Rouyn–Noranda, Quebec), Golden Pond and Estrades (both Casa Berardi, Quebec), and Trout Lake, Manitoba. Brief descriptions of the Golden Pond and Estrades deposits have been given by Phillips (1986 and 1987b), respectively. With the exception of Golden Pond, where gold is the primary product in 1989-90, gold is generally a trace, but valuable, economic component. In the case of the Mobrun and Trout Lake deposits, only the flotation tailings were examined. Two samples were examined from different parts of the Golden Pond deposit. The mineralogy of the Trout Lake deposit and a discussion of the mineral characteristics that affect metal recoveries have been given by Healy (1987).

The Ketza River deposit, Yukon, is a limestone-hosted stratabound, auriferous massive sulfide deposit of Cambrian age, containing only traces of the base metals. Currently, only the superjacent oxide ore is worked (Phillips 1987a). Pyrrhotite and arsenopyrite are the main sulfide minerals present. The polymetallic HW massive sulfide deposit on Vancouver Island, British Columbia, is hosted within the volcanic–sedimentary coastal Insular Belt, and is Triassic in age (Walker 1983). It shares many characteristics with the nearby Lara deposit. The giant pyritic Windy Craggy deposit in northern British Columbia contains minor base and precious metals, hosted within a mafic volcanoclastic–sedimentary section of late Triassic age (MacIntyre 1985).

Ore deposits of the Appalachians are represented by the Ordovician Elmtree deposit in northern New Brunswick. The deposit consists of narrow quartz veinlets that carry sulfides and associated gold (Watson 1988). Pyrite and arsenopyrite are the dominant minerals.

The Congress deposit, south-central British Columbia, is of Triassic age and is a vein and replacement-type deposit hosted by volcanic rocks and sediments of the Bridge River Group. The deposit is disseminated and contains pyrite, arsenopyrite and stibnite (Cooke & Barakso 1986). The Olympias deposit, Greece, is of early Cretaceous to late Jurassic age and belongs to the Tethys greenstone belt (Nicolaou & Kokonis 1980). The sulfide minerals are pyrite, arsenopyrite, sphalerite, galena and chalcopyrite. The Sheba deposit, Transvaal, South Africa lies within the Archean Barberton Greenstone belt (Phillips *et al.* 1984). Arsenopyrite and pyrite are the main minerals present in the quartz veins, lenses and massive pyritic ores.

Samples of mill feeds, composite ores, concentrates and tailings were used for analysis. Polished blocks 2.5 cm across were prepared from the +53 μm size fraction of each sample, by mounting the grains in evacuated epoxy admixed with copious amounts of carbon to eliminate charging during microanalysis. The grains were examined microscopically after mounting and polishing to a 0.1 μm fine surface. Only grains free of scratches, pits, or other surface blemishes were selected for ion-probe microanalysis, each grain being circled with a diamond marker. The grains also were examined with optical and scanning electron microscopes to detect the presence of inclusions of other minerals, in particular gold minerals (detection limit 0.5 μm). After analysis, each grain was checked again to ensure that no second phase had been exposed to the primary ion beam.

Analytical Method

Ion microprobe

The ion microprobe (Secondary Ion Mass Spectrometer) facility at Surface Science Western has been calibrated to determine concentrations of precious metals in sulfide minerals down to the sub-ppm range. It presently is the most sensitive *in situ* microanalytical technique available (Chryssoulis *et*

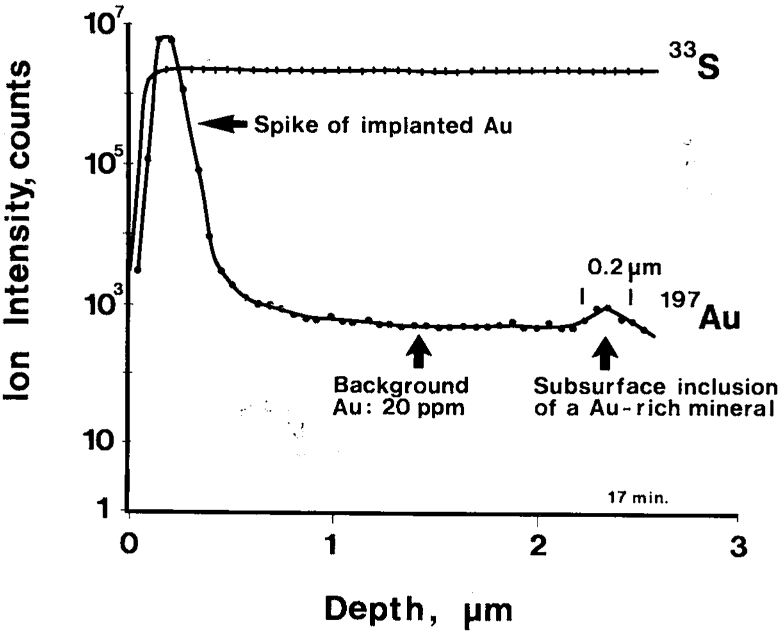

FIG. 1. Ion-microprobe depth profile of a sulfide grain, illustrating the technique of internal standardization and identification of submicroscopic gold mineral inclusions.

TABLE 2. CONCENTRATIONS OF GOLD IN PYRITE*

Deposit	N	x ± A	min.	max.
Golden Pond Ore A	10	1.10 ± 0.90	<MDL	4.1
Ore B	14	0.23 ± 0.24	<MDL	1.4
Mobrun	104	1.41 ± 0.23	<MDL	5.6
Estrades	59	0.67 ± 0.53	<MDL	12.0
Trout Lake	46	0.72 ± 0.38	<MDL	6.8
HW	92	0.25 ± 0.09	<MDL	2.8
Windy Craggy (coarse pyrite)	20	0.15 ± 0.10	<MDL	0.6
(fine pyrite)	8	1.37 ± 0.50	0.43	2.7
Lara	88	0.16 ± 0.12	<MDL	3.4
Congress	79	1.2 ± 0.61	<MDL	21.0
Elmtree	82	24.1 ± 5.3	0.9	107.8
Olympias (As-poor pyrite)	6	3.6 ± 2.0	1.0	12.0
(As-rich pyrite)	26	36. ± 12.	4.1	110.

* Concentrations in ppm determined by ion microprobe.
N: Number of grains analysed,
MDL: Minimum detection limit (0.25 ppm).

al. 1989). The instrument used is a CAMECA model IMS-3f. The method of standardization used for the quantification of gold is internal, in which a known amount of ^{197}Au is implanted into the surface layer of the grains, one µm deep (Chryssoulis *et al.* 1987). Because the ion-microprobe technique is destructive and involves the progressive sputtering of the sample surface by the primary ion beam, leaving behind a crater, depth profiling of the analyzed grain shows the background signal of the specimen beneath the peak due to the implanted gold. The intensity of the background signal is quantified by standardization relative to the known dose of ^{197}Au. Details of standardization, quantification, operating conditions and analytical accuracy and precision are given by Chryssoulis *et al.* (1987).

Counting periods per sample ranged from about 5 to 20 minutes. The As content of the grain also is monitored during analysis, with 10 ppm As easily detectable. The in-depth profiling capability of the technique also offers the possibility of identifying subsurface sub-micrometer-scale inclusions of gold minerals within a sulfide grain, thus rendering greater accuracy to the determination of the truly structurally bound gold. An ion-microprobe depth profile, illustrating the standardization technique and identification of subsurface inclusions of an Au-rich mineral, is shown in Figure 1.

Electron microprobe

A JEOL JXA-8600 microprobe, coupled with an energy-dispersion spectrometer, was used to determine As concentrations in pyrite. Natural pyrite and arsenopyrite standards were used. The analyses were performed at 15 kV, with a specimen current of 25 µA.

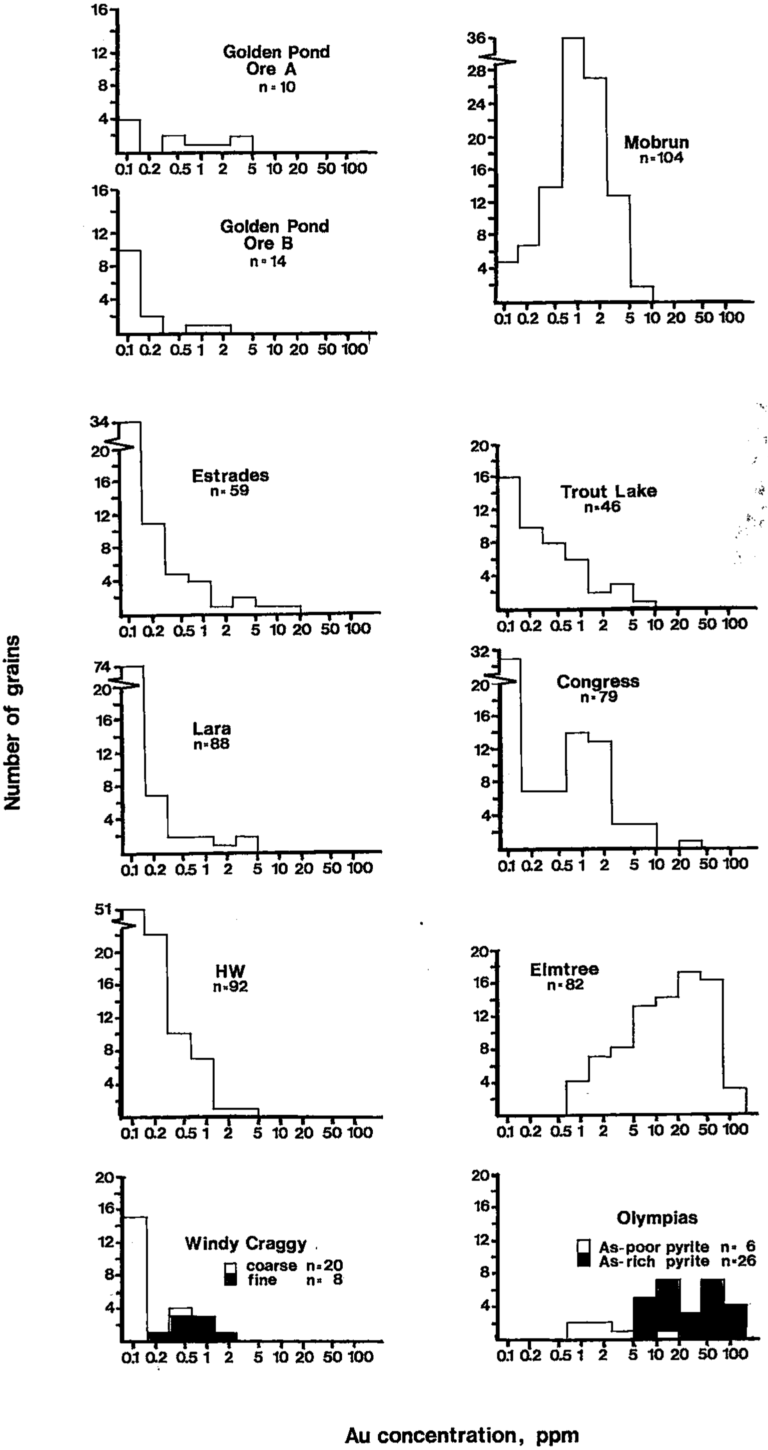

FIG. 2. Distribution of gold concentrations in pyrite, as determined by ion-microprobe microanalysis of particles from different deposits.

RESULTS

Gold was not detected in all mineral grains analyzed. The nominal minimum detection limit (MDL) for Au in sulfide matrices is 250 ppb. The average gold concentration of a mineral in a particular ore and the confidence interval on the mean at a 95% significance level are given.

Pyrite

Concentrations of "invisible gold" in pyrite appear to have a great range, from less than the MDL to greater than 100 ppm. Although concentrations in pyrite are generally minor, except in the arsenian varieties, the abundance of pyrite in most ores, relative to the other sulfide minerals, does mean that "invisible gold" in pyrite can nevertheless account for a significant proportion of the total gold in the ore. Table 2 shows the number of pyrite grains analyzed, average gold content and range of gold content in each ore. The distribution of "invisible gold" in pyrite from selected ores is expressed in histogram form (Fig. 2).

In the Mobrun ore, the mean concentration of "invisible gold" in pyrite from tailings is 1.41 ± 0.23 ppm. In the Golden Pond ore, pyrite shows some evidence of a difference in distribution between the two ores sampled. In ore A, the mean concentration is 1.10 ± 0.90 ppm and in ore B, 0.23 ± 0.24 ppm. In the Estrades ore, the mean concentration of "invisible gold" in pyrite is 0.67 ± 0.53 ppm. In the Trout Lake ore, the average concentration is 0.72 ± 0.38 ppm. Despite these rather low concentrations and the fact that concentrations of "invisible gold" in arsenopyrite are an order of magnitude greater, pyrite is an important gold-carrier mineral in the Mobrun, Trout Lake and Estrades ores, by virtue of its abundance. It accounts for nearly 70% of the gold in the Mobrun tailings, 26.6% in the Trout Lake tailings, and 5.8% in the Estrades mill head. In the ores from Golden Pond, where there is more arsenopyrite, "invisible gold" in pyrite accounts for only 0.2 and 0.06% of the total gold in the two samples of ore.

TABLE 3. CONCENTRATIONS OF GOLD IN ARSENOPYRITE*

Deposit	N	x ± λ	min.	max.
Golden Pond				
Ore A (coarse)	35	13.2 ± 5.0	0.3	72.8
(fine)	9	39.1 ± 13.2	17.5	77.4
Ore B (coarse)	37	23.1 ± 10.3	1.3	158.
(fine)	12	98.9 ± 61.2	10.6	402.
Estrades	10	54. ± 36.	<MDL	170.
Trout Lake	44	30.2 ± 8.6	2.	112.
Ketza River	87	11.9 ± 2.2	1.3	46.
Lara	10	10. ± 4.7	1.9	22.
Congress (coarse)	16	38. ± 17.	1.7	100.
(fine)	25	1630. ±1330.	25.	13000.
Elmtree	44	123. ± 61.	0.4	912.
Olympias	32	49. ± 24.	2.3	370.
Sheba	34	929. ± 150.	81.	1900.

* Concentrations in ppm determined by ion microprobe.
N: Number of grains analysed,
MDL: Minimum detection limit (0.3 ppm).

Typically, the Canadian Shield ores contain two or more types of pyrite, distinguished from one another by textural criteria, indicating inhomogeneous metamorphism, multiphase ore genesis, or both. In the four ores mentioned above, the abundance of "invisible gold" in the pyrite was found to be independent of textural type, although the evidence of Wilson & Rucklidge (1987) from the Owl Creek deposit, Ontario, has shown gold concentrations to be higher in fine-grained, "porous" pyrite, which also is arsenian.

The comparable Lara and HW ores contain minor amounts of "invisible gold" in pyrite. In the Lara ores, the average concentration is 0.16 ± 0.12 ppm. In the HW ores, the average concentration is 0.25 ± 0.09 ppm, with no significant differences between ore types. Two types of pyrite are present in the Windy Craggy ore, a coarse-grained, dominantly euhedral type, and a fine-grained, deformed, fractured and brecciated variety. The fine-grained pyrite contains more "invisible gold" (1.37 ± 0.50 ppm) than the coarse-grained variety, which is the more abundant (0.15 ± 0.10 ppm). Pyrite from the Congress ore contains only negligible amounts of "invisible gold". The mean concentration is 1.20 ± 0.61 ppm, although isolated values exceeding 20 ppm were recorded. The Elmtree pyrite contains considerable "invisible gold". The average gold concentration is 24.1 ± 5.3 ppm. Most of the pyrite grains present in the ore contain some As, present as inhomogeneously distributed regions of arsenian pyrite within As-poor pyrite. There is an apparent positive correlation between the bulk Au and As contents of pyrite grains (see discussion and Fig. 9).

The Olympias pyrite is similar to the Elmtree pyrite, with zones of arsenian pyrite within most pyrite particles analyzed. Regions of pyrite particles that contain less than 0.5% As contain minor "invisible gold" (2 ppm), but regions of arsenian pyrite contain an average of 36 ± 12 ppm gold. Compositional zoning of As within the pyrite is widespread, and the two types are intimately intergrown. There is a correlation between the 'bulk' As content of the grain and the invisible gold in the pyrite.

Arsenopyrite

All the ores studied contain major to minor

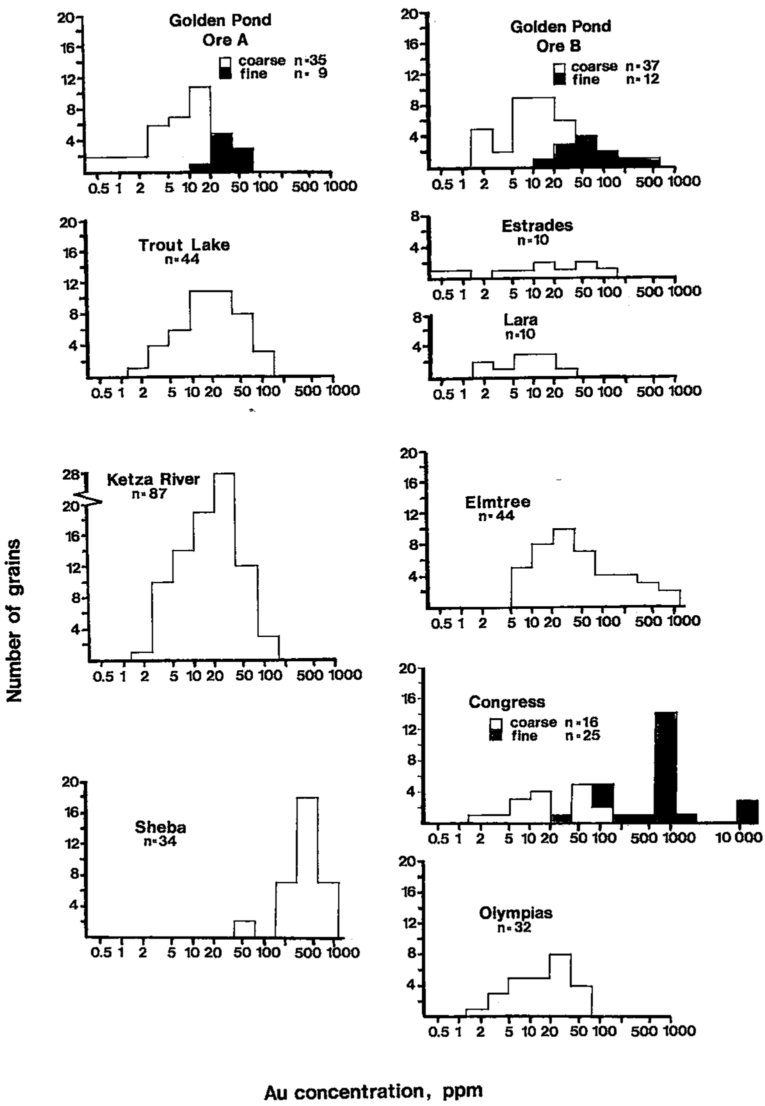

FIG. 3. Distribution of gold concentrations in arsenopyrite, as determined by ion-microprobe microanalysis of particles from different deposits.

arsenopyrite, except the Mobrun, HW and Windy Craggy ores, where the mineral accounts for less than 0.05 vol.% of the ore. Almost all arsenopyrite grains analyzed contain significant quantities of "invisible gold". Average concentrations (Table 3) range from 10 ppm (Lara) to 1630 ppm (Congress, fine-grained type). The distribution of concentrations is presented as histograms in Figure 3. In refractory gold ores in which arsenopyrite is a major mineral, "invisible gold" in arsenopyrite can account for a majority of the gold in the sample.

The Estrades and Trout Lake samples contain only small amounts of arsenopyrite; 0.36 ± 0.02% in the Estrades ore and 0.20 ± 0.04% in the Trout Lake flotation tailings. Concentrations of invisible gold in arsenopyrite from these ores are near the lower end of the concentration range observed, 54 ± 36 ppm and 30.2 ± 8.6 ppm, respectively. The Golden Pond ore shows a clear bimodal distribution of concentrations of "invisible gold" in the two ore samples. The average concentrations of the two populations are 18.3 ± 5.7 ppm in ore A, and 41.4 ±

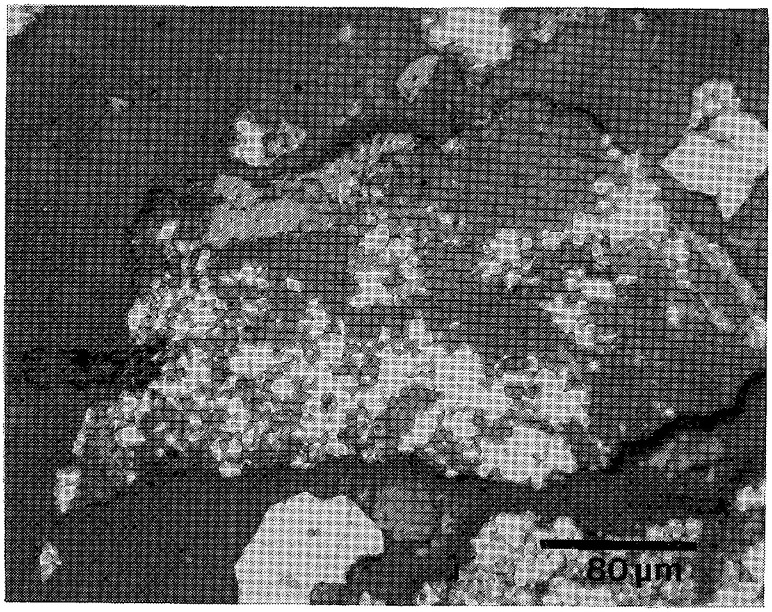

FIG. 4. Photomicrograph of sulfide ore from Congress mine, indicating fine-grained arsenopyrite enclosed within calcite, mica and quartz.

18.6 ppm in ore B. This relationship is the opposite of the case for pyrite in the two ores, in which ore A contains the greater concentration of gold of the two ores. Closer inspection of the data reveals a distinction between coarse-grained and fine-grained arsenopyrite, in which the fine-grained type contains significantly higher concentrations of "invisible gold", three times as high in ore A and four times as high in ore B. The variations in average "invisible gold" content of arsenopyrite between the two ores may be explained by the relative proportions of the two types present. In all three ores from the Canadian Shield, arsenopyrite is the only mineral to contain significant "invisible gold".

The Lara ore contains less than 0.1% arsenopyrite, as small (50 μm) grains within the matrix. Concentrations of "invisible gold" are low, 10 ± 4.7 ppm. Nevertheless, in this case, arsenopyrite is the only mineral to contain significant invisible gold. Arsenopyrite from the Ketza River deposit contains an average "invisible gold" concentration of 11.9 ± 2.2 ppm.

In the Congress ore, arsenopyrite is the most abundant sulfide. There is a distinct difference in the concentrations of "invisible gold" in the two types of arsenopyrite present: a coarse-grained type, and a fine-grained type, the latter being typically euhedral needles of less than 20 μm and entirely enclosed within calcite, mica and quartz (Fig. 4). The fine-

TABLE 4. CONCENTRATIONS OF GOLD IN MARCASITE, PYRRHOTITE, CHALCOPYRITE, GALENA, TETRAHEDRITE AND BORNITE*

Deposit	N	$x \pm \lambda$	min.	max.
Marcasite				
Estrades	18	0.91 ± 0.55	<MDL	4.1
Congress	2	0.25 ± 0.50	<MDL	0.5
Pyrrhotite				
Ketza River	25	0.48 ± 0.18	<MDL	1.8
Chalcopyrite				
Lara	9	0.01 ± 0.03	<MDL	0.12
HW (coarse cpy)	9	0.19 ± 0.10	<MDL	0.5
HW (fine cpy)	12	3.0 ± 1.3	0.7	7.7
Mobrun	14	1.1 ± 0.8	0.15	6.0
Estrades	12	0.13 ± 0.09	<MDL	0.4
Galena				
HW	4	1.78 ± 1.11	0.6	3.4
Lara	17	0.10 ± 0.04	<MDL	0.28
Estrades	2	0.3 ± 0.2	0.2	0.4
Tetrahedrite				
HW (polymetallic ore)	32	5.1 ± 3.7	<MDL	59.
(other ores)	33	0.31 ± 0.15	<MDL	2.6
Bornite				
HW	16	0.67 ± 0.20	0.2	1.6

* Concentrations in ppm determined by ion microprobe.
N: Number of grains analysed,
MDL: Minimum detection limit (0.25 ppm).

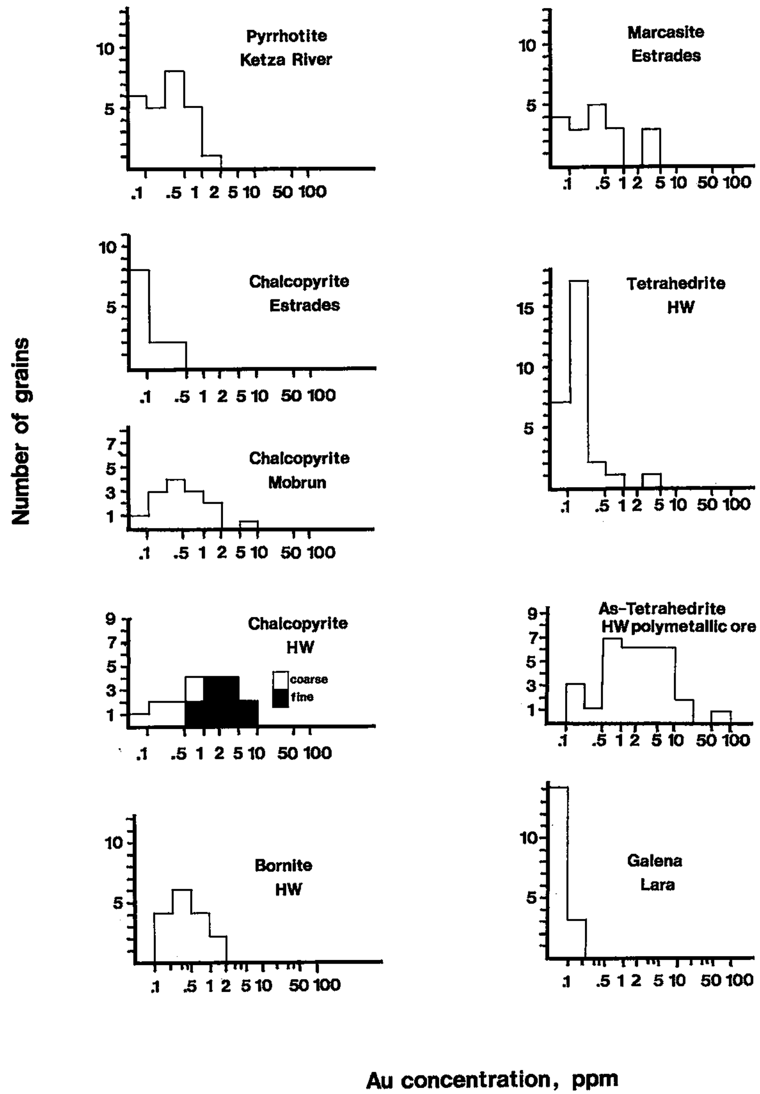

FIG. 5. Distribution of gold concentrations in marcasite, pyrrhotite, chalcopyrite, galena, tetrahedrite and bornite as determined by ion-microprobe microanalysis of particles from different deposits.

grained type contains, on average, fifty times as much "invisible gold" as the coarse-grained type. The average concentrations are 38 ± 17 ppm and 1630 ± 1330 ppm, respectively. Measured concentrations in the fine-grained type range from 1.7 ppm to 13,000 ppm (1.3 wt.%).

In the Elmtree ore, in which arsenopyrite is 30% of the sulfide minerals, concentrations of "invisible gold" in arsenopyrite are 123 ± 61 ppm on average, which is an order of magnitude greater than in the Canadian Shield ores examined. Arsenopyrite from Olympias contains, on average, 49 ± 24 ppm gold. The Sheba ore, in which arsenopyrite is the most abundant sulfide mineral in the sample studied, contains very large concentrations of "invisible gold". The mean concentration is 929 ± 150 ppm.

Other minerals

The gold concentrations in other sulfides are given in Table 4. Distribution histograms are presented in Figure 5.

Marcasite

The Congress and Estrades ores contain significant amounts of marcasite that has replaced pyrite. In both cases, "invisible gold" concentrations in the marcasite are comparable to those in the coexisting pyrite. Average concentrations are 0.25 ± 0.50 ppm (Congress) and 0.91 ± 0.55 ppm (Estrades).

Pyrrhotite

Pyrrhotite was analyzed in the Ketza River ore, where it is the dominant sulfide mineral. The average gold concentration is 0.48 ± 0.18 ppm.

Chalcopyrite

Chalcopyrite previously has been demonstrated to be an excellent host for silver in solid solution (Harris *et al.* 1984, Cabri *et al.* 1984). However, the results of this study indicate that the mineral is generally a poor host for gold. The concentration of "invisible gold" in chalcopyrite was determined in four ores. Average concentrations are 0.01 ± 0.03 ppm (Lara), 0.13 ± 0.09 ppm (Estrades), and 1.1 ± 0.8 ppm (Mobrun). Gold concentrations in coarse-grained chalcopyrite from HW are 0.19 ± 0.1 ppm. However, etching of the sample reveals a second type of chalcopyrite that is much finer-grained and occurs as aggregated and highly twinned grains. This type contains 3.0 ± 1.3 ppm gold.

Galena

Average concentrations of "invisible gold" in galena from Lara, Estrades and HW are 0.10 ± 0.04 ppm, 0.3 ± 0.2 ppm and 1.78 ± 1.11 ppm, respectively.

Tetrahedrite-tennantite

Tetrahedrite-tennantite was analyzed in different ore facies within the HW deposit. Tetrahedrite samples from the bedded Cu-Zn ore, cupriferous pyrite ore and bornite-rich ore contain comparable concentrations of "invisible gold", averaging 0.31 ± 0.15 ppm. Arsenian tetrahedrite from the polymetallic ore facies contains rather higher concentrations, 5.1 ± 3.7 ppm. The depth profiles of a number of tetrahedrite grains from HW encountered submicroscopic grains of electrum, each less than 0.5 μm in diameter (Fig. 6).

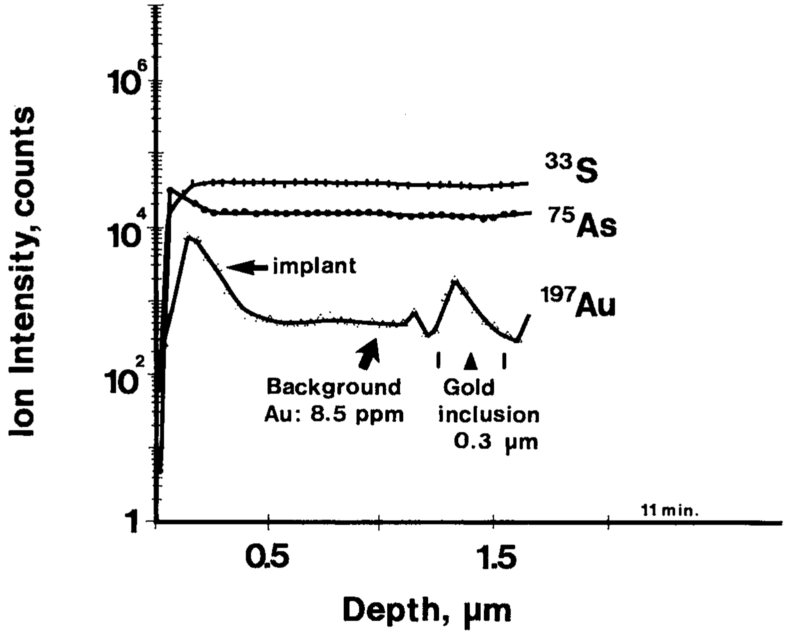

FIG. 6. Depth profile obtained by ion-probe microanalysis of an arsenian tetrahedrite grain from the HW ore, showing subsurface, submicroscopic inclusions of gold.

Bornite

Ten percent of the HW ore contains bornite rather than chalcopyrite. The average gold concentration is determined to be 0.67 ± 0.20 ppm.

DISCUSSION

Mineral chemistry

The results of this study indicate that arsenopyrite and arsenian pyrite are both good hosts for "invisible gold", but that arsenic-poor pyrite, chalcopyrite, pyrrhotite and other sulfide minerals generally are not. The work of Cabri *et al.* (1989) has shown that, at least in the Sheba arsenopyrite, the "invisible gold" is present in solid solution. Interestingly, arsenic is the most commonly used pathfinder element in geochemical exploration for gold (Boyle 1965, Webb 1958).

Finding specific explanations for the relationship between gold and arsenic within the sulfide structure is not an easy task, since there is very little known about the location and chemical state of Au in these structures. Arsenopyrite is a complex mineral species because of its considerable nonstoichiometry, the ratio As:S ranging from 1.22 to 0.82 (Kostov 1981). In pyrite and arsenopyrite, as with other sulfide minerals, the bonding is essentially covalent. Because of the structural complexity and the variety of chemical bonds in sulfides, variations in crystal chemistry, stereochemistry and the presence of delocalized bonding, it is not possible to approach substitution in sulfides in the same way as for silicate minerals, by comparing ionic radii. Ionic radii cannot reliably be used for sulfide minerals (Vaughan & Craig 1978).

Boyle (1979) suggested that Au substitutes for As in arsenopyrite. This hypothesis is largely based on comparisons of radii of covalently bonded As and Au. The covalent radius of Au in aurostibite $AuSb_2$ is 1.40 Å and that of As in FeAsS is 1.39 Å (Marion *et al.* 1986). Adherents to this hypothesis contend that the similar size of the As and Au atoms explains the relative ease of incorporation of Au into arsenopyrite relative to pyrite.

Refinement of this hypothesis was possible based on recent microprobe studies of gold in arsenopyrite and pyrite. Johan *et al.* (1989) used electron-probe data from gold-rich arsenopyrite (> 0.21 wt.% Au) and stoichiometric calculations to propose that Au is substituting for the excess As, which actually is present in Fe sites. Cabri *et al.* (1989) found that based on results of electron- and ion-probe microanalysis of arsenopyrite from the Sheba mine (gold content 350 - 4,400 ppm), gold-bearing arsenopyrite requires a minimum of about 43.3 wt.% As to contain more than 350 ppm Au.

Similarly, a threshold value of 0.2 to 0.4 wt.% arsenic was observed in the gold-rich pyrite from the Elmtree and Olympias deposits (gold content range from 0.3 to 110 ppm), beyond which there is a definite correlation of gold with arsenic. The correlation coefficients are 0.77 and 0.66, respectively. The proposed double substitution of Au for excess As that occupies Fe sites may be explained based on the work of Wood & Strens (1979), in which the structure of disulfide minerals is discussed. The structure of these minerals is either of AX_2 type (pyrite), AXY type (arsenopyrite) or AY_2 type (löllingite), where A is a metal (Fe, Ni, Co), X is S and Y may be As, Sb or Bi. Although the sulfide structure does not involve ions in the 'rock salt' sense, the bonding between metals and nonmetals does allow the component atoms to bear a charge. Wood & Strens showed that in all three types, the metal atoms (Fe, in pyrite and arsenopyrite) are octahedrally coordinated by the paired anions, which may be regarded as *sp³* hybridized to form filled bonding orbitals, with the following closed-shell configurations: $[S_2]^{2-}$ in pyrite, $[AsS]^{3-}$ in arsenopyrite and $[As_2]^{4-}$ in löllingite.

In these structures, each nonmetal atom is bonded to one other anion (its pair) and to three metal atoms. Wood & Strens (1979) also showed that the formal negative charges on the $[S_2]^{2-}$, $[AsS]^{3-}$ and $[As_2]^{4-}$ dianions require formal positive charges on the metal atoms of equal valency. That these charges exist is largely based upon measurements of magnetic susceptibility. The authors concluded that in the case of pyrite (or its dimorph, marcasite), Fe is present as Fe^{2+}, and in arsenopyrite, as Fe^{3+} ions. They also pointed out that arsenopyrite is a semiconductor with a very low magnetic moment, implying that adjacent pairs of Fe^{3+} ions are bonded, resulting in the observed alternating long and short Fe–Fe bond distances.

A simple pyrite structure can thus be written $[Fe]^{2+}[S_2]^{2-}$. Arsenic is a common minor element in the pyrite. If As is introduced into the structure, some of the anion pairs will be $[AsS]^{3-}$ pairs, meaning that there will be a charge imbalance with the metal. If such an imbalance of charge exists because of incorporation of As in the structure, it can be met by trivalent cations replacing the divalent iron. Such ions may be As^{3+}, Au^{3+}, Sb^{3+}, *etc.* This hypothesis may account for the observed link between gold and arsenic incorporation in pyrite. In arsenopyrite, which can be expressed $[Fe]^{3+}[AsS]^{3-}$, it is presumably easier for trivalent metal cations to substitute for Fe^{3+} than in pyrite.

If the argument favoring Au substitution for As in the Fe sites is correct, the presence of the $[AsS]^{3-}$ species would appear to be necessary before substantial quantities of gold can enter the sulfide structure. This inference is supported by the thresholds of As

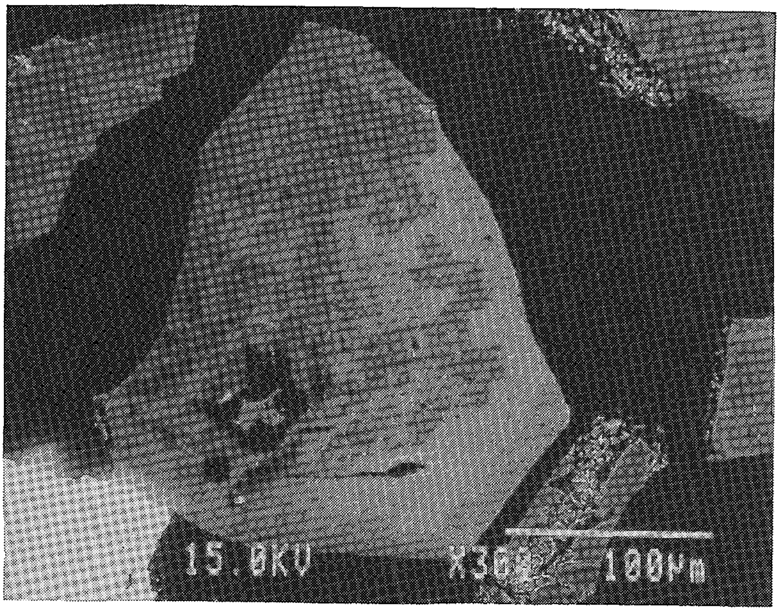

FIG. 7. Back-scattered electron image of a pyrite grain from the Olympias ore, showing concentric zonation of arsenic within the grain. Light areas are arsenic-rich, dark areas are arsenic-poor.

content referred to above. Based on this hypothesis, the following minerals, which have the arsenopyrite or modified pyrite structure with the $[AsS]^{3-}$ paired dianion and have excess arsenic in the Fe sites, may also be able to incorporate "invisible gold": glaucodot [(Co,Fe)AsS], cobaltite [CoAsS] and gersdorffite [(Ni,Co,Fe)AsS].

The studies of gold ores by Mössbauer spectroscopy carried out by Wagner *et al.* (1986) and by Marion *et al.* (in press) have successfully shown that gold in pyrite and arsenopyrite is structurally bound and is bonded covalently. However, these authors have experienced some difficulty, because of the bulk nature of the technique and the large MDL for gold (100 ppm), in confirming the state of that chemical bonding. By its very nature, the Mössbauer technique cannot shed light on the mechanism of incorporation of the gold or its valency.

Pyrite

In the ores that contain arsenian pyrite, Elmtree, Olympias, Golden Pond and Trout Lake, there is a strong positive correlation between the concentrations of Au and As in pyrite in all cases except Trout Lake.

In the Elmtree and Olympias ores, a study with the scanning electron microscope revealed that many of the pyrite grains are zoned with respect to As (Fig. 7). Electron-probe microanalyses show that the optically brighter areas in the back-scattered image correspond to regions of greater As content. The patterns of As distribution are largely irregular. However, notably in the Olympias case, and occasionally in the Elmtree case, the As-rich regions are clearly seen to be concentric. In both the Elmtree and Olympias pyrite, electron-probe microanalyses of the light and dark areas in the pyrite grain reveal two distinct populations of pyrite: a "normal" pyrite containing less than 0.5% As, and an arsenian variety with As contents ranging from 1.5 to 4 wt.% (Fig. 8). Most of the pyrite grains analyzed contain a mixture of the two types.

In the pyrite particles that have both arsenic-rich and arsenic-poor regions, the arsenic-rich areas were analyzed for gold. These areas were located on the ion probe by imaging for ^{75}As. Effort was made to contain the analysis area of 60 μm in diameter within the arsenic-rich region of the pyrite particle. However, 'dilution' with arsenic-poor pyrite up to a maximum of 20% by volume is possible during analysis. The 'dilution' effect will result in a measured concentration of gold in the arsenian pyrite that is lower than the true value. This effect in turn will increase the scatter of data points in Figure 9 and result in a less inflected least-squares-fit line through the analytical points. In the pyrite from Elmtree and Olympias, the threshold values for arsenic, beyond which there is a strong correlation of gold and arsenic concentrations, are approximately 0.2 and 0.4 wt.%

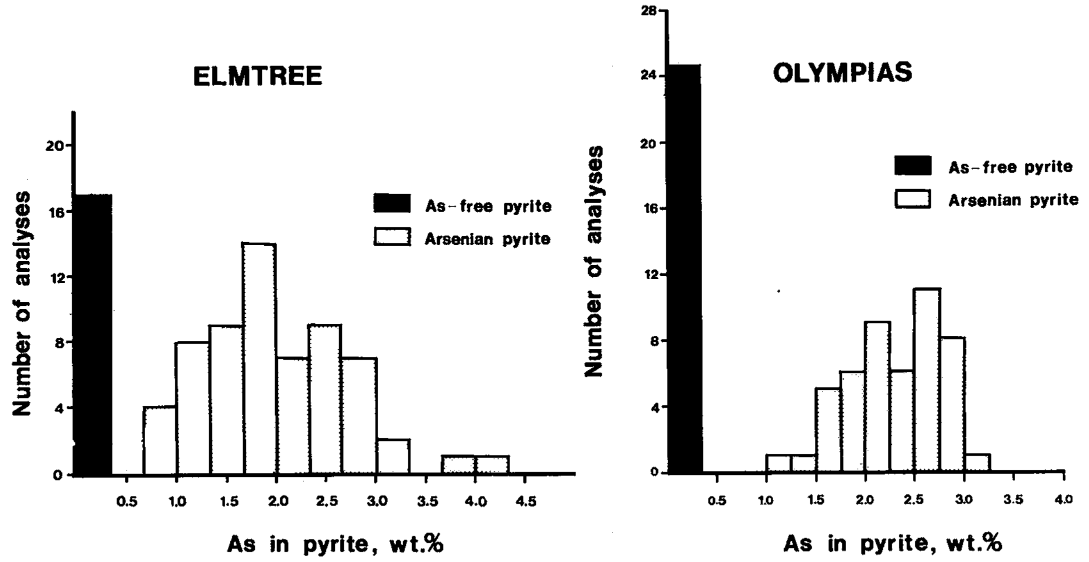

FIG. 8. Histogram of As content of pyrite from the Elmtree and Olympias ores, showing bimodal distribution of As between normal pyrite, with less than 0.5 wt.% As, and arsenian pyrite, which contains more than 2.0 wt.% As.

arsenic. The correlation coefficient is 0.77 for Elmtree and 0.66 for Olympias. The observed threshold may indicate that pyrite incorporates gold significantly (> 1 ppm Au) only after the arsenic content has reached a certain threshold value. Thus in the Trout Lake pyrite, the arsenic concentration ranges between less than 10 ppm to 4100 ppm (mean 500 ± 247 ppm As), and there is no significant correlation (0.187) between As and Au concentrations in individual pyrite grains.

Based on synthesis experiments, the maximum As that can be incorporated in pyrite under equilibrium conditions is about 0.1 wt.% (Clark 1960). However, a recent study by Fleet *et al.* (1989) has identified natural pyrite with up to 8 wt.% arsenic. The arsenian pyrite occurs as fine oscillatory zones as narrow as 0.5 μm.

Grain size of sulfide minerals and "invisible gold"

Our studies have shown that where there is more than one generation of a particular sulfide mineral present, each must each be treated as a separate phase, because contents of "invisible gold" may differ significantly. The fine-grained type contains the higher gold concentrations, by as much as an order of magnitude. This finding has been demonstrated for the arsenopyrite of the Congress and Golden Pond ores, chalcopyrite from HW, and also may be true for other ores in which there are great ranges in the "invisible gold" concentration in the arsenopyrite or other minerals. The existence of more than one generation is not precluded by the absence of optically visible distinctions based on paragenetic or textural criteria. The association of the fine-grained arsenopyrite with the silicate gangue in the Congress ore suggests that possibly two ore-forming events occurred, and that the fine-grained arsenopyrite and its contained gold were deposited during the earlier event, and subsequently reworked during the later episode. Explanations should be sought for the inverse correlation between grain size and gold concentration and for the enrichment of the fine-grained type in arsenic.

CONCLUSIONS

1. "Invisible gold" appears to be preferentially concentrated in arsenopyrite, which is the main sulfide mineral incorporating gold into its structure. This ready acceptance of gold is apparently related to its crystal chemistry. Concentrations of "invisible gold" should be sought in minerals that adopt the arsenopyrite structure.
2. Concentrations of "invisible gold" in pyrite are not as large as in arsenopyrite. Possible reasons are the differences in crystal chemistry and the absence of As. Only if As is present in the pyrite in amounts greater than 0.2–0.4 wt.% does there appear to be significant incorporation of Au into the structure.
3. On the evidence of the samples studied here, the

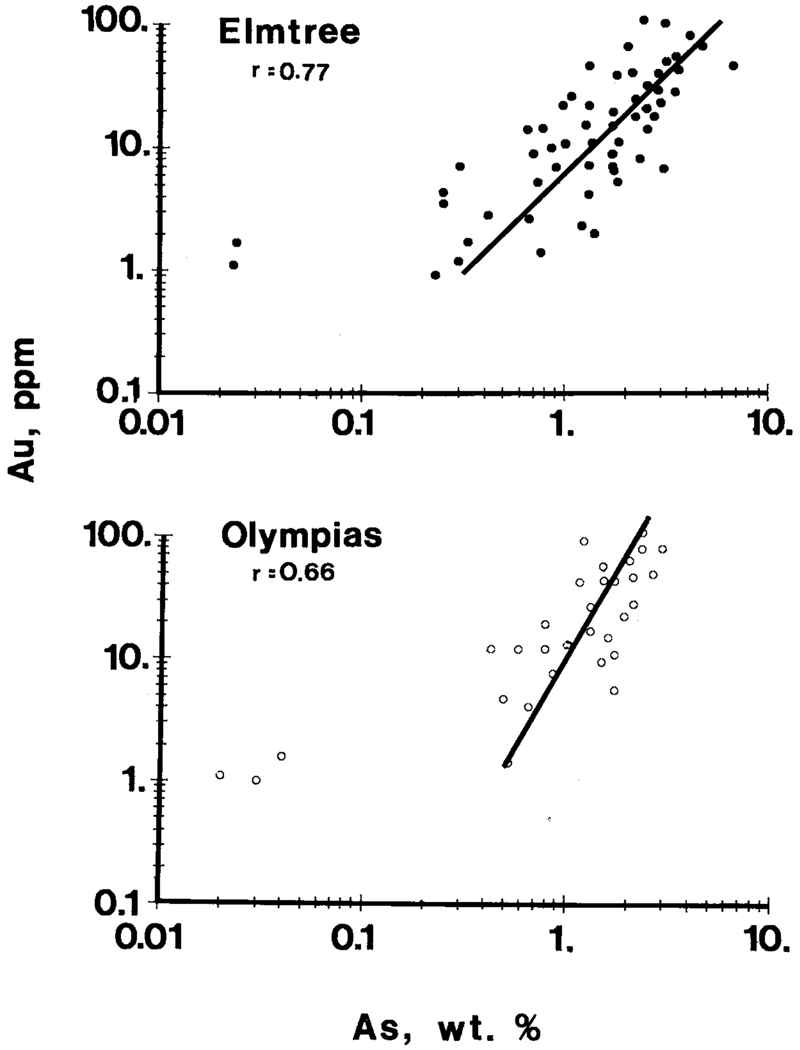

FIG. 9. Plot of As content against concentration of "invisible gold" in pyrite and arsenian pyrite from the Elmtree and Olympias deposits, indicating the correlation between gold and arsenic in each case.

size of the mineral grain, particularly arsenopyrite, seems to reflect the concentration of "invisible gold" present. Where two generations are present, "invisible gold" tends to be significantly concentrated in the type having a finer grain-size.

4. Concentrations of "invisible gold" in As-poor pyrite, pyrrhotite and chalcopyrite are minor, usually not exceeding 2 ppm in the samples studied. However, even at such minor concentrations, appreciable proportions of gold may be accommodated within such minerals in a deposit.

5. This study has shown that concentrations of gold in sulfide minerals vary considerably from deposit to deposit. Factors that control the concentration of structurally bound gold in a sulfide mineral include the gold content of the ore-forming solution, the prevailing physicochemical parameters during ore genesis or metamorphism, the chemistry of the host, and the simultaneous formation of such gold minerals as native gold, electrum and gold tellurides. The presence of submicroscopic intracrystalline inclusions of gold in a sulfide depends on the suitability of the host substrate for gold nucleation, initial gold solubility and solubility decrease with changing conditions leading to exsolution.

6. Further data obviously are required to gain a bet-

ter understanding of gold concentration in the common sulfide minerals. In particular, consideration should be given to possible patterns of "invisible gold" mineralogy common to deposits of a particular genetic type or geological setting. "Invisible gold" concentrations or the partitioning of gold between two or more phases may reveal genetic relationships among ore minerals and may show dependencies upon temperature or other physical variables.

7. Indirect evidence gathered to date suggests that Au replaces the excess arsenic that occupies iron sites in arsenopyrite that is both arsenic- and gold-rich. Further studies are required to determine unequivocally the chemical state and the site of gold in the crystal structure of sulfides and sulfarsenides.

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