

A Multidisciplinary Study of Invisible Gold in Arsenopyrite from Four Mesothermal Gold Deposits in Siberia, Russian Federation

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Abstract

Characterization of gold in four Siberian mesothermal gold deposits was done through a multidisciplinary investigation (including ore microscopy, INAA, SIMS, EPMA, and ¹⁹⁷Au Mössbauer spectroscopy). The deposits are Olympiada and Veduga in the Enisei Mountain Range and Nezhdaninskoye and Sentachan in the Verkhoyansk-Kolyma area, in which vein and disseminated orebodies are hosted by sedimentary sequences metamorphosed to amphibolite (Olympiada) and greenschist facies. Ore minerals include arsenopyrite and pyrrhotite (or pyrite) as major constituents with minor scheelite, and sphalerite, chalcopyrite and native gold as minor constituents (with $\pm$ austrobitite, galena, gudmundite, tetrahedrite, stibnite, and berthierite). Some of the gold mineralization is metallurgically refractory in all four deposits, largely due to the presence of "invisible" gold in arsenopyrite, and to a lesser extent, in pyrite. Several generations of arsenopyrite are recognized in the auriferous zones of the Veduga, Nezhdaninskoye, and Sentachan deposits. Textural observations indicate late deposition of native gold with respect to arsenopyrite. No evidence was found of arsenopyrite recrystallization and the crystallization of native gold is considered to result from an evolution of fluids rather than redeposition of gold.

Wide variations in the gold contents of arsenopyrite occur within deposits, within samples, and within individual grains. INAA analyses of individual arsenopyrite grains (30–70 μm in size) show that the gold

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concentration ranges from <0.2 to 762 ppm for Olympiada, from 6.5 to 393 ppm for Veduga, from 2.0 to 938 ppm for Nezhdaninskoye, and from 71 to 292 for Sentachan. EPMA and X-ray distribution maps using the electron microprobe reveal a heterogeneous gold distribution within individual arsenopyrite grains, with gold-rich areas usually depleted in arsenic and gold. The Au contents range from <0.03 to 0.47 wt percent for Olympiada, from <0.03 to 0.37 wt percent for Veduga, from <0.03 to 0.14 wt percent for Nezhdaninskoye, and from <0.03 to 0.26 wt percent for Sentachan. The gold concentration of arsenopyrite determined by SIMS varies as follows: Olympiada, from 0.07 to 2,298 ppm; Veduga, from 63.98 to 1,141.60 ppm; Nezhdaninskoye, from 1.17 to 386.64 ppm; and Sentachan, from 26.7 to 424.5 ppm. Pyrite from Olympiada contains from <0.03 to 0.53 ppm Au, and from Nezhdaninskoye, from <0.23 to 12.97 ppm Au. SIMS ion imaging confirmed the gold heterogeneity and the depth profiles which occasionally detected invisible gold occurring as micro inclusions, ranging from <0.02 to 0.075 μm in diameter. ^{197}Au Mössbauer spectra of arsenopyrite concentrates from the Veduga, Nezhdaninskoye, and Sentachan deposits exhibit mainly a component with isomer shifts between 3.3 and 3.6 mm/s which is interpreted as strong evidence of the presence of chemically bound gold in the arsenopyrite crystal structure. The spectra of samples from the Veduga deposit also contain minor amounts of native gold, for which negative isomer shifts near -1.2 mm/s are expected. Metallic gold dominates in the ^{197}Au Mössbauer spectra of samples from the Olympiada deposit, but varying amounts of chemically bound gold are also visible in the spectra, some attributed to aurostibite.

It is concluded that the ores from these deposits are refractory, partly because the gold occurs in arsenopyrite as chemically bound gold as well as submicroscopic metallic particles probably as small as 2 nm. This study also shows that Au-bearing arsenopyrite is usually depleted in As with respect to its stoichiometric composition, but correlation of Au enrichment to Fe deficiency was not found. It is inferred from ^{197}Au Mössbauer spectroscopy that substitution of Fe^{3+} for Au^{3+} is most likely. The temporal change in different modes of gold occurrence (i.e., as native gold or invisibly in sulfides) in the mineralized zones and veins is interpreted to result from an evolution of fluids rather than to be a recrystallization phenomenon. Dissemination of Au-bearing sulfides within the altered halos infers that a pervasive fluid-rock interaction was an effective mechanism for deposition of minerals and gold. Absorption of gold complexes onto sulfide surfaces is also suggested to have played an important role in the deposition of native gold during the latest episodes in the formation of the deposits.

Introduction

THE ASSOCIATION of gold with sulfide minerals has been demonstrated by numerous investigators (e.g., Bürg, 1930; Haycock, 1937; Boyle, 1979). Arsenopyrite is a common and significant gold-bearing sulfide mineral (Cabri, 1992) and there has been a long-standing debate as to whether the gold occurs as submicroscopic or colloidal-size particles, or whether it is incorporated in the crystal structure of the host mineral. New advances in analytical techniques such as secondary ion mass spectrometry (SIMS), ^{197}Au Mössbauer spectroscopy, and high-resolution transmission electron microscopy (HRTEM) make it possible to achieve a better understanding of the chemical state, distribution patterns, and nature of gold in arsenopyrite. The use of these techniques has demonstrated that gold invisible to detection by SEM ($\sim <0.1 \mu\text{m}$) occurs in arsenopyrite from many deposits as submicroscopic, colloidal-size, and solid solution gold (Cabri et al., 1989; Cathelineau et al., 1989; Fleet et al., 1989; Marcoux et al., 1989; Chrysosoulis and Cabri, 1990; Cook and Chrysosoulis, 1990; Bortnikov et al., 1993; Mumin et al., 1994; Oberthür et al., 1997). The occurrence of gold in different modes within the same deposit raises the question of the relative timing of the gold precipitation mechanisms to form Au^0 or gold in solid solution (cf. Neumayr et al., 1993), as well as the factors controlling gold-bearing arsenopyrite deposition. In addition to being of academic interest, the presence of "invisible" gold in sulfides is of practical importance because these ores require the use of alternative recovery processes to the commonly used cyanide leaching. Data on the distribution of invisible gold within the ores and within a particular mineral are extremely valuable to mineral-dressing engineers.

The problem under discussion has assumed increased importance recently because large-tonnage disseminated gold

deposits with refractory ores are now the main source of gold production in many countries (cf. Hausen et al., 1997). Two of the largest gold deposits of the Russian Federation (Olympiada and Nezhdaninskoye), which are currently being mined, contain refractory ores. The ore reserves of the Olympiada deposit are estimated to be 750 metric tons Au (24.1×10^6 troy oz), according to the *Kommersant Daily* (Moscow, Aug. 16, 1996); the ore reserves of the Veduga deposit, which is located within the same ore camp, are estimated to be about 75 t Au (2.4×10^6 troy oz). Total proved and estimated ore reserves for the Nezhdaninskoye deposit are 500 t Au (16.1×10^6 troy oz) as well as 2,000 t Ag (64.3×10^6 troy oz). The estimated gold reserves of the Sentachan antimony deposit are about 100 t Au (3.2×10^6 troy oz) and the gold is produced as a by-product. The grades of the Sentachan ores are 25 percent Sb, 37 g/t Au, and 13.4 g/t Ag. Annual production includes 9,500 t of high-grade ores containing 38 percent Sb and 75 g/t Au. Exploitation of the Sentachan deposit indicates gold losses, which are attributed by assays to gold in disseminated sulfides in an alteration halo. The potential for heap leaching some of these ores has recently been discussed (Genkin et al., 1997). Because of their refractory nature, it was considered desirable to examine these deposits in more detail, in order to provide data which can be used to improve gold recovery.

The purpose of this study was to determine: (1) the amount of gold that can be incorporated in arsenopyrite from several deposits, (2) the distribution of gold within individual grains, (3) the nature of the chemical state of such gold, and (4) the relative timing of gold precipitation within arsenopyrite and of native gold. To find the answers, the authors used a multidisciplinary examination of arsenopyrite with the help of SIMS, EPMA, INAA, and ^{197}Au Mössbauer spectroscopy. We use the terms "invisible" gold and "submicroscopic" gold

interchangeably, and the term "chemically bound" gold as a generic term to denote that the gold is held within the structure of a mineral, either as a one-on-one replacement or in defect sites that are not of the end-member structure.

Geologic Setting

The deposits studied are situated within fold belts rimming the ancient Siberian platform, Russian Federation (Fig. 1). The Olympiada and Veduga mesothermal gold deposits are part of the old well-known North Eniseiski mining district that lies within the Enisei Mountain Range (Genkin et al., 1994). The Nezhdaninskoye mesothermal gold deposit and the Sentachan antimony-gold deposit occur in the Verkhoyansk-Kolyma Mesozoids which extend along the northeast margin of the ancient Siberian platform (Parfenov, 1991).

Gold deposits in the Enisei Mountain Range

The Enisei Mountain Range is a part of the Precambrian Baikaside fold belt that extends along the southwest and southeast margins of the Siberian platform. It consists of amphibolite- to greenschist-grade carbonate-terrigeneous and carbonaceous rocks and mafic and intermediate volcanic rocks of Early Proterozoic age, overprinted by a regional northwest-trending fold structure developed during an Upper Proterozoic folding event. The North Eniseiski mining district is underlain by carbonate terrigenous rocks of the Early Proterozoic Sukhopit series, which are intruded by porphyritic granites and biotite granites. The Olympiada and Veduga deposits lie within gold-bearing belts located within the junction zone of the Panimba anticlinorium and the Bol'shepit synclinorium (Votakh, 1968). Two major east-northeast-trending brittle-ductile structures, the Tatar and Ishimbian fault zones, control the distribution of gold deposits in this district. They consist of a series of subparallel fractures and subsidiary high-angle bedding-plane faults that show an en echelon distribution with a northwest-trending envelope. The

rocks within these fault zones display plicated-imbricated structures and intense cleavage and metamorphic foliation.

The Olympiada deposit occurs within rocks of the middle Kordian subunit of early Riphean age comprising a succession of micaceous quartz-, micaceous carbonate-quartz, carbonaceous muscovite-quartz, and sericite-quartz-carbonate schists, and carbonate rocks. The lower part of this succession comprises the core of the Medvezhinskaya anticline and the upper part is in the limbs of adjacent synclines. Retrograde alteration around the deposit has produced micaceous quartz-carbonate, carbonaceous sericite-quartz, and carbonaceous zoicite-quartz rocks containing widespread disseminated sulfide minerals. The deposit comprises several strata-bound horizons and lenses with disseminated and stringer sulfides and scheelite mineralization occurring along the northern limb and part of the hinge zone of the Medvezhinskaya anticline over an area up to 2.5 km along strike and to a depth of 200 m. The strata-bound character of the ores reflects the primary structural pattern of the metamorphic host rocks. Typically these rocks are banded, foliated, reticulate, and puckered.

The Veduga deposit occurs in Early Proterozoic green-schist carbonate terrigenous rocks within the Tatar fault zone. The host rocks are gray fine-grained to black carbonaceous phyllitic shales and coarsely foliated greenish-gray sericite-chlorite schists. These rocks were carbonatized and silicified during retrograde alteration. Quartz-sericite, nearly monomineralic sericitic, and quartzitic rocks form an inner zone of alteration halos. Orebodies consist of strata-bound lenses of sericitic and quartzitic rocks containing abundant disseminated sulfide mineralization. Banded structures, defined by alternating silicate and sulfide bands, are most typical for this deposit. Gold correlates with the amount of sulfide minerals in the altered rocks. Sulfide minerals occur as tiny veinlets 1.0 to 1.5 cm wide within these rocks. Quartz-carbonate-sulfide veinlets were observed in these rocks as well.

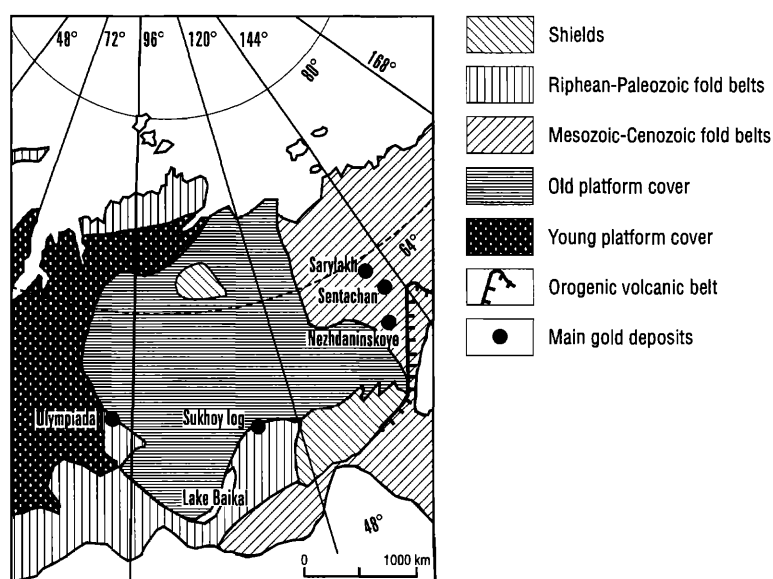


FIG. 1. Simplified geologic map of the Siberian platform and its folded margins showing the location of the main gold deposits.

Gold deposits in the Verkhoysansk-Kolyma fold belt

The Nezhdaninskoye deposit lies within the South Verkhoysansk synclinorium in the outer part of the Verkhoysansk-Kolyma orogenic belt (Parfenov, 1991). It is confined to the Dyba flexurelike anticline and a junction of the south-north-trending Nezhdaninsk shear zone with the northeast-trending Suntarsk fault zone. The deposit is hosted in Lower to Upper Permian siltstones and sandstones metamorphosed to greenschist grade. The sedimentary sequence was intruded by the Kurum massif (amphibole-biotite granodiorite), a number of small diorite and quartz-diorite stocks, and dikes of gabbro-diorite, amphibole and biotite lamprophyre, and diorite. More than 50 orebodies over an area 10 km along the strike and to depth of 1.5 km occur in the core of an anticline. Their width ranges from 2 to 40 m. Mineralization is hosted mostly in high-angle faults and sinistral faults of the Nezhdaninsk system, with a roughly north-south direction. Morphologically the orebodies consist of sulfide impregnations in the altered host rocks, quartz sulfide veinlets, concordant to discordant quartz sulfide veins and lenses. Low-grade disseminated pyrite and arsenopyrite mineralization in altered rocks is of most economic importance.

The Sentachan gold-antimony deposit is located within the Sentachan fault, approximately 300 m northeast of the Adycha Taryn fault zone (Indolev et al., 1980; Parfenov et al., 1988), a 40-km-wide band of intensely and multiply deformed terrigenous sedimentary rocks which extends up to 900 km in a northwesterly direction. Gold quartz and gold-antimony deposits are controlled by the dextral faults which are subsidiary to the Adycha-Taryn fault zone (Berger, 1978). The deposit occurs in shales, siltstones, and sandstone of Norian and Rhaetian ages that comprises a monocline. Three main orebodies occur within the Sentachan fault, as lenslike lodes 0.2 to 6 m in width and 80 m in length. The central parts of the orebodies are massive quartz-stibnite veins. They are transformed to several separate quartz lenses at the northwestern flank of the mineralization host zone. Veins are accompanied by numerous quartz-ankerite veinlets and halos of disseminated pyrite along the hanging wall; the footwall is marked by carbonatized sandstone with finely disseminated pyrite. Brecciated quartz veins fill the steeply dipping fissures; stibnite is a dominant mineral in the gently dipping parts of zones. Quartz fragments are cemented by fine-grained quartz-stibnite aggregates. Boudins of milky quartz are observed crosscut by tiny chlorite-ankerite-quartz veinlets with rare stibnite.

Samples Studied

Sampling of the deposits studied was carried out during the course of a long-term investigation of the mineralogy and distribution patterns of gold in the deposits. Sampling of the Nezhdaninskoye and Sentachan deposits began in 1972 and the Olympiada and Veduga deposits were sampled in 1992. In addition, hand specimens from the Olympiada deposit, collected during the period 1980-1991 (provided by G. Ivanova and N. Sergeev) are representative of all the important morphological varieties of the orebodies. Samples for this study were selected on the basis of previous extensive studies of the ores and sulfide concentrates by ore microscopy, assays,

AA, and NAA. In particular, insufficient visible gold was found by ore microscopy to account for the assays. Assays, AA, and NAA showed a correlation between arsenopyrite abundance and gold content, with a high gold concentration in arsenopyrite separates. Arsenopyrite concentrates for Mössbauer and other analyses were made from crushed material. After sieving, heavy liquid separations were made of the $-0.5 + 0.25$ - and $-0.25 + 0.1$ -mm sieve fractions using methylene iodide, followed by electromagnetic separations of the heavy fractions. Examination under the binocular microscope showed the concentrates to be better than 95 percent arsenopyrite.

Sampling from the Olympiada deposit was restricted to available drill cores which explored the nonoxidized mineralization from 380- to 780-m vertical depth and 700 m along strike. More than 200 thin and polished sections were examined by transmitted and reflected light microscopy. Samples for this study were collected from drill holes 451 (sample O-4 at 375-m depth and sample O-5 at 364-m depth) and 382 (sample 204 at 164.0-m depth) which explored orebody 4 for intervals enriched in arsenopyrite and gold. These samples represent two types of mineralization from the eastern part of the deposit. Sample O-4 is an amphibolite-carbonate-quartz-margarite schist with disseminated arsenopyrite and minor pyrite, pyrrhotite, berthierite, native gold, and aurostibite. Samples O-5 and 204 consist of a muscovite-quartz-carbonate banded rock with disseminated arsenopyrite, minor pyrite, and pyrrhotite. Sample 116 was taken from the main adit driven to explore orebody 2. It consists of quartz with disseminated arsenopyrite and is representative of the western area of the deposit.

Samples from the Veduga deposit were taken from prospecting trenches, drill cores, and an adit which explored an orebody from the surface to a depth of 360 m, extending more than 500 m along strike. The samples are representative of all the auriferous metasomatic rocks (quartz rich, sericite rich, and altered phyllitic siltstones). Three samples (148, 140, and 152), representing the most economically important auriferous zone (assaying up to 19 ppm Au), were sampled from an adit.

Samples of arsenopyrite from the Nezhdaninskoye deposit are typical of altered quartz-sericite-carbonate rocks with disseminated arsenopyrite and pyrite. They were collected from prospecting trenches, drill cores, and from underground within orebody 1 from the 1,300-m level (adit 6, sample 233), from the 1,230-m level (adit 115, sample 115), and on the 1,200-m level (adit 19, sample 69). Sample 251 was collected from a drill hole core on the 250-m level. Orebody 56 was sampled on the 720-m level (adit 31, samples 2 and 11) and on the 550-m level (drill hole 546, sample 546).

Sampling of arsenopyrite from the Sentachan deposit was restricted to a surface trench which exposed a major orebody (orebody 2). Five samples of quartz-sericite-ankerite rocks containing disseminated arsenopyrite and pyrite were collected near the contact of a quartz-stibnite vein.

Analytical Methodology

A number of different analytical techniques were used in this study, including both bulk analytical and microanalytical methods. These methods cover a wide range of minimum

detection levels, from sub-ppb to a few hundred ppm Au. The bulk analytical methods of analysis used are instrumental neutron activation analysis (INAA) and ^{197}Au Mössbauer spectroscopy. The microanalytical methods used are electron probe microanalysis (EPMA), scanning electron microscopy (SEM), and secondary ion mass spectrometry (SIMS). Details of analytical conditions for each method are given in the Appendix.

Results

Ore mineralogy: Arsenopyrite and gold paragenetic relations

Field and microscopic studies revealed the following common features of arsenopyrite and native gold mineralization in the four deposits studied:

1. The earliest gold-bearing pyrite and arsenopyrite are disseminated within metasomatic quartz-sericite-carbonate rocks controlled by fractures or surrounding the auriferous veins as constituents of alteration halos.
2. Native gold is extremely rare in alteration halos and late with respect to the sulfide minerals.
3. Native gold is more abundant in late mineral assemblages.
4. Native gold is associated with late arsenopyrite, pyrite, and sphalerite which form bands, veinlets, and patches cutting across quartz veins.

The ore mineralogy and paragenesis of the individual deposits is discussed in more detail below.

Olympiada deposit: This study and a compilation of earlier mineralogical studies (Lee and Shokhina, 1986; Genkin et al., 1994; Afanas'eva et al., 1995) show that the auriferous bodies consist of several (and overprinting) successive paragenetic mineral assemblages, of which the earliest includes quartz and scheelite. Scheelite is disseminated within the banded carbonaceous sericite-quartz and zoisite-carbonate-quartz metasomatic rocks, within massive carbonate rocks, or as tiny quartz-scheelite stringers.

Arsenopyrite is the most important mineral in the ores of this deposit. In the quartz-carbonate-micaceous schists it occurs in association with pyrrhotite and pyrite in sulfide-rich bands parallel to the schistosity of the host rocks (Fig. 2A). The thickness of the sulfide-rich bands ranges from 1–2 to 20 mm. Arsenopyrite is dominant in some bands, whereas pyrrhotite is a principal mineral in others. Such a relationship may be interpreted as the result of a selective replacement of bands of different composition and suggests coeval crystallization of arsenopyrite and pyrrhotite in the alteration halo. Arsenopyrite also occurs as isolated crystals in the schists, forming idiomorphic crystals ranging from 5 to 10 μm and from 1 to 2 mm in size. Prismatic and needle shapes are typical for the arsenopyrite crystals, which are irregularly distributed within the orebodies. Some fine (1–2 mm wide) sulfide bands contain rare segregations of diversely sized arsenopyrite grains. In rare cases, tiny arsenopyrite crystals form rimlike cockade textures around the pyrrhotite aggregates (Fig. 3A), indicating that arsenopyrite may be younger than pyrrhotite. An overgrowth of pyrrhotite by rhombohedral arsenopyrite porphyroblasts has also been observed (Fig. 3A)

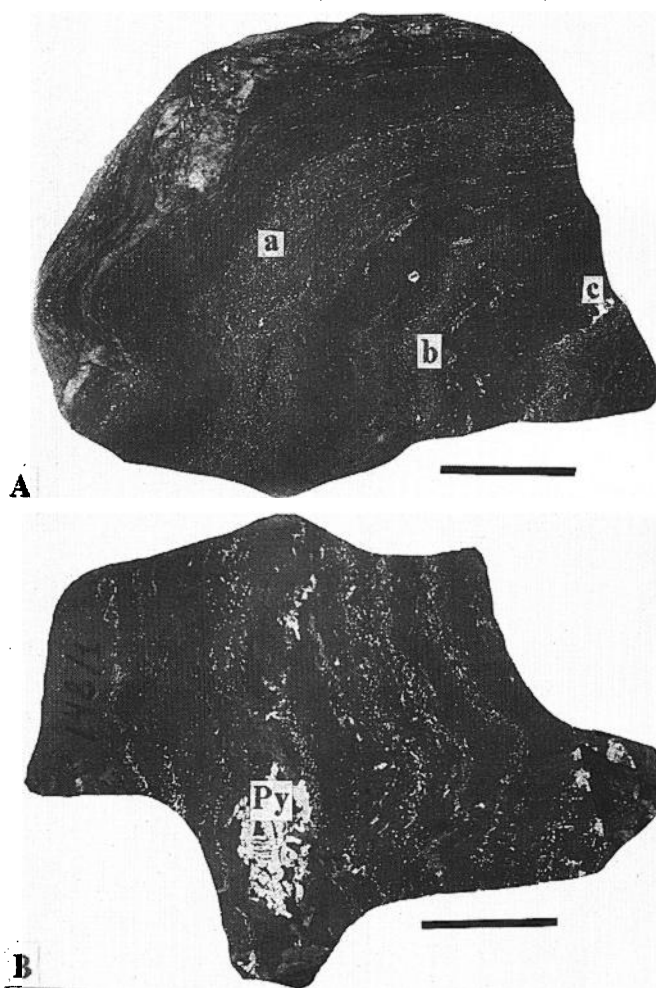


FIG. 2. Photographs showing the fabrics of auriferous ores. A. Banded structure of micaceous carbonate-quartz sulfide-bearing schists. Folded sulfide bands are composed of arsenopyrite + pyrrhotite + pyrite aggregates (a), pyrrhotite + arsenopyrite assemblage (b), and pyrrhotite (c). Olympiada deposit, polished hand specimen, bar = 2 cm. B. Folded sulfide bands in sericite rocks consist of arsenopyrite II crystals and pyrrhotite + arsenopyrite III intergrowths. Py = pyrite. Veduga deposit, polished hand specimen, bar = 2 cm.

and skeletal porphyroblasts of arsenopyrite replace the pyrrhotite aggregates (Fig. 3B). Arsenopyrite is also intergrown with pyrite, occurring as inclusions in larger pyrite porphyroblasts. In sample O-4, native gold occurs in association with arsenopyrite, pyrrhotite, and pyrite, as tiny grains (2–68 μm) overgrowing arsenopyrite crystals (Fig. 4A), and also as inclusions and fracture fillings in arsenopyrite. Aurostibite is also associated with arsenopyrite, occurring as inclusions or overgrowths with grains ranging from about 2 to 25 $\times$ 105 μm in diameter (Fig. 4B). Such textural intergrowths indicate that native gold and aurostibite are late minerals in this assemblage. However, there is no evidence that crystallization of native gold resulted from an overprint of a late process because evidence of dissolution or recrystallization of arsenopyrite and pyrite was not observed. The latest mineral assemblage consists of stibnite, berthierite, quartz, and carbonate. This mineral assemblage occurs as tiny veinlets which cut

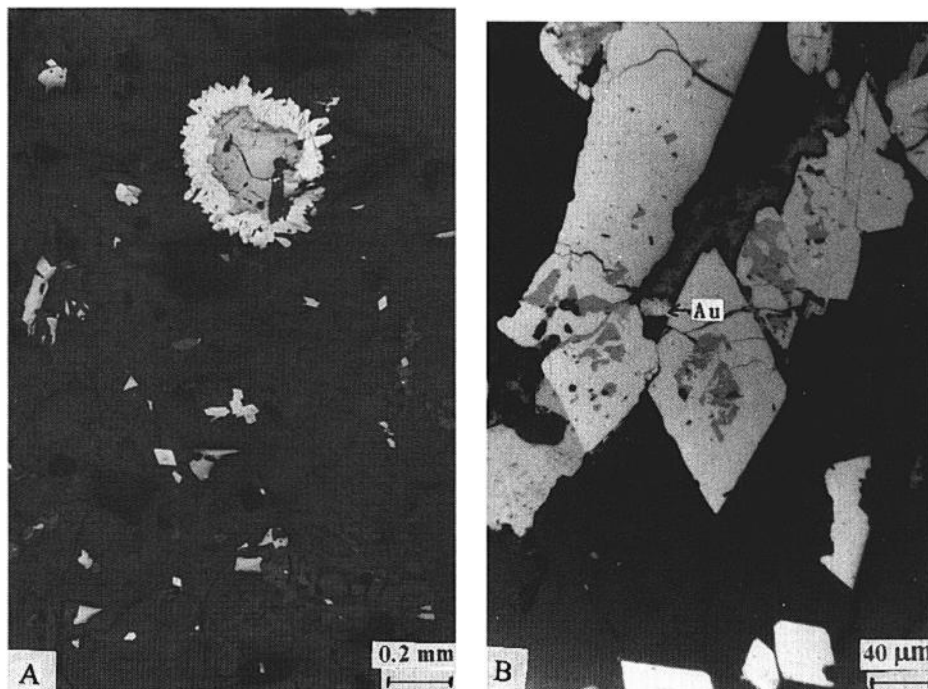


FIG. 3. Microphotographs showing arsenopyrite intergrowths. A. Radiating arsenopyrite crystals overgrowing earlier pyrrhotite. Olympiada deposit. B. Arsenopyrite porphyroblasts (light gray) replacing pyrrhotite (medium gray). Native gold (Au) fills intergranular spaces between arsenopyrite grains. Olympiada deposit.

quartz-scheelite veinlets and the sulfide-bearing layers of banded metasomatic rocks and is subordinate in the ores.

Veduga deposit: The main opaque ore minerals are pyrite, arsenopyrite, and pyrrhotite. Crystallization of quartz, pyrite, arsenopyrite, and pyrrhotite occurred as patches and small lenses, predating auriferous mineralization. The earliest sulfide mineral aggregates are observed beyond the contours of the auriferous orebody and are interpreted to have formed during metamorphic processes.

The first paragenetic mineral assemblage within the auriferous orebody consists of arsenopyrite II (principal sulfide), native gold, pyrite, and minor sartorite (PbAs_2S_4). These minerals are disseminated in sericitic rocks (rarely in quartz-sericite rocks) which represent the inner zone of an alteration halo 900 m wide and up to 7 km long, confined to the shear and mylonite zone. The textural intergrowths of sulfides, sericite, and quartz (pseudomorphic aggregates replacing metamorphic minerals) indicate their coeval crystallization during metasomatic replacement of country rocks. Arsenopyrite II aggregates form bands, sometimes folded (Fig. 2B), in the sericite metasomatic rocks, where it occurs as isolated needle-like crystals, ranging from 0.05 to 0.8 mm long. Arsenopyrite II was also observed as inclusions within pyrite grains (Fig. 5A). Native gold in tiny grains (up to 20 μm) rarely overgrows arsenopyrite crystals (Fig. 5C), showing evidence of late crystallization of gold with respect to the sulfide minerals.

The next assemblage in the paragenesis consists of an arsenopyrite III-pyrrhotite-quartz-carbonate assemblage in the form of short veinletlike (Fig. 5B), lenslike, or nestlike pyrrhotite-quartz-carbonate aggregates in the above-mentioned bands and in the sericite rocks. This arsenopyrite is fine-grained (1–10 μm). This assemblage is interpreted to have

been deposited later because these aggregates cut the sericite and arsenopyrite II aggregates.

The third assemblage consists of stibnite, gudmundite, galena, native gold and aurostibite. These minerals were observed in the quartz-carbonate veinlets which cut the arsenopyrite II-bearing sericite rocks. Native gold is a late mineral in relation to the antimony sulfides, replacing berthierite and gudmundite. Aurostibite inclusions are associated with this replacement phenomenon. The gold-bearing assemblage of antimony minerals was observed in the sericitic rocks without arsenopyrite II and is therefore considered to be evidence that late native gold cannot be interpreted to result from redeposition of native gold associated with arsenopyrite II. The last event in the paragenesis consists of barren quartz-carbonate veinlets cutting the stibnite-carbonate veinlets.

Nezhdaninskoye deposit: The ore-forming processes were initiated by formation of alteration halos which are confined to shear zones. The alteration halos are zoned, with the inner zone consisting of quartz-ankerite + sericite + pyrite I + arsenopyrite I. Arsenopyrite I and pyrite occur in the rocks as random disseminations considered to be coeval with quartz, sericite, and ankerite. The formation of this assemblage is the result of replacement of Fe-rich carbonates [$\text{Fe}/(\text{Fe} + \text{Mg}) > 0.2$] and sericite by Fe-deficient carbonate [$\text{Fe}/(\text{Fe} + \text{Mg}) < 0.2$] and sericite, arsenopyrite I, and pyrite I through influx of arsenic and sulfur (Bortnikov et al., 1998). This study showed that quartz veins containing arsenopyrite II and pyrite II, together with native gold, formed later since they cut all zones of the alteration halos. Arsenopyrite II and pyrite II are coarse grained and occur within thin veinlets in the country rocks or irregular patches and bands in quartz veins. These minerals commonly occur at contacts of the

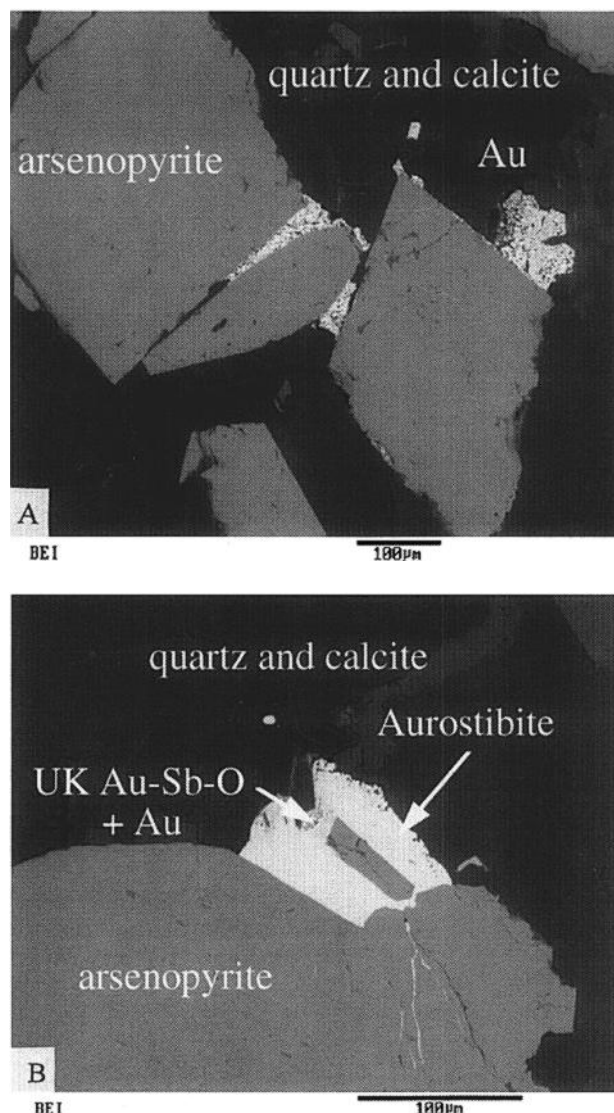


FIG. 4. A. Details showing native gold filling spaces and rimming arsenopyrite grains. B. Aurostibite shown replacing an arsenopyrite crystal at the grain margin and in very thin veins. Also shown is an undefined Au-Sb oxide, UK (that appears brown in polished section) closely intergrown with native gold and occurring as a rim on aurostibite. Olympiada deposit, sample O-4.

veins. The sulfide bands are a few millimeters to 20 cm wide and several meters long. Arsenopyrite II appears to be largely restricted to selvages or to laminations in the host rock fragments. Pyrite II and arsenopyrite II are concentrated in groups and aggregates of numerous individual grains up to 1×2 cm in size. The grain size of both sulfides is quite variable and ranges between 0.1 and 2 mm. Both minerals display mutual boundaries or are intergrown as idiomorphic individuals that indicate their coeval crystallization. These minerals fill the intergranular space of milky vein quartz and are tentatively assumed to be later than the quartz. Rare native gold occurs in association with arsenopyrite II and pyrite II aggregates. Gold is paragenetically late in relation to sulfides and quartz. It overgrows or heals tiny cracks in the sulfide grains (Fig. 5D, E). Gold appears in a vast variety of shapes and

grain sizes. It occurs usually as thin xenomorphic sheets 0.08 to 0.16 mm in size or as equidimensional grains ranging from 0.16 to 0.25 mm in size. The late generation of native gold II occurs in an association with fine-grained arsenopyrite III, pyrite III, sphalerite, galena, and tetrahedrite that comprise the ore minerals in quartz veinlets. Mutual boundary textures of native gold II with arsenopyrite III, tetrahedrite, and chalcopyrite and their occurrence in the thin veinlets of quartz (Fig. 5F) suggest the simultaneous crystallization of these minerals.

Sentachan deposit: Compilation of the data of Indolev et al. (1980), together with personal observations (N.S.B. and G.N.G.), makes it possible to distinguish several successive mineral assemblages in the orebodies. The earliest assemblage consists of barren quartz veins in which the quartz is cataclazed, brecciated, and crosscut by later mineral aggregates. The next mineral assemblage contains arsenopyrite I and pyrite I disseminated in quartz-sericite-ankerite halos controlled by faults and surrounding quartz-stibnite veins, with arsenopyrite I decreasing rapidly in abundance at about 5 to 7 cm from a vein contact. This assemblage occurs in the form of veinlets within the alteration halo and crosscuts barren quartz veins. Arsenopyrite I is widespread in foliated zones where it occurs as inclusions and frequently at contacts with siltstone fragments in the quartz veins. It also occurs in selvages of mineralized zones or quartz veins or as inclusions in early milky-white quartz, but it usually occurs as isolated grains in quartz. Arsenopyrite I is also observed as porphyroblasts, usually about 1 to 2 mm, and up to 5 mm in size. It rarely is associated with pyrite I, which it replaces. Pyrite I is widespread in the foliated and cataclazed zones, forming mutual boundaries with metasomatic quartz, which infers coeval crystallization. The quartz, pyrite I, and arsenopyrite I are fractured, with the cracks filled by stibnite. Only a few grains of native gold were found disseminated in quartz-sericite-ankerite rocks after microscopic examination (G.N.G.) of hundreds of polished sections.

Next in the paragenesis is a galena-sphalerite-sulfosalt assemblage which fills subsidiary fissures to a major fracture filled with a quartz vein. Galena-sphalerite-sulfosalt aggregates replace ankerite, arsenopyrite I, and pyrite I and are restricted to areas where the quartz has been recrystallized. Arsenopyrite II, associated with galena, sphalerite, and sulfosalts, is rare and fine grained. Native gold occurs in association with tetrahedrite and sphalerite and is replaced by stibnite. Aurostibite is found at gold-stibnite contacts. However, native gold occurs preferentially at the corroded contacts of relict quartz and stibnite.

Arsenopyrite III commonly occurs as rare inclusions in monomineralic massive stibnite veins where idiomorphic arsenopyrite crystals (0.005–0.02 mm in size) are concentrated in clusters associated with quartz. Replacement of arsenopyrite III by native gold occurs and an enrichment in native gold was sometimes observed where stibnite mineralization is overprinted onto the earliest arsenopyrite and pyrite aggregates.

Analytical Results

INAA data

The results of INAA for Au are shown in Figure 6. Twenty-three arsenopyrite grains from the Olympiada deposit

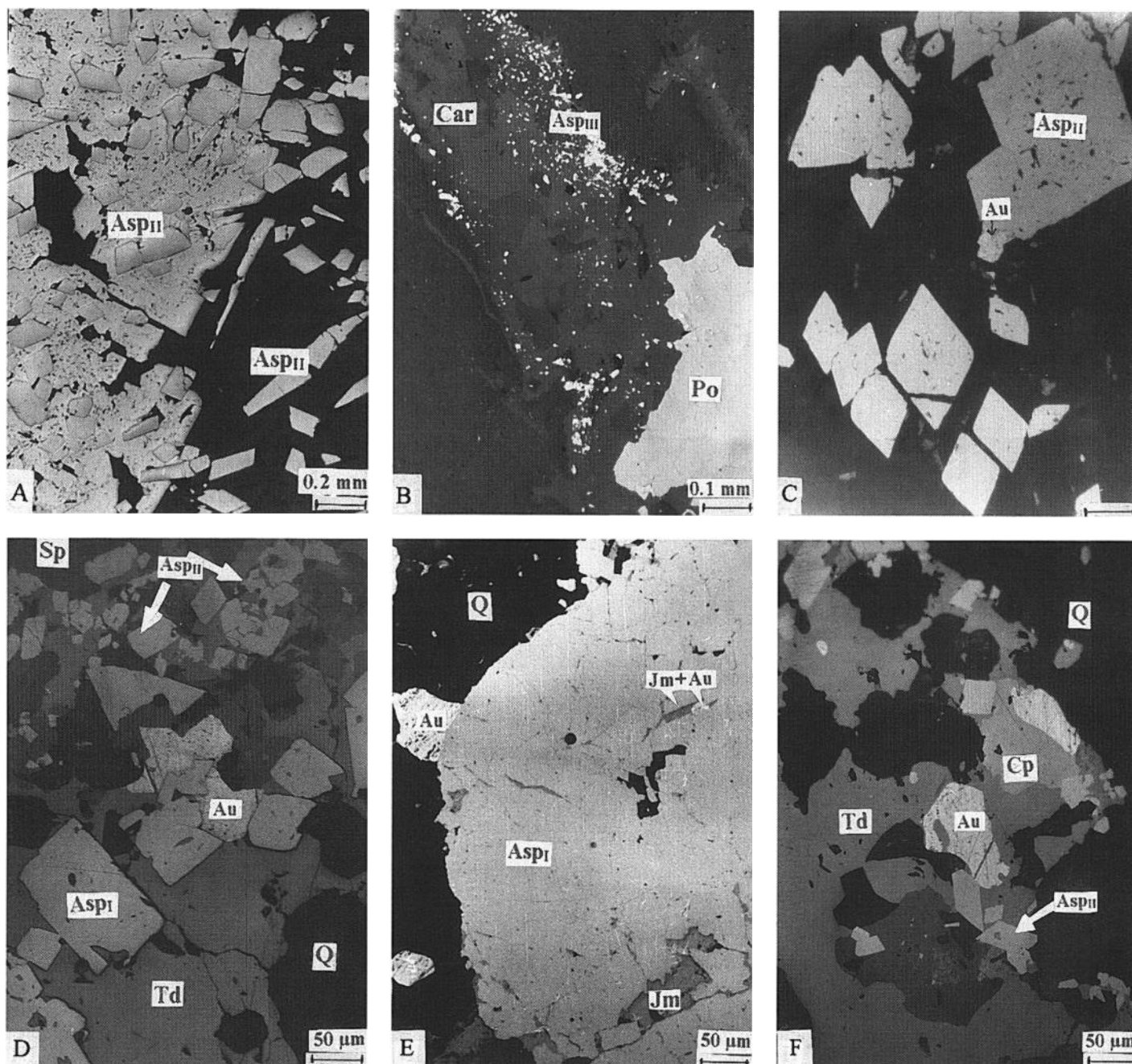


FIG. 5. A. Inclusions of arsenopyrite II crystals within a pyrite porphyroblast. Veduga deposit. B. Pyrrhotite-arsenopyrite III-carbonate veinlets in sericite rocks. Veduga deposit. C. Native gold overgrows an arsenopyrite porphyroblast. Veduga deposit. D. Crystals of arsenopyrite I and arsenopyrite II intergrowths with sphalerite, tetrahedrite, and electrum. Electrum replaces arsenopyrite I. Nezhdaninskoye deposit. E. Native gold overgrowths with arsenopyrite I. Tiny jamesonite-electrum veinlets fill cracks in arsenopyrite. Nezhdaninskoye deposit. F. Sulfide-electrum intergrowths with mutual boundaries suggest coeval precipitation of minerals. Nezhdaninskoye deposit. Abbreviations: Asp = arsenopyrite (generations in Roman numerals), Au = native gold, Car = carbonate, Cp = chalcopyrite, Jm = jamesonite, Q = quartz, Po = pyrrhotite, Py = pyrite, Sp = sphalerite, Td = tetrahedrite.

weighing from 5 to 854 μg were studied. The Au content of individual grains ranges from 0 to 762 ppm in the O-4 separate and from 0 to 238 ppm in the O-5 separate. These data lie within the range of gold concentrations (1.2–2,130 ppm) reported previously for 47 arsenopyrite grains from this deposit (Genkin et al., 1994). These data indicate considerable

variation in the Au content from separate to separate and from grain to grain. The frequency diagram (Fig. 6) shows that arsenopyrite grains with Au contents of 0 to 50 ppm prevail in these two samples.

Nine arsenopyrite grains weighing 4 to 29 μg were analyzed from the Veduga deposit. The Au concentrations vary from 7

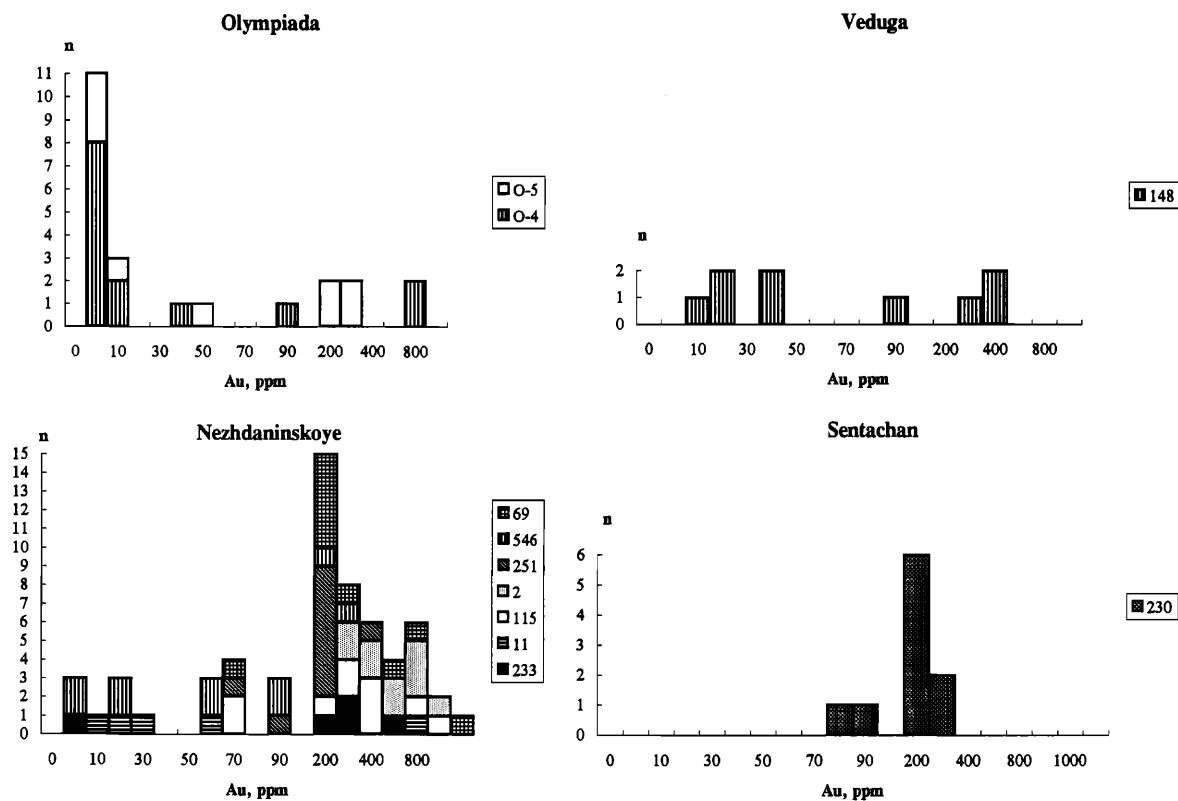


FIG. 6. Instrumental neutron activation analysis data. Frequency diagrams of gold contents in arsenopyrite.

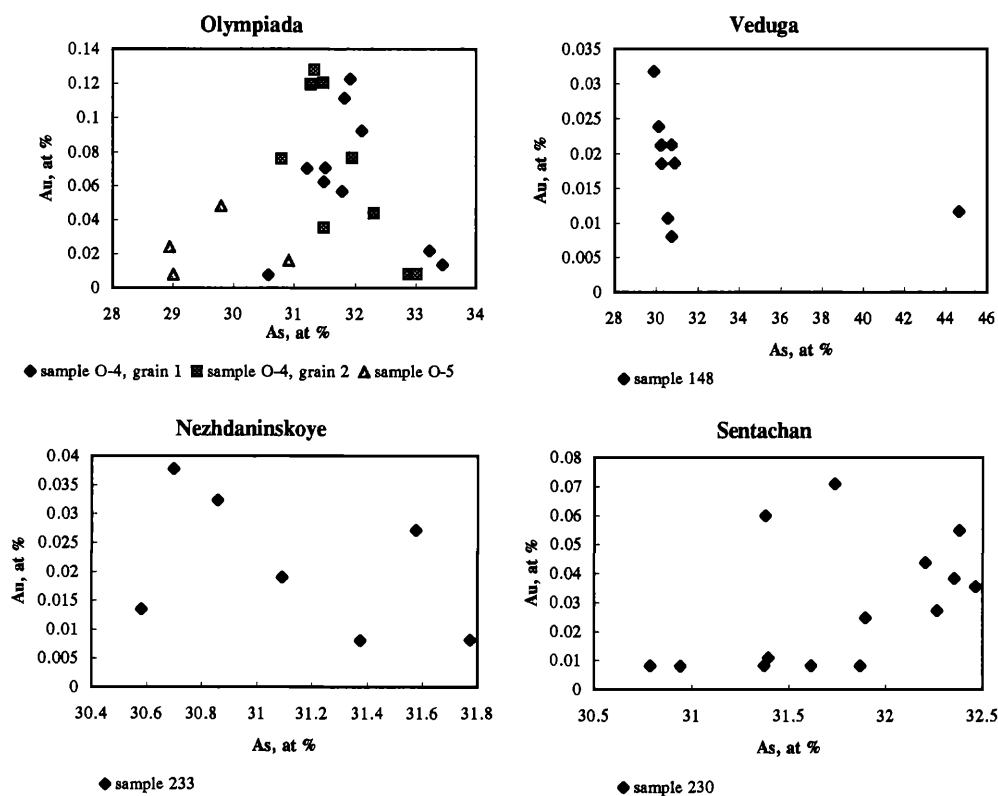


FIG. 7. Plot of electron microprobe data for arsenopyrite. As content vs. Au content.

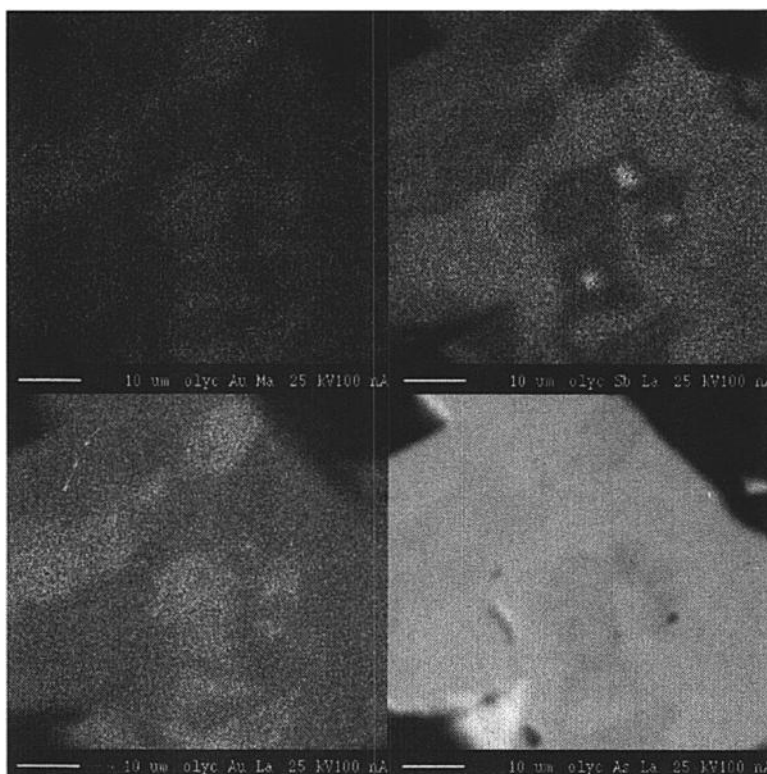


FIG. 8. Electron microprobe X-ray distribution maps for arsenopyrite grain O-5 from the Olympiada deposit. These illustrate an irregular distribution of gold within the crystals and show that the relatively gold-rich areas correlate with areas of lower antimony and arsenic contents.

to 393 ppm, Co from 139 to 1,641 ppm, and Sb 0 to 898 ppm. The frequency distribution for Au is shown in Figure 6.

Sixty arsenopyrite grains from five separates were examined from the Nezdansinskoye deposit and the Au contents found to be in the range of 2 to 938 ppm, but the concentration varies considerably from grain to grain. Prismatic and needle-like arsenopyrite have nearly the same compositions. The studied grains contain antimony and cobalt as trace elements, ranging from 0 to 4,637 ppm Co and from 0 to 2,088 ppm Sb. There appears to be no relationship between the concentrations of Au and that of other minor constituents; the Au frequency distribution is shown in Figure 6, suggesting a median gold concentration between 200 and 400 ppm for all samples.

Ten grains from a single separate were analyzed from the Sentachan deposit. The Au content lies between 71 to 292 ppm. Low cobalt contents were detected in these grains (37–133 ppm), whereas the Sb concentration is rather high (1,060–2,425 ppm). Most grains have a gold content near 200 ppm (Fig. 6).

Electron microprobe data

Electron microprobe spot analyses (Fig. 7) and element mapping of arsenopyrite (Figs. 8 and 9) revealed the distribution patterns of invisible gold within individual grains and determined the nature of the relationship between the Au content, the stoichiometry of arsenopyrite, and major and trace elements in the samples studied.

Element mapping of grains from the Olympiada deposit shows the gold to be distributed as mosaiclike domains in some grains (Fig. 8) and in other grains as veinlets along apparently healed fractures. These and similar maps indicate that gold-bearing areas are depleted in Sb and As. Spot analyses across some of the gold-bearing areas revealed that the Au content varied from below detection limits (i.e., 0.02 wt % or 0.005 at. %) to 0.47 wt percent in different grains. In areas where the composition of arsenopyrite is close to stoichiometric, gold was not detected. However, the highest concentrations of gold were found where the (As + Sb)/S ratio was <1 (Fig. 7). The As content ranges from a nearly stoichiometric value of 33.4 to as low as 28.9 at. percent. Nevertheless, there is no correlation between the Au and As contents.

Antimony and cobalt are minor constituents of the Au-bearing arsenopyrite, with concentrations of these elements varying from grain to grain and within a grain. In grains from sample O-4, areas with higher Sb and Co contents are not generally associated with gold. In sample O-5, gold was only found above the detection limits in one grain out of about 40 examined, illustrating the extremely irregular distribution of gold both between and within grains of arsenopyrite.

The gold contents in both arsenopyrite II and III from the Veduga deposit were examined. Although gold was detected in spot analyses, element maps did not show a clear distribution of gold within the grain due to the short dwell times when using the instrument in the mapping mode. Spot analy-

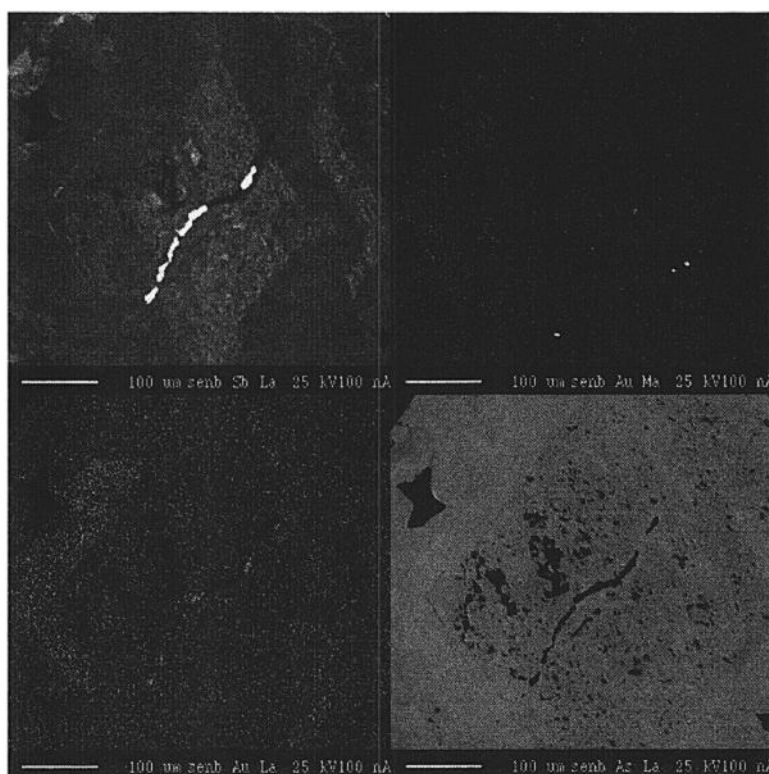


FIG. 9. Electron microprobe X-ray distribution maps for the central area of an arsenopyrite grain from the Sentachan deposit. Gold appears to have a partly regular distribution, but only on one side of the grain. Antimony is concentrated in a zone mirroring the gold, also toward the center of the grain and in stibnite (together with some gold) which occupies a fracture. Note on the Au $M\alpha$ map some interference from three tiny grains of zircon.

ses using the Au $L\alpha$ line showed gold values up to 0.12 wt percent. Again, the highest gold value is associated with nonstoichiometric As-deficient arsenopyrite (Fig. 7). Antimony and cobalt are the main trace elements detected in arsenopyrite, but their behavior differs. The antimony content seems to be uniformly distributed within the area studied but at a low level up to 0.05 wt percent. The cobalt concentration is low and there is no strong evidence of its correlation with gold. Invisible gold was not detected by EPMA in the tiny grains of arsenopyrite III from pyrrhotite-carbonate veinlets. Representative analyses show higher Sb and Co contents than for arsenopyrite II.

Mapping with the electron microprobe established that there was little evidence of specific zoning within an arsenopyrite grain from the Nezhdaninskoye deposit. Spot analyses determined gold contents in one grain of up to 0.14 wt percent, with no clear relationship between gold and the other elements, except that gold is again associated with a nonstoichiometric, arsenic-deficient arsenopyrite (Fig. 7).

A single grain out of the ten analyzed from the Sentachan deposit was found to contain gold above the minimum detection limits. It displays pronounced chemical zoning, particularly with respect to the gold and antimony contents. Figure 9 shows that the arsenopyrite core and outer zone have low gold contents. The core is overgrown by an intermediate, 100- μ m-wide zone enriched in gold on one side, whereas the opposite side of the core is rimmed by a zone enriched in antimony. The electron microprobe spot analyses show that

the zone enriched in Au contains up to 0.26 wt percent Au and is depleted in arsenic. In addition to the major constituents and Au, the grain contains Sb and Co.

Ion microprobe analyses and ion imaging

Olympiada: Grains of arsenopyrite and pyrite were analyzed, with some ion images, from two subsets of samples O-4 and O-5. The first subset was restricted to 10 arsenopyrite grains from O-4, and nine arsenopyrite and five pyrite grains from sample O-5. A much larger number of grains was analyzed for the second subset which was derived from splits of the arsenopyrite concentrates previously analyzed by Mössbauer spectroscopy. The results will be discussed separately because they illustrate problems that can arise in interpreting SIMS data based on analysis of too few grains or in the interpreting the analyses by ^{197}Au Mössbauer spectroscopy without detailed mineralogical characterization.

Arsenopyrite from the first subset (sample O-4) contains small quantities of gold ranging from 0.22 to 0.75 ppm for 10 grains, five of which were reanalyzed (R numbers in Table 1). The grains reanalyzed gave Au concentrations that are systematically lower than those determined when first analyzed (in parentheses): D1R, 0.09 (0.22); D2R, 0.19 (0.36); D5R, 0.36 (0.52); D8R, 0.13 (0.36); and D10R, 0.16 (0.29), all in ppm. Because gold concentrations at such low levels are usually inhomogeneous and because the analyses were done on different days and parts of the grains, such agreement between analyses is considered to be good. Two grains of

TABLE 1. Ion Microprobe Analyses of Gold in Arsenopyrite and Pyrite Grains

Sample and mineral	Analysis number	Au (ppmw)	Comments
Olympiada (O-4)			
Arsenopyrite	D1	0.22	Needlelike, with muscovite inclusions
Arsenopyrite	D2	0.36	Irregular shape, with apatite, quartz inclusions
Arsenopyrite	D3	0.24	Blocky shape, As-rich zones at edges, berthierite inclusion
Arsenopyrite	D4	0.57	
Arsenopyrite	D5	0.52	
Arsenopyrite	D6	0.33	Depth profile shows ~0.1 μ m subsurface Au-rich zone
Arsenopyrite	D7	0.26	
Arsenopyrite	D8	0.36	
Arsenopyrite	D9	0.75	
Arsenopyrite	D10	0.29	
Arsenopyrite	D8R	0.13	In old crater grain D8
Arsenopyrite	D5R	0.36	In old crater grain D5
Arsenopyrite	D1R	0.09	New area of grain D1
Arsenopyrite	D1R-2	0.09	Near edge at pointed end of grain D1
Arsenopyrite	D10R	0.16	Nearer edge grain D10
Arsenopyrite	D2R	0.19	Nearer edge grain D2
Olympiada (O-5)			
Arsenopyrite	C1	25.69	Subsurface Au-rich inclusions and/or zone?
Arsenopyrite	C1R	0.67	
Arsenopyrite	C2	0.61	
Arsenopyrite	C2R	0.63	
Arsenopyrite	C4	0.51	
Arsenopyrite	C5	75.44	Ion image shows subsurface Au-rich inclusions, mass spectrum
Arsenopyrite	C6	0.40	
Arsenopyrite	C7	1.23	
Arsenopyrite	GR9R	27.64	Small grain in pyrite C9
Arsenopyrite	GR8R	2.97	Small grain in pyrite C8
Arsenopyrite	C10	84.25	Small grain in calcite (new grain)
Arsenopyrite	C10R	80.22	Small grain in calcite repeat
Pyrite	C3	275.30	Subsurface Au-rich inclusions/zone?
Pyrite	C4	<0.23	
Pyrite	C8	<0.33	
Pyrite	C8R	<0.23	
Pyrite	C9	1.75	Mass spectrum
Pyrite	C9R	0.37	
Pyrite	PY-C9	0.53	Avoiding small arsenopyrite inclusions
Pyrite	PY-C8	0.03	Avoiding small arsenopyrite inclusions
Veduga 148			
Arsenopyrite	B1	63.98	Mass spectrum
Arsenopyrite	B4	192.79	Mass spectrum
Arsenopyrite	B5	1141.60	
Arsenopyrite	B6	433.97	Mass spectrum
Arsenopyrite	B7	273.84	
Arsenopyrite	B8	414.42	
Arsenopyrite	B9	76.21	
Arsenopyrite	B10	198.41	
Arsenopyrite	B12	233.05	
Arsenopyrite	B13	99.45	
Arsenopyrite	B14	143.70	
Arsenopyrite	B15	404.92	Ion image shows inhomogeneous Au distribution
Nezhdaninskoye 233			
Arsenopyrite	E1	103.99	Ion image shows Au-free band along grain edge
Arsenopyrite	E2	137.85	As-poor zone in center by SEM
Arsenopyrite	E3	271.89	Ion image shows Au-free band along grain edge
Arsenopyrite	E4	125.16	
Arsenopyrite	E5	176.77	
Arsenopyrite	E6	134.12	
Arsenopyrite	E7	189.45	
Arsenopyrite	E8	99.40	
Arsenopyrite	E9	94.94	
Arsenopyrite	E10	68.79	

TABLE 1. (Cont.)

Sample and mineral	Analysis number	Au (ppmw)	Comments
Nezhdaninskoye 11			
Arsenopyrite	A1	22.26	
Arsenopyrite	A2	361.06	
Arsenopyrite	A3	46.49	Ion image Au-free band at grain edge which is As poor by SEM
Arsenopyrite	A4	5.59	
Arsenopyrite	A5	267.55	
Arsenopyrite	A6	1.17	
Arsenopyrite	A7	249.97	
Arsenopyrite	A8	386.64	
Arsenopyrite	A9	13.72	As/S zoning observed with SEM
Arsenopyrite	A10	147.06	
Arsenopyrite	A11	43.39	
Arsenopyrite	A12	3.87	
Pyrite	APY1	3.69	Mass spectrum
Pyrite	APY1R	<0.23	
Pyrite	APY2	6.42	Mass spectrum
Pyrite	APY2R	12.97	
Pyrite	APY3	<0.33	Depth profile shows subsurface Au micro-inclusions
Pyrite	APY3R	<0.23	Mass spectrum
Pyrite	APY4	3.25	
Pyrite	APY4R	0.36	Mass spectrum
Pyrite	APY5	2.59	
Pyrite	APY5R	<0.23	Mass spectrum
Pyrite	APY6	<0.33	
Pyrite	APY6R	0.93	Mass spectrum
Pyrite	APY7	0.69	Depth profile shows Au micro-inclusion
Pyrite	APY8	2.62	
Sentachan 230			
Arsenopyrite	S1	139.8	Block shaped
Arsenopyrite	S2	102.0	Prismatic
Arsenopyrite	S3	192.9	Block shaped
Arsenopyrite	S4	314.6	Block shaped, ion imaged
Arsenopyrite	S5	100.0	Block shaped
Arsenopyrite	S6	102.5	Block shaped
Arsenopyrite	S7	368.4	Block shaped
Arsenopyrite	S8	84.4	Block shaped
Arsenopyrite	S9	424.2	Block shaped
Arsenopyrite	S10	97.7	Block shaped
Arsenopyrite	S11	327.6	Rhombohedral
Arsenopyrite	S12	26.7	Block shaped

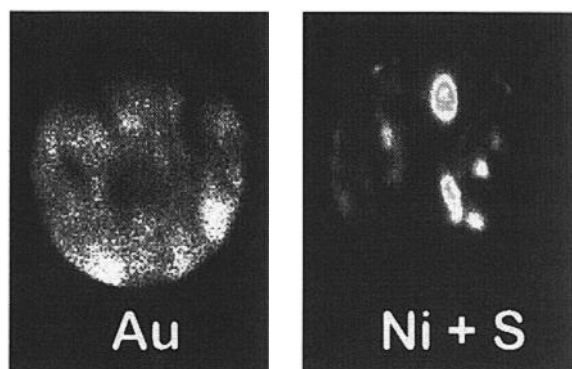


FIG. 10. Ion images of arsenopyrite from sample O-4/2 showing a relatively nonhomogeneous distribution of the gold mass 196.9722 and of Ni + S (94.0706). Diameter of image field is 62.5 μm .

arsenopyrite from sample O-4 were also examined by direct ion imaging. The gold and nickel distributions were found to be inhomogeneous and do not correlate with each other (Fig. 10). No correlation with arsenic could be discerned due to the high arsenic counts from the sample.

Similar-sized arsenopyrite grains from the first subset for sample O-5 were also reanalyzed. Repeat analyses of grain C2, done on different days, gave reproducible results: 0.61 and 0.63 ppm Au. However, grain C1 contained a relatively high Au content (25.69 ppm); when reanalyzed on another day and on another part of the grain, a much lower Au concentration (0.67 ppm Au) was determined, consistent with that of grain C2. Grain C5, which also gave a high value (75.44 ppm Au) was reexamined by imaging and was found to contain "hot spots" that are interpreted as being due to subsurface Au inclusions (Fig. 11) which could account for the initial high value. These data suggest that the two high values are anomalous because of the presence of subsurface

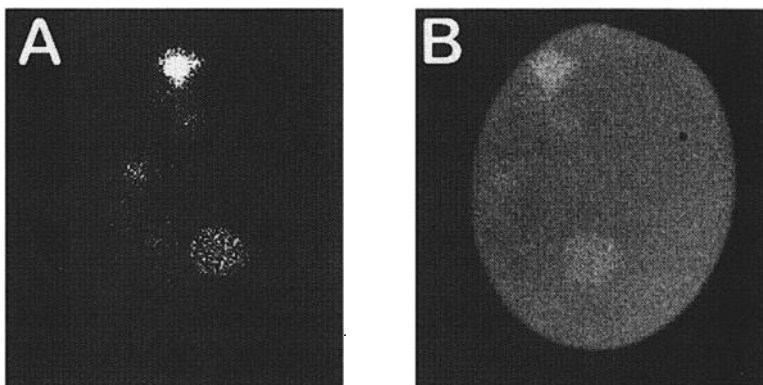


FIG. 11. Ion images of arsenopyrite grain C5 to illustrate (A) localized concentrations of gold, and (B) overlay of the gold mass 196.9765 onto a matrix iron sulfide mass of 177.8748. Olympiada deposit, sample O-5. Diameter of image field is 62.5 μm . Reproduced from Cabri and McMahon (1996, fig. 6, with permission from the Minerals, Metals, and Materials Society).

inclusions of native gold. However, small arsenopyrite grains included in pyrite gave higher gold values (2.97–84.25 ppm) than the larger arsenopyrite crystals (0.40–1.23 ppm). A few pyrite grains were also examined from this sample; they had Au concentrations ranging from less than the minimum detection level (0.069–0.33 ppm) up to 1.75 ppm Au, excluding a single very high value ascribed to subsurface gold inclusions (Table 1). Repeat analyses (done on different days) of two grains gave very similar values, except for one: C8, <0.33, <0.23, <0.069 and C9, 1.75, 0.37, 0.53 ppm Au. In any case, it is difficult to assign a value for the gold content of the pyrite grains because they also contain tiny inclusions of arsenopyrite which were found to be very much richer in gold. Therefore, prior to analysis of a much larger number of grains from the concentrates analyzed by Mössbauer spectroscopy, we concluded that arsenopyrite in sample O-4 had a very low content (less than about 0.57 ppm) and that arsenopyrite in sample O-5 had a somewhat higher gold content (up to 84.25 ppm, and an average of about 13.2 ppm Au), with evidence of the presence of some submicroscopic inclusions of native gold in both arsenopyrite and pyrite.

Veduga: Twelve arsenopyrite grains were analyzed from

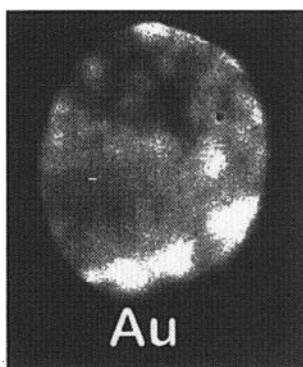


FIG. 12. Ion images of arsenopyrite from Veduga, sample 148, grain B15, showing a nonhomogeneous distribution of the gold mass 197.0067 which is concentrated along the edge of the grain. Diameter of image field is 62.5 μm ; the straight border at 5:30 denotes the edge of the grain.

sample 148. The average concentration was 305.6 ppm Au with a range from 63.98 to 1,141.60 ppm Au (Table 1). Reexamination of grain B15 by imaging the gold ions showed an

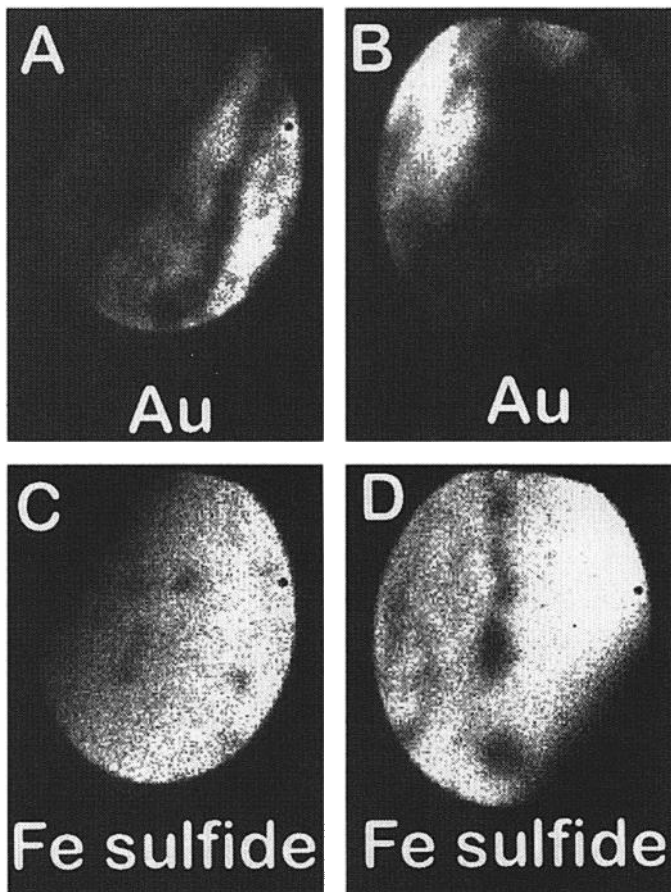


FIG. 13. Ion microprobe images of the two opposite edges of an arsenopyrite grain (E3) from Nezhdaninskoye, sample 233, which show depletion of gold mass 196.9675 along the edge in the top left side (A) and in the opposite edge of the grain on the bottom right side (B). Diameter of image field is 62.5 μm .

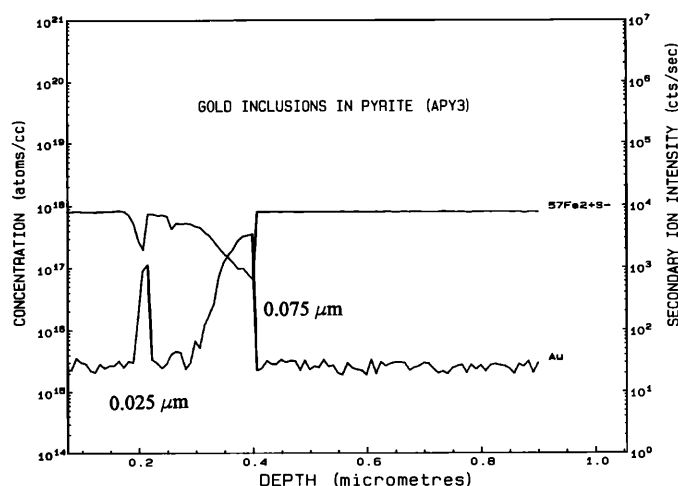


FIG. 14. SIMS depth profile of a pyrite grain from the Nezhdaninskoye deposit which illustrates the presence of and effects on the depth profile of two very small inclusions of gold (0.025 and 0.075 μm in diameter).

inhomogeneous gold distribution within the 62.5- μm -diameter analysis area (Fig. 12).

Nezhdaninskoye: Two samples were analyzed from this deposit and gave similar average gold concentrations in arsenopyrite: 140.24 ppm Au for 10 grains from sample 233 and 129.06 ppm Au for 12 grains from sample 11 (Table 1). Sample 233 has a narrower range for the gold concentrations, from 68.79 to 386.64 ppm, whereas sample 11 has a wider range, from 1.17 to 386.64 ppm Au. Imaging two grains from sample 233 and one from sample 11 showed that, for the grains examined, there is a gold-free zone along their edges (Fig. 13). Later examination by SEM of grain A3 (sample 11) showed that there is a coincidental As-poor band along the grain edge. SEM examination of an arsenopyrite grain from sample 233 showed, in contrast, a well-defined As-poor zone in the central portion of the grain. Eight grains of pyrite from sample 11 were also analyzed, of which six were analyzed twice (Table 1). It was found that pyrite had a range of concentrations from less than the minimum detection level (0.23–0.33) to 12.47 ppm Au. An average value for pyrite, calculated including those values less than the minimum detection level, equals 2.45 ppm Au. The depth profile of one grain (A3) clearly showed evidence of the presence of very small subsurface inclusions of native gold which range in diameter from about 0.025 to 0.075 μm (Fig. 14).

Sentachan: Twelve arsenopyrite grains were analyzed from sample 230; they had an average content of 190.05 ppm Au and a range from 26.7 to 368.4 ppm Au. Direct ion imaging was done on four areas of a large rhombohedral-shaped arsenopyrite grain containing a microvein of stibnite. Images of the following masses were selected to study the distribution of gold: $^{54}\text{Fe} + ^{32}\text{S}$ and ^{75}As (for background), $^{123}\text{Sb} + ^{32}\text{S}_2$, $^{121}\text{Sb} + ^{32}\text{S}_2$, and $^{60}\text{Ni} + ^{34}\text{S}$. It was not possible to resolve zoning for arsenic because the signal was too intense. As shown in Figure 15, the distribution of gold appears to be relatively inhomogeneous and correlates approximately with that of nickel. On the other hand, the distribution of antimony does not correlate with either gold or nickel.

^{197}Au Mössbauer spectroscopy

The results of the ^{197}Au Mössbauer experiments are compiled in Table 2. The spectra are shown in Figures 16 to 18. The samples from the Veduga, Nezhdaninskoye, and Sentachan deposits (Figs. 16 and 17) mainly contain chemically bound gold. The isomer shifts of the chemically bound gold in these ores all lie within the expected range of +3 to +4 mm/s expected for gold in arsenopyrite. The spectra of the Veduga samples exhibit minor metallic components representing between about 6 and 17 percent of the total gold. Even when the substantial statistical errors are taken into account, the metallic component in the Veduga ores appears to have a more negative isomer shift than pure metallic gold (Table 2). No convincing explanation can presently be given for this observation, although one may suspect that nano-sized particles of metallic gold in sulfide matrices may yield such extreme isomer shifts.

The four samples from the Olympiada deposit exhibit more varied ^{197}Au Mössbauer spectra (Fig. 18). Within the limits of error, sample Olympiada 204 contains only metallic gold with a mean isomer shift (Table 2) corresponding to gold with a silver content of 6 ± 4 at. percent. The spectrum of the Olympiada 116 concentrate is very similar, with a metallic

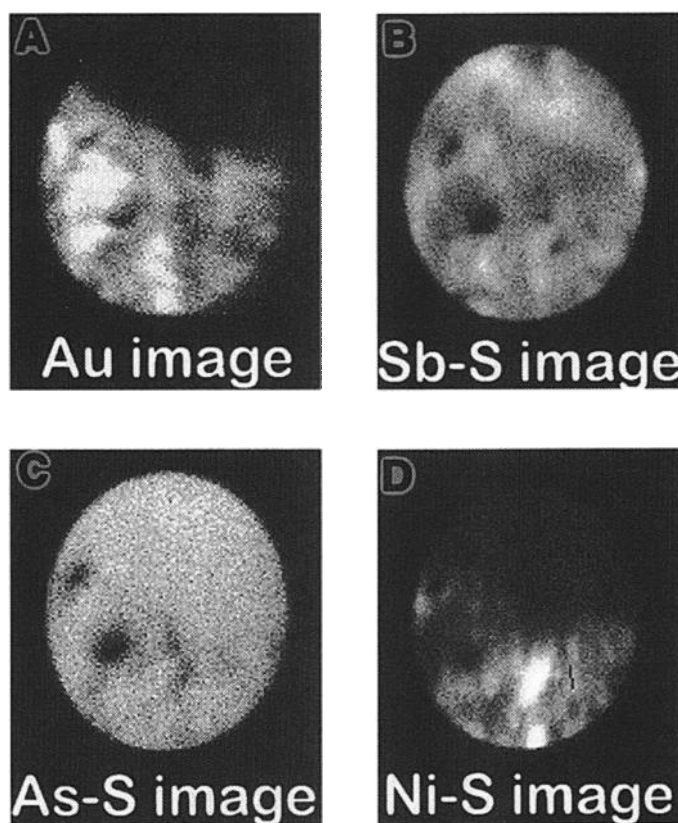


FIG. 15. Another area of the same grain shown in Figure 9 which illustrates the distribution of several masses. The ion microprobe images were taken sequentially in the order presented, which may distort comparisons for estimates of correlation. However, it can be seen that there is an area of arsenopyrite which is relatively gold and nickel free (A and D, respectively) but which appears to contain an increased concentration of antimony sulfide (B) and arsenic sulfide (C). A. Gold mass 196.9923. B. Antimony sulfide mass 184.9239. C. Arsenic sulfide mass 138.9081. D. Nickel sulfide mass 94.0706.

TABLE 2. Mean Isomer Shifts (mm/s) and Relative Amounts (%) of Chemically Bound and Metallic Gold

Deposit	Sample no.	Isomer shifts		Relative %	
		Chemically bound gold	Metallic gold	Chemically bound gold	Metallic gold
Olympiada	O-4	2.39 ± 0.08	-1.14 ± 0.07	45 ± 2	55 ± 2
Olympiada	O-5	2.00 ± 0.64	-1.30 ± 0.10	21 ± 9	79 ± 9
Olympiada	204		-1.12 ± 0.09	<3	>97
Olympiada	116	3.44 ± 0.68	-0.95 ± 0.13	5 ± 3	95 ± 3
Veduga	148	3.01 ± 0.06	-1.83 ± 0.20	83 ± 4	17 ± 4
Veduga	152	3.30 ± 0.02	-1.51 ± 0.14	94 ± 1	6 ± 1
Veduga	140	3.27 ± 0.06	-1.54 ± 0.30	93 ± 3	7 ± 3
Nezhdaninskoye	233	3.58 ± 0.06		>95	<5
Nezhdaninskoye	11	3.54 ± 0.04		>95	<5
Sentachan	230	3.54 ± 0.09		>95	<5

The relative amounts of chemically bound and metallic gold were calculated from the line intensities in the ^{197}Au Mössbauer spectra with $f(\text{Au comb.})/f(\text{Au metallic}) = 1.45$ (Friedl et al., 1992) for the ratio of the Lamb-Mössbauer factors of chemically bound and metallic gold; chemically bound gold is in arsenopyrite for all samples except for O-4, where it is in austrobitite, and in O-5 where its nature remains unclear; in these two cases, the relative amounts of chemically bound and metallic gold were calculated with $f(\text{AuSb}_2)/f(\text{Au metallic}) = 0.8$ (Erickson et al., 1971; Thomson et al., 1974)

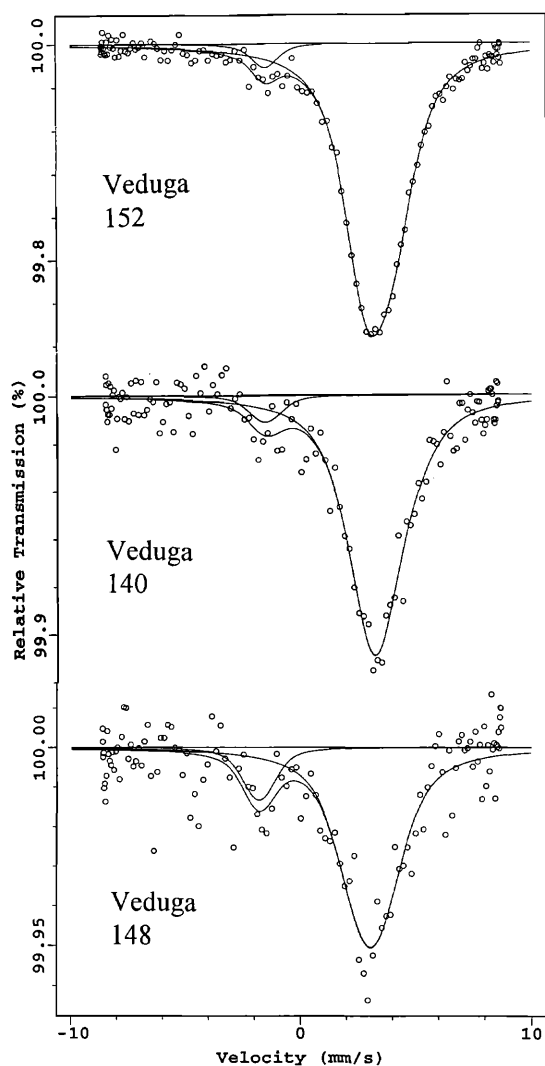


FIG. 16. ^{197}Au Mössbauer spectra of arsenopyrite concentrates from the Veduga deposit showing the presence of chemically bound gold in arsenopyrite and a minor amount of metallic gold.

component corresponding to gold with a silver content of 17 ± 6 at. percent. The spectrum of O-4 consists of two well-defined lines with nearly equal intensities. The isomer shift of one of these is -1.20 ± 0.07 mm/s, which suggests that this line represents virtually pure metallic gold. The line at $+2.39 \pm 0.08$ mm/s has an isomer shift that does not fall in the range of $+3$ to $+4$ mm/s expected for chemically bound gold in arsenopyrite. There are two known gold minerals that give rise to single-line Mössbauer patterns with isomer shifts near 2.3 mm/s, namely austrobitite, with a shift of $+2.33 \pm 0.02$ mm/s (Friedl et al., 1992), and the rare mineral criddleite, $\text{TlAg}_2\text{Au}_3\text{Sb}_{10}\text{S}_{10}$ (Harris et al., 1988), with an isomer shift of $+2.36 \pm 0.01$ mm/s (Friedl et al., 1992). Because the presence of austrobitite was subsequently confirmed in polished sections made from the same arsenopyrite concentrate previously analyzed by ^{197}Au Mössbauer spectroscopy, we can confidently assign the component at $+2.39 \pm 0.08$ mm/s to austrobitite. The ratio of the Lamb-Mössbauer factors of austrobitite and metallic gold, $f(\text{AuSb}_2)/f(\text{Au metallic})$ is about 0.8 (Erickson et al., 1971; Thomson et al., 1974). The relative amounts of metallic gold and the chemically bound gold in austrobitite for sample O-4 (Table 2) were calculated with this value. Further discussion of the results for this sample and sample O-5 is given below.

Additional study of samples O-4 and O-5

The low gold contents for arsenopyrite obtained by SIMS for these two samples initially were of concern because it was thought that samples containing no visible gold minerals, together with such low gold contents, would not produce a ^{197}Au Mössbauer spectrum at all, yet spectra were observed with an intensity suggesting an overall gold content on the order of 100 ppm or more. In addition, the wide range in gold concentration for a limited number of SIMS analyses for sample O-5 suggested a lognormal distribution or the presence of more than one population. Sufficient material remained for additional SIMS analyses of arsenopyrite grains from both samples and for an assay of sample O-5.

A representative split of sample O-5 was analyzed by conventional fire assay at CANMET (J. Cloutier, analyst) and was found to have 92.11 and 95.68 ppm Au, much higher

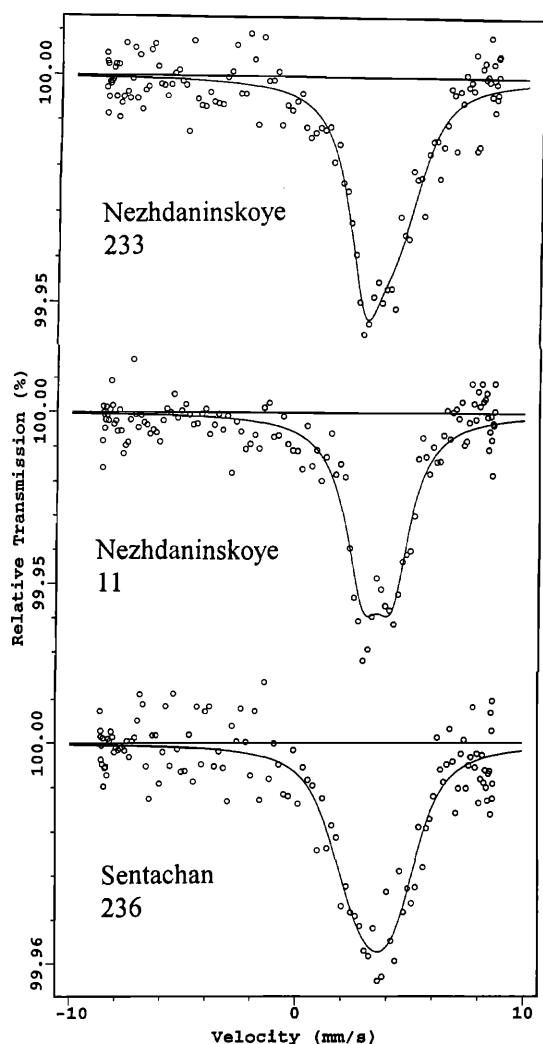


FIG. 17. ^{197}Au Mössbauer spectra of arsenopyrite concentrates from the Nezhdaninskoye and Sentachan deposits showing the presence of chemically bound gold in arsenopyrite.

than expected because arsenopyrite grains contained only from 0.40 to 84.25 ppm Au in the first subset SIMS analyses. In addition, the high values were only found in small arsenopyrite grains included in pyrite; other high values were thought to be due to subsurface gold inclusions. SIMS analyses of an additional 30 randomly selected arsenopyrite grains combined with the nine previous analyses give a new average value of 77.1 ppm Au (116–434.6 ppm), in much better agreement with the bulk assays. Analysis of this many grains from the high concentration end of the lognormal distribution gives a better reflection of the bulk assay. The Mössbauer data for this sample indicate that about 79 percent of the total is metallic gold and 21 percent is chemically bound, with an isomer shift of about 2.0 mm/s (Table 2). Because no gold or gold minerals were found by ore microscopy and because there is SIMS evidence of subsurface submicroscopic gold particles, we conclude that subsurface submicroscopic gold represents the bulk of the gold in this sample. In this context, it is important to note that gold particles as small as

2 nm yield Mössbauer spectra that are practically identical to those of native gold (Santucci et al., 1996; Stievano et al., 1998). However, the nature of the weak and ill-defined shoulder on the positive velocity side of the peak of metallic gold remains unclear. It has too small an isomer shift to represent gold chemically bound in arsenopyrite, for which isomer shifts between +3 and +4 mm/s are expected. Since there is no mineralogical evidence for aurostibite in sample O-5, it appears improbable that this ill-defined shoulder rep-

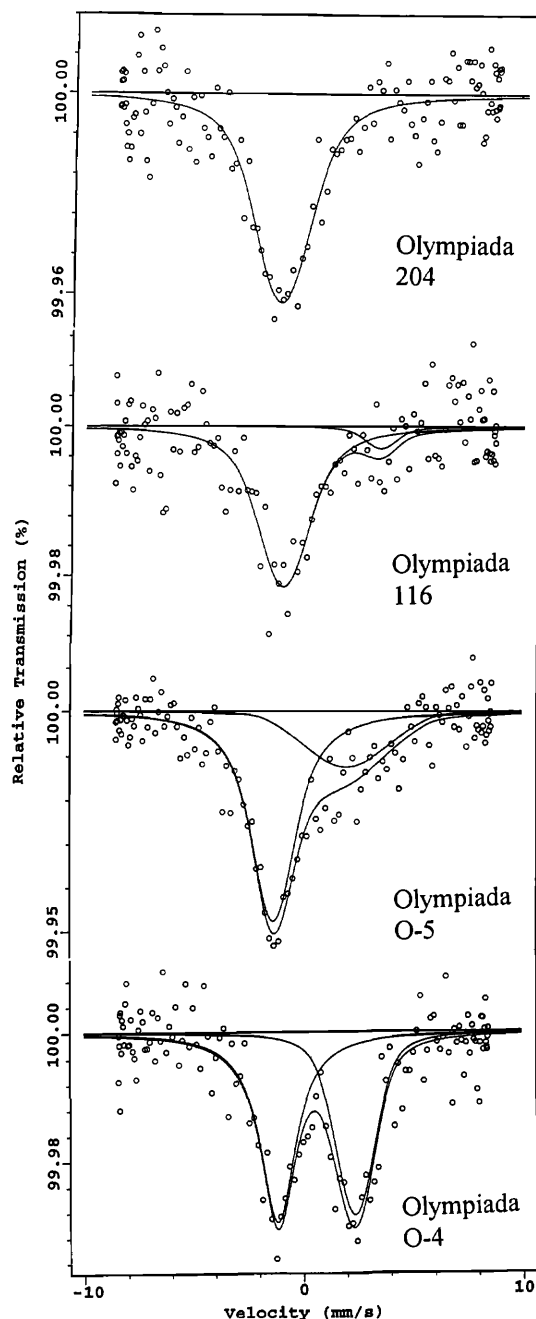


FIG. 18. ^{197}Au Mössbauer spectra of arsenopyrite concentrates from the Olympiada deposit showing the presence of metallic and chemically bound gold. The chemically bound gold occurs in aurostibite in sample O-4.

resents this mineral, although the isomer shift of the shoulder is compatible with aurostibite.

A ^{197}Au Mössbauer spectrum of sample O-4 was interpreted to contain about 45 percent chemically bound gold in the form of aurostibite and 55 percent metallic gold (Table 2). In this case, aurostibite and gold grains were observed by optical microscopy giving substance to the interpretation. Though there was insufficient material left for a bulk chemical assay, an additional 65 grains of arsenopyrite were analyzed by SIMS in order to obtain a better understanding of its gold content. The average of SIMS analyses of both subsets is 52.5 ppm Au, with a wide range from 69 ppb to 2,298 ppm. This again demonstrates the need to analyze a significant number of grains to obtain a realistic average value. There is no evidence of chemically bound gold in arsenopyrite by ^{197}Au Mössbauer spectroscopy. However, the proximity of the relatively strong line of aurostibite may make it difficult to detect a weaker component for chemically bound gold in arsenopyrite (+3 to +4 mm/s).

Discussion

Comparison of results using different techniques

The results obtained in this investigation can, in most cases, be compared and understood in terms of the characteristics and limitations of each analytical method employed, as well as in terms of the ore mineralogical studies. It was shown, by using two different bulk analytical methods (INNA and ^{197}Au Mössbauer spectroscopy), that invisible gold in most cases is concentrated in arsenopyrite. Likewise, invisible gold concentrations in arsenopyrite were measured by EPMA and SIMS, and in pyrite by SIMS. In general terms, the gold content found by INNA, EPMA, and SIMS is comparable and fits within the ranges for the different samples. The INNA data show no correlation between grain shapes and gold concentration, but they do show a correlation between the highest Au, Co, and Sb contents and the smallest arsenopyrite grains in samples O-4 and O-5. The heterogeneous gold distribution and the different volumes and areas analyzed by EPMA ($\sim 5\ \mu\text{m}^3$ and $1\ \mu\text{m}^2$) and by SIMS ($1,500\text{--}3,000\ \mu\text{m}^3$ and $62.5\text{-}\mu\text{m}$ -diam circle) make direct comparisons of the results obtained by the two different microbeam techniques very difficult, even when done on the same grains (Cabri et al., 1991). This study also shows how difficult it can be to characterize the nature of invisible gold in sulfide minerals, even when using a multidisciplinary approach. However, a combination of SIMS analyses (to locate subsurface inclusions of gold and to determine gold in solid solution) together with ^{197}Au Mössbauer spectroscopy (to determine the chemically bound gold and particulate gold) may be considered a useful approach to characterize the gold distribution. Other techniques such as X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) could shed light on the valency of invisible gold and the details of the crystal structure, respectively. However, all such studies must be done on samples well-characterized by traditional mineralogical techniques.

Siting of gold within arsenopyrite

Interpretation of ^{197}Au Mössbauer spectra indicates that metallic gold in arsenopyrite concentrates from the Olympi-

ada deposit prevails and represents about 55 to 95 percent of the total gold concentration. This is partly supported by ore microscopy (of sample O-4 only) and by SIMS images which showed the presence of small discrete areas of gold concentrated in Olympiada arsenopyrite (interpreted as subsurface gold particles). However, as discussed above, ^{197}Au Mössbauer spectra of gold particles as small as 2 nm are similar to those of native visible gold. Metallic gold in arsenopyrite concentrates ranges up to about 17 percent in samples from the Veduga deposit. The electron microprobe images were unable to reveal particulate gold in the areas enriched in this metal. SIMS depth profiling of pyrite from the Nezhdaninskoye deposit also showed evidence of possible particulate gold ($0.025\text{--}0.075\ \mu\text{m}$ in diameter) and the interpretation of ^{197}Au Mössbauer spectra of an arsenopyrite concentrate indicates that metallic gold represents <5 percent of the samples.

The gold content of arsenopyrite in the deposits studied lies within the range previously found in most arsenopyrite samples (Cabri, 1992). Invisible gold exceeding 10,000 ppm (1.0 wt %) has been reported for arsenopyrite in three deposits: 1.52 wt percent in the Villeranges deposit, France (Boiron, 1987; Johan et al., 1989), with similar values in the Congress mine, Canada (Cook and Chrysosoulis, 1990), and 1.15 wt percent in the Le Châtelet deposit, France (Johan et al., 1989). Wu et al. (1990) were successful in the synthesis of arsenopyrite containing 1.7 wt percent Au, which may be considered as close to the maximum concentration of gold that can be incorporated in the crystal structure of arsenopyrite.

The substitutional mechanism of gold in arsenopyrite is not yet well understood and many mechanisms have been proposed. Boyle (1979) suggested that Au may occupy the As sites in the arsenopyrite structure. This assumption is based on the similar radii of these elements when bonded covalently. For example, the covalent radius of Au in aurostibite is 1.40 Å and that of As in arsenopyrite is 1.39 Å. Based on the crystal structure of arsenopyrite and EPMA of gold-bearing arsenopyrite from Le Châtelet and Villeranges, Johan et al. (1989) suggested that the substitution mechanism $2\text{As}[\text{Fe}] \rightleftharpoons (\text{Au}, \text{Sb}) + \text{Fe}$ took place. They considered the possibility of mixed populations of As and S sites in the arsenopyrite structure determined by Buerger (1936) and a systematic deficiency in the Fe content in both synthetic and natural arsenopyrite as evidence of this substitution scheme. They pointed out that the existence of Fe^{3+} in the nonpolar state of the arsenopyrite crystal structure could imply the presence of Au^{3+} in this mineral. The coupled substitution of Au for Fe and As for S or one Au and one As for two Fe has been proposed for gold-bearing arsenian pyrite (Arehart et al., 1993). X-ray photoelectron spectroscopic measurements are interpreted to show that gold enters the arsenopyrite structure as Au^{3+} rather than as a neutral (Au^0) metal (quoted in Arehart et al., 1993). On the other hand, Cardile et al. (1993) found that gold absorbed on As_2S_3 and Sb_2S_3 colloidal substrates has ^{197}Au Mössbauer spectra similar in appearance to those of Au_2S with isomer shifts and quadrupole splittings characteristic of Au^{1+} , coordinated to two S electron donors in an approximately linear geometry. Li et al. (1994) proposed a negative valence state of gold in arseno-

pyrite and pyrite, as it substitutes for sulfur atoms or is chemically bound with sulfur by the covalent bond. Cook and Chrysosoulis (1990) supported the suggestion of double substitution of Au for excess As that enters Fe positions. Their conclusions were derived from the crystal structures of disulfide minerals. Iron atoms in arsenopyrite as well as in pyrite and löllingite are octahedrally coordinated by anion pairs (Wood and Strens, 1979). An As atom in the arsenopyrite structure is bonded to one S atom and to three Fe atoms. If a quasimolecular $[\text{AsS}]^{3-}$ configuration in arsenopyrite occurs, that infers that iron is present as Fe^{3+} ions. Thus, the arsenopyrite structure may be considered to have $[\text{Fe}]^{3+}$, $[\text{AsS}]^{3-}$, and Au^{3+} ions that may substitute for Fe^{3+} . Au^{3+} substituting for Fe^{3+} on octahedrally coordinated iron sites in arsenopyrite would also explain the small or even vanishing electric quadrupole splittings observed in the Mössbauer spectra. Fleet and Mumin (1997) point out that invisible gold is incorporated in sulfides with anomalous As contents and depleted in Fe. They suggest that very small clusters of Au atoms could be attracted to sulfide surfaces due to a surface charge and also proposed that the arsenopyrite formula may be expressed as $(\text{Fe}, \text{As}, \square)(\text{As}, \text{Sb})_{1 \pm x} \text{S}_{1 \pm x}$. The ^{197}Au Mössbauer results, however, contradict the cluster hypothesis since clusters as small as 2 nm already show metallic isomer shifts whereas chemically bound gold in arsenopyrite usually exhibits isomer shifts of 3 to 4 mm/s. On the other hand, some arsenopyrites exhibit a metallic gold rim that might be derived from small gold clusters.

SIMS direct ion imaging of three arsenopyrite grains from the Nezhdaninskoye deposit shows Au-poor rims (e.g., Fig. 13). However, SEM study showed contrasting behavior of As zoning with respect to the Au concentration: in sample 11 As deficiency correlates with Au deficiency, whereas in sample 233, the As-rich zone correlates with the Au-poor rim. More recently, Tarnocai et al. (1997) show by EPMA of arsenopyrite from the Campbell mine (Ontario) that $(\text{As} + \text{S})_{\text{atomic}}$ is relatively constant at ≈ 66 at. percent and that the $(\text{As}/\text{S})_{\text{atomic}}$ ratio shows an increase in Au-rich rims, as observed by direct ion SIMS images. They conclude that both data indicate that relative depletion in Fe occurs with Au enrichment, supporting the interpretation that Au substitutes for Fe rather than As.

Other than a relationship of gold with nonstoichiometric arsenopyrite, EPMA did not shed further light on possible correlations. EPMA also enabled us to determine that Fe is partly substituted for by Co in arsenopyrite, within the accuracy of the analyses. This is consistent with the assumption that the Fe sites are fully occupied in the arsenopyrite crystal structure.

It is difficult to deduce the manner in which invisible gold is bonded to its neighbors, or even what these neighbors are, on the basis of the Mössbauer spectrum. It is clear, however, that the invisible gold cannot be bonded in either the linear two-fold coordination typical for the monovalent, or the planar fourfold coordination typical for the trivalent valence state, because in both cases a large quadrupole splitting would be expected (Bartunik et al., 1970; Parish, 1982). The most appealing interpretation is that the gold replaces iron in both arsenopyrite and pyrite. In stoichiometric arsenopyrite, it would then be surrounded by a distorted octahedron of three As and three S atoms as nearest neighbors, but the actual

number and arrangement of neighbors may vary due to deviations from stoichiometry that are common in arsenopyrite (Bortnikov, 1993) and possibly lead to disorder in the host lattice. Gold-bearing pyrites are usually found to contain some arsenic, which is concentrated in the gold-rich zones of the crystals (Marion et al., 1991; Fleet et al., 1993). Therefore the siting of gold in pyrite may not be very different from that in arsenopyrite, except that a wider variation in the numbers of S and As neighbors appears possible, which would result in a wider range of isomer shifts (Friedl, 1993; Friedl et al., 1995). The absence of a substantial quadrupole splitting of the Mössbauer line of chemically bound invisible gold in arsenopyrite and pyrite is to be expected if the gold occupies Fe sites, which have a rather symmetrical environment of six nearest As and S neighbors. If the gold replaces As in the $[\text{AsS}]^{3-}$ molecular units, the absence of a substantial quadrupole splitting is difficult to understand. Moreover, the magnitude of the isomer shift of Au in arsenopyrite appears to confirm the replacement of iron (Friedl et al., 1995).

Variability in gold content of arsenopyrite within deposits

This study has indicated a considerable variability in the gold distribution in arsenopyrite on different levels. The gold concentration of arsenopyrite varies considerably within individual grains, from grain to grain, on a centimeter scale, and within a single deposit. The largest range, from the minimum detection level to 4,700 ppm Au, for an individual grain was determined by EPMA for arsenopyrite from the Olympiada deposit. The gold distribution in individual arsenopyrite grains is more uniform in the Nezhdaninskoye and Sentachan deposits. In some grains of arsenopyrite, gold is distributed as mosaiclike domains and in others gold concentration or impoverishment occurs in marginal zones. Although considerable variation was found for the gold concentrations in arsenopyrite from three deposits (Olympiada, Veduga, and Nezhdaninskoye), arsenopyrite with very little gold detected by SIMS (at the ppb level) was only found in the Olympiada deposit. Though the data obtained are considered to be limited, it is possible to assign a different gold distribution for different generations of gold. For example, it appears that the earliest arsenopyrite I from the Nezhdaninskoye deposit is richer in gold than the coarser grained arsenopyrite II from the auriferous veins and the fine-grained arsenopyrite III from the sulfide-sulfosalt veinlets which contain from 1.5 to 48 ppm (nine SIMS analyses, $\text{avg} = 12.4 \pm 9.4$ ppm) and from 10.5 to 35 ppm (10 SIMS analyses, $\text{avg} = 22.4 \pm 5.8$ ppm), respectively (Bortnikov et al., 1993).

We still do not possess sufficient knowledge to evaluate quantitatively the factors controlling the gold concentration in arsenopyrite. No experimental study was done to determine the distribution coefficient of gold between fluid and arsenopyrite. The deviation of the distribution coefficient from unity will change the ratio of Au and Fe in the fluid as arsenopyrite crystallization proceeds. The grains will tend to display a zonation of Au concentration from core to exterior. Such a phenomenon has been observed for grains from the Olympiada and Sentachan deposits. If the fluid flows through a hydrothermal system, grains with different compositions will precipitate if the ratio of Au and Fe activities changes from an initial value. The irregular distribution patterns of

gold in arsenopyrite may have resulted from changes in physico-chemical parameters alone. There is evidence that gold-bearing arsenopyrite precipitated under fluctuating physico-chemical conditions. Substantial variations in the As/S ratio of this mineral are considered to be strong evidence of oscillating sulfur activity and temperature (Barton, 1970). Gradients in pH, redox-condition, and H_2S fugacity would be expected during an infiltration of ore fluid. Coprecipitation of gold with arsenopyrite may depend on a surface phenomena rather than on equilibrium between the fluid and the interior of a precipitating arsenopyrite crystal. The coordination number of cations located in the various surface sites increases as a crystal grows, changing the value of the distribution coefficients.

Timing and mechanisms of gold precipitation

The main feature of the deposits studied is that different modes of gold occur within the auriferous mineralized zones and veins. Gold occurs as a solid solution in sulfide minerals, mainly in arsenopyrite, and as native gold or electrum in all four deposits. Very small subsurface inclusions of native gold, ranging in diameter from about 0.025 to 0.075 μm , were also found in some arsenopyrite grains examined. Gold also occurs as aurostibite in some of the deposits. In addition to these modes, metallic gold occurs as submicroscopic particles in arsenopyrite grains from the Olympiada deposit in a manner not as yet completely understood. The existence of both chemically bound gold incorporated in sulfide minerals and native gold mineralization has been reported for many mesothermal deposits and may be regarded as the rule for gold deposits of this type, as pointed out by Oberthür et al. (1997).

Field and microscopic studies clearly indicate that invisible and native gold are spatially and temporally separated within orebodies as a rule, which may suggest influx of new solutions of different composition. Gold-bearing sulfide mineralization prevails at the Olympiada, Veduga, and Nezhdaninskoye deposits. Native gold in veins is important in the Nezhdaninskoye deposit and is predominant in the Sentachan deposits. It should be noted that the proportion of the two modes of gold mineralization also varies within individual deposits, similar to the situation found at the Ashanti gold mine (Ghana) by Mumin et al. (1994) and Oberthür et al. (1997). Gold-bearing arsenopyrite (as well as pyrite) formed contemporaneously with retrograde alteration halos controlled by shear zones and is paragenetically linked with crystallization of the metasomatic minerals quartz, sericite, and carbonates. Therefore, a principal mechanism responsible for the deposition of such wall rock-hosted gold from a fluid is through fluid-rock reactions. The formation of this style of mineralization has been shown here to precede deposition of native gold, which is rarely distributed within the alteration halos, occurring rather in veins and veinlets. Textural observations, such as overgrowths of native gold on arsenopyrite or filling of fractures in sulfides by native gold, clearly indicate its late deposition with respect to sulfides. However, it should be noted that the age relationships of gold-bearing arsenopyrite and submicroscopic subsurface particles of gold found by SIMS imaging and depth profiles in several grains is not yet fully understood.

Chemically bound gold must have coprecipitated with arse-

nopyrite because we find it difficult to see how gold can be introduced into earlier arsenopyrite and pyrite by interaction of a late gold-bearing solution. In support of this hypothesis is the refractory nature of arsenopyrite and pyrite (Barton, 1970) and the low rates of dissolution of these minerals and of diffusion of large cations. Precipitation of primary gold as a solid solution in sulfide and sulfarsenide minerals was also proposed by Mumin et al. (1994) for the Bogusu-Prestea deposits in Ghana. In addition, SEM and SIMS images show that the primary distribution patterns of chemically bound gold in arsenopyrite have been preserved and that the mineral has not been recrystallized. Native gold was usually observed as grains unrelated to arsenopyrite or else attached as overgrowths, consistent with the assumption that the early chemically bound gold is preserved in the sulfarsenide-sulfide minerals' structure during late mineralization processes. It may thus be concluded that the fluids which metasomatically transformed the host rocks were undersaturated with respect to gold. Calculations for typical mesothermal environments show that, at 400° to 300°C, pH of 4 to 6, salinity of 6 wt percent NaCl equiv, and 0.01 molal total dissolved sulfur at the pyrite-pyrrhotite boundary, the molal concentration in a fluid saturated with respect to gold does not exceed 0.1 to 100 ppb (Romberger, 1990). Gold concentrations ranging from 20 to 100 ppb have been directly measured in near-surface hot waters (Tilling et al., 1973; Weissberg et al., 1979). Therefore, in the case of mesothermal ores one might infer values two to three orders of magnitude lower than for those predicted from calculations done for fluids saturated with respect to gold.

Quartz veins or veinlets which carry mainly native gold mineralization are formed later than the alteration halos in most deposits because they crosscut all zones of alteration halos and fragments of altered rocks within the veins. The Nezhdaninskoye deposit, where simultaneous crystallization of late fine-grained gold-bearing arsenopyrite and electrum is inferred, may represent a possible exception (see Fig. 5D).

The late deposition of native gold in the deposits studied may be explained in several ways. A previously suggested model is that gold was released from the gold-bearing sulfides during postdepositional redistribution and concentration (Marcoux et al., 1989; Mumin et al., 1994) or by recrystallization via metamorphism (Arehart et al., 1993; Neumayr et al., 1993; Larocque et al., 1995 a,b). Late introduction of gold deposited from fluids of different composition has been argued by Cathelineau et al. (1991) and Boiron et al. (1992, 1996). Their conclusions were based on microstructural and fluid inclusion studies as well as textural investigations with the help of cathodoluminescence SEM images.

The common occurrence of native gold in fractures and veins in arsenopyrite may be considered as evidence for the introduction of the gold-bearing fluids in the late stages and the evolution of the chemistry of a fluid and the depositional physico-chemical parameters. These phenomena were well argued by Boiron et al. (1996). We believe that the fact that grains of native gold, as a rule, are confined to arsenopyrite surfaces or fractures in arsenopyrite can be explained by the important role of adsorption processes as a depositional mechanism. The sulfide-fluid interfaces have been shown to play an important role in concentrating heavy metals under

high temperatures and low oxygen fugacity (Jean and Bancroft, 1985, 1986; Hyland and Bancroft, 1989; Knipe et al., 1991, 1992). The adsorption of chloride complexes of Au^{3+} and Au^{1+} by pyrite, pyrrhotite, sphalerite, and galena and of thio gold $^{1+}$ complexes by amorphous As_2S_3 and Sb_2S_3 has been shown experimentally (Jean and Bancroft, 1985; Renders and Seward, 1989). Jean and Bancroft (1985) proposed a two-step gold depositional mechanism onto the sulfide surfaces involved in adsorption of gold complexes to surface sites followed by gold reduction. Möller and Kerstein (1994) suggested that electrochemical accumulation of gold on pyrite and arsenopyrite may play an important role in the deposition of this metal from solutions. Therefore, crystallization of native gold by metal adsorption on to sulfide surfaces from a fluid undersaturated with gold is inferred. This is in contrast to the data of Cardile et al. (1993) who demonstrated that significant Au^0 was absent on sulfide substrates but that the gold was present as Au^{1+} and that the bonding is in linear coordination to two S atoms. When the surface Au^{1+} eventually grows into chemically bound gold in the interior of arsenopyrite crystals, however, it transforms to Au^{3+} , and at least, changes its coordination, as is shown by the vanquished quadrupole splittings in the ^{197}Au Mössbauer spectra. The latter process best explains the incorporation of chemically bound gold during deposition of arsenopyrite and pyrite from hydrothermal solutions.

Field and textural observations (brecciation, overprinting relations, ribboned and laminated vein textures) clearly indicate that the orebodies were formed as result of multistage processes within active tectonic environments. This may give rise to the infiltration of fluids of different composition or it may enhance fluid evolution through commonly inferred processes such as fluid-rock interaction or phase separation.

Conclusions

1. There were two main stages of gold deposition: early chemically bound Au and submicroscopic gold in arsenopyrite and pyrite (possibly as small as 2 nm) associated with wall-rock alteration; and native gold in veins or as fracture fillings and overgrowths on auriferous arsenopyrite.

2. Gold occurs in arsenopyrite in the four deposits, both as chemically bound Au and as submicroscopic metallic particles. At Olympiada, it occurs mostly as microscopic and submicroscopic particles of metallic gold and aurostibite, usually either associated with or included in arsenopyrite.

3. Gold-bearing arsenopyrite is usually depleted in As with respect to its stoichiometric composition, but correlation of Au enrichment to Fe deficiency has not been found. It may be inferred from ^{197}Au Mössbauer spectroscopy that substitution of Fe^{3+} for Au^{3+} is most likely.

4. There is no evidence that late native gold originated from recrystallization of auriferous sulfides. Late native gold represents a second stage of gold deposition, which attests to the evolution of the mineralizing fluid through time or to the involvement of more than one fluid. Evidence of two stages of gold precipitation is inferred from a pervasive fluid-rock interaction for disseminated Au-bearing sulfides within the alteration halos and absorption of gold complexes onto the sulfide surfaces for late native gold, resulting in overgrowths of native gold.

5. Finally, this study has confirmed the refractory nature of the ore from four large Siberian gold deposits and that arsenopyrite is an important and common carrier of invisible gold.

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APPENDIX

Instrumental Neutron Activation Analysis (INAA)

The INAA technique, which is highly sensitive for detection of Au concentrations in small samples with weights down to $1\mu\text{g}$, was used to attempt to understand how gold is distributed among the different tiny arsenopyrite crystals (30–70 μm in size). The individual grains of arsenopyrite selected for analysis were weighed on a microanalytical balance and sealed in polyethylene film. For activation, the polyethylene packages were wrapped in filter paper and aluminum foil. The standard samples were prepared in the same manner. The samples were activated for 17 h in the IRT reactor at the Moscow Engineering Physical Institute with a neutron flux of $1 \times 10^{13} \text{ s cm}^{-2}$. The nuclide, the gamma line used for analysis (KeV), and cooling times after activation in the reactor (days) used for the determination of Au, Sb, and Co were ^{197}Au , 412, 8 to 10; ^{120}Sb , 564, 8 to 10; ^{124}Sb , 602 and 1691, 40 to 50; ^{60}Co , 1332, 40 to 50.

Electron Probe Microanalysis (EPMA)

The operating conditions for a Cameca SX-50 used at the Natural History Museum [London] were accelerating voltage 25 kV and beam current 100 nA (on the Faraday cup). These conditions represent a compromise between the high voltages and currents recommended by Robinson and Graham (1992) and the normal analytical conditions of 20 kV and 20 nA. Standards used were pure metals and arsenopyrite of known composition. The radiations measured were Fe $K\alpha$, S $K\alpha$, As $K\alpha$, Au $L\alpha$, Sb $L\alpha$, Co $K\alpha$. For a 100-s dwell time on peak and background, the calculated minimum detec-

tion levels for the trace elements are Au, 200 ppm; Sb, 100 ppm; Co, 150 ppm. Background levels were carefully placed to avoid slopes, overlapping peaks, and in the case of gold, a hole in the background between 31.5° and 31.6° on the LiF crystal used. This instrument was also used in the scanning mode to map areas defined by spot analyses as having gold concentrations higher than the detection limits of about 0.02 wt percent.

Secondary Ion Mass Spectrometry (SIMS)

Among the reasons which make the use of SIMS attractive to investigate problems in mineralogical and related sciences are minimum limits of detection of less than one part per million by weight (ppmw), depth-profiling capabilities permitting the detection of buried inclusions, the ability to determine isotope abundances, and the possibility of imaging the specimen with any desired secondary ion to produce maps of element distribution. MacRae (1995) has reviewed the application of SIMS in geology, and the large body of literature that exists in its application for the determination of trace concentrations of precious metals in various minerals was reviewed and discussed by Cabri and McMahon (1995). Unfortunately, the quantification of SIMS data can be hindered by several complicating factors. These include matrix effects, which refer to differences in sensitivity for a given element in samples of different compositions resulting from changes in ionization efficiency and sputtering yield, as well as variations in instrument parameters and ion collection

TABLE A1. Summary of SIMS Experimental Parameters

Primary ion beam and polarity	Cs ⁺
Secondary ion polarity	Negative
Matrix masses measured	⁵⁶ Fe, ⁵⁷ Fe ₂ + ³² S
Primary beam current	200–450 nA
Primary beam accelerating voltage	10 kV
Impact energy	14.5 kV
Field aperture diameter	750 μ m
Contrast diaphragm diameter	400 μ m
Raster	250 μ m
Image field	150 μ m
Diameter of analysis area	62 μ m
Implant standards	Arsenopyrite, pyrite
Implantation fluence, species	2.5×10^{13} ions ¹⁹⁷ Au/cm ²
Mass resolution	~2,000 m/ Δ m
Energy offset	None
Minimum detection limits: arsenopyrite	22–412 ppb Au
pyrite	69–331 ppb Au
Depth of analyzed profiles	0.3–2.0 μ m

efficiencies. In order to account for matrix effects, the use of relative sensitivity factors has been adopted for the quantification of SIMS data. The relative sensitivity factor is a multiplying factor used to convert the experimentally measured ion count rate to atom density and is unique to the sample matrix, operating conditions, and reference mass.

All work in the present study was performed using a Cameca IMS-4f double-focusing magnetic sector secondary ion mass spectrometer at the Canada Centre for Mineral and Energy Technology (Ottawa). The SIMS operating conditions are listed in Table A1, except for a dynamic transfer system that was used for the last analyses. All samples had been previously coated with a thin film of carbon to prevent charging. In order to alleviate the problem of mass interferences associated with the ¹⁹⁷Au mass, the mass spectrometer was operated under conditions of high mass resolution ($m/\Delta m \sim 2,000$), which allowed an adequate separation of the masses of interest from the undesired interferences caused by molecular secondary ions (CsS²⁻ at mass 196.850 amu and FeAsS²⁻ at mass 196.799 amu). The differences observed in the relative intensities of the molecular interferences (Fig. A1) are due mainly to variations in the As content of the two grains. However, the general triplet of peaks remains recognizable, enabling very rapid magnet calibrations for all depth profiles. Calibration proceeded for extremely low Au concentrations by noting the theoretical distance separating both interfering masses and ¹⁹⁷Au, and setting the magnet based on this separation with the peak of the strongest interference. For higher concentrations of Au, the peak is readily observable and the magnet can be calibrated on it directly. However, the actual value of the mass is based on a local calibration. For this step, performed during initial alignment procedures, a synthetic platinum-containing iron sulfide was used, and the magnet calibrated using the ¹⁹⁸Pt fingerprint mass spectra described by Cabri and McMahon (1995). Therefore, different calibration settings in this step will lead to different values for the experimentally observed peak for gold. By using the ¹⁹⁷Au interferences to advantage as a ¹⁹⁷Au mass spectra fingerprint, magnet calibrations for the depth profile are greatly simplified.

Depth profiles on implanted standards were then performed, following the procedure described by Cabri and McMahon (1995). The ¹⁹⁷Au mass and one or two other masses (e.g., ⁵⁶Fe, ⁵⁶Fe₂ + ³²S) were recorded in order to monitor the system stability and the integrity of the sample, as well as to provide a reference mass for relative sensitivity factor calculations. At the conclusion of the depth profile, the average count rate for matrix mass ⁵⁶Fe or ⁵⁶Fe₂ + ³²S over the entire depth profile was used for the relative sensitivity factor calculations. Usual procedures were to perform two consecu-

tive depth profiles on the implant standard, followed by one or two more at the end of the analyses of the minerals. This technique was followed rather than that of using previously derived calibration curves, because it is more sensitive to slight day-by-day changes in instrumental parameters and the primary and secondary beam alignments, as well as to more long-term changes in the sensitivity of the electron multiplier. Furthermore, a minimum detection level can be defined for every analysis day, which will be different owing again to slight changes in instrumental parameters as well as memory effects, whereby Au atoms sputtered on to instrument components from previously analyzed high gold-containing minerals or gold-coated specimens can raise the minimum detection limit. Following the depth profiles in the implant standard, the crater depths were measured using a Tencor Alpha-Step 200 profilometer several times in both directions across the crater. The relative sensitivity factor values were then determined using the SIMS Instrument Control System software, version 4.0, from Charles Evans and Associates. Depth profiles were then made on each mineral selected for analysis, using the same analytical procedures as for the implant standards. The counts for ¹⁹⁷Au and the reference matrix mass were obtained from each spectrum and used, together with the relative sensitivity factor value, to calculate the concentration of gold in ppm by weight (e.g., Larocque et al., 1995a).

Direct ion images of selected elemental and molecular ion species were acquired by operating the instrument in the ion microscope mode while retaining high mass resolution. In this technique, which is similar to optical microscopy in principle, a primary ion beam of large diameter illuminates the sample surface. Secondary ions are emitted from all points illuminated by the beam in a planar electrostatic field such that the lateral distribution of these secondary ions is retained through the double-focusing mass spectrometer system. Following energy and mass filtering, the resulting image is recorded on a resistive anode encoder, a pulse-counting, position-computing device capable of localizing ion signals in the image plane of the detector, as well as recording the ion intensity in this image. For the present study, acquisition times ranged from 60 to 200 s, de-

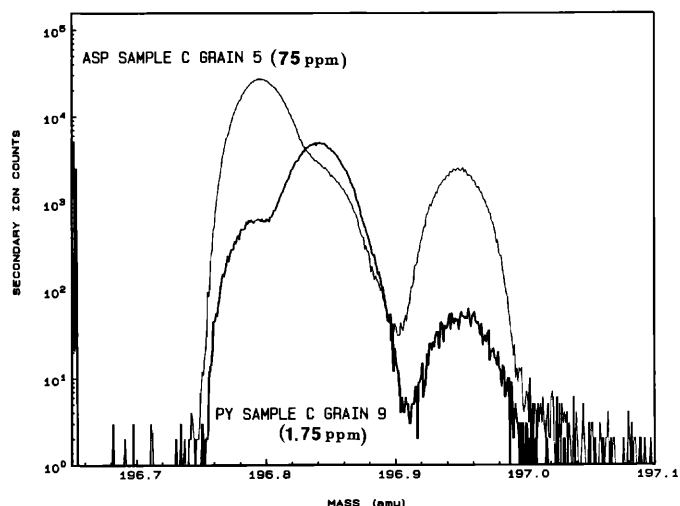


FIG. A1. An overlay of the mass spectrum of an arsenopyrite grain (C5, 75 ppm Au) and a pyrite grain (C9, 1.75 ppm Au) to illustrate the separation of interference masses from the gold peak at high mass resolution. Though similar, the interference peaks in arsenopyrite and pyrite are different in detail. Note also the superposition of the gold peaks, which is a measure of the stability of the 4f instrument. Both grains are from Olympiada deposit, sample O-5. Reproduced from Cabri and McMahon (1996, fig. 1, with permission from the Minerals, Metals, and Materials Society).

pending upon the concentration and sensitivity of the selected species.

¹⁹⁷Au Mössbauer Spectroscopy

The chemical state of gold atoms in arsenopyrite has been examined by ¹⁹⁷Au Mössbauer spectroscopy. During the last decades, Mössbauer spectroscopy (Gutlich et al., 1978) has become a valuable tool for identifying the chemical state of gold in gold ores (Marion et al., 1986, 1991; Wagner et al., 1986, 1988, 1989, 1994a; Friedl et al., 1992). In particular, invisible gold, whose detection eludes most other methods, could be shown to be a nonmetallic, chemically bound form of gold giving rise to a Mössbauer pattern that is easily distinguishable from that of even nanometer-size particles of metallic gold and electrum.

The time required to record the ¹⁹⁷Au Mössbauer spectrum of a gold ore depends on the gold content. The absorber thickness of sulfide gold ores is limited by the photoelectric absorption of the γ -rays to about 4 g/cm² of the ore. If an ore sample contains 100 g/t of gold, such an absorber contains 0.4 mg Au per cm², which for a single line yields a depth of the Mössbauer effect, i.e., a decrease of the count rate at resonance of about 0.05 percent. It takes several days to measure such a spectrum with acceptable accuracy. Lower gold contents require longer measuring times, which increase inversely proportional to the square of the gold content: half as much gold requires fourfold measuring time. Hence at gold contents below 50 g/t of gold, the experiments become tedious, and 20 g/t is considered to be a practical detection limit at present. The only way of increasing the sensitivity beyond that limit would be a substantial increase in the count rate at the output of the gamma spectrometer. At present, the count rate of 77 keV quanta is limited to about $2 \cdot 10^5$ s⁻¹ by dead-time effects in the electronic counting chain (Friedl, 1993). The application of ¹⁹⁷Au Mössbauer spectroscopy is limited, therefore, to ores or ore concentrates containing more than about 20 to 50 ppm of gold.

Owing to its face-centered-cubic (fcc) structure, pure metallic gold exhibits no quadrupole splitting. Its Mössbauer resonance is an un-broadened line at -1.23 mm/s with respect to a Pt metal source. Au-Ag alloys, i.e., argentine gold or electrum, also yield single lines, but these are somewhat broadened and shifted toward more positive velocities. The shape of these lines can usually be described by a Gaussian distribution of line positions around the mean isomer shift values (IS). Either the full width at half maximum (FWHM) or the variance of the Gaussian distribution can be used as a measure of the macroscopic or microscopic inhomogeneity of the gold-silver alloys in a specimen. The mean isomer shift of Au_{1-x}Ag_x alloys increases nearly linearly with silver content *x* from -1.23 mm/s for pure gold to +0.68 mm/s for dilute gold in silver (Huray et al., 1971; Friedl et al., 1992). The component attributable to the chemically bound gold in sulfide minerals is usually a broadened line with a mean isomer shift between +3 and +4 mm/s (Marion et al., 1986, 1991; Wagner et al., 1986,

1988; Yvon et al., 1991; Friedl et al., 1992, 1995; Friedl, 1993). The Mössbauer patterns of metallic and chemically bound gold are thus clearly distinguishable. Sometimes the resonance line shape of the chemically bound gold is asymmetrical. These patterns can be described by a Gaussian distribution of isomer shifts and correlated, small quadrupole splittings (Friedl, 1993). The essential parameter is the mean isomer shift (Table 2). Presumably the different line widths and asymmetries encountered for chemically bound gold in sulfide ores can be attributed to distributions of gold sites with different numbers of As and S ligands surrounding the gold, but details of this are still a matter of speculation (Friedl et al., 1995).

It is also worth noting that the gold chemically bound in the structures of pyrite or arsenopyrite gives rise to Mössbauer patterns that are different from those of all gold minerals that have so far been studied by Mössbauer spectroscopy (Friedl et al., 1992; Wagner et al., 1992, 1994a and b; Udubasa et al., 1993). This permits one to rule out the situation where the nonmetallic gold component in pyrite or arsenopyrite occurs as submicroscopic inclusions of a common gold mineral.

Gold ores often contain metallic gold (both visible and as invisible submicroscopic particles) and chemically bound gold which is mostly contained in arsenopyrite or pyrite structures. In such cases the relative amount of gold in the two modifications can be derived from the relative line intensities in the Mössbauer patterns. To this end one must know the ratio of the Lamb-Mössbauer factors, *f*, of the two species. For chemically bound gold in arsenopyrite or pyrite and metallic gold, the relevant ratio, *f*(Au bound)/*f*(Au metallic), was found to be 1.45 and 1.65, respectively (Friedl et al., 1992; Friedl, 1993). For gold-silver alloys the Lamb-Mössbauer factors are practically the same as for pure metallic gold (Friedl et al., 1992). The value of 1.45 was used to determine the relative amounts of metallic and chemically bound gold from the relative line intensities in the Mössbauer spectra.

The measurements were made with both the source and the absorber cooled to 4.2 K in a liquid He bath cryostat. The sources consisted of about 200 mg of enriched ¹⁹⁶Pt metal that had been irradiated in a thermal neutron flux of $2 \cdot 10^{13}$ ncm⁻² s⁻¹ for one or two days. The gamma rays were detected by an intrinsic Ge detector and the count-rate in the window of the 77 keV Mössbauer line was between $1 \cdot 10^5$ and $2 \cdot 10^5$ s⁻¹. The spectra were fitted with Gaussian distributions of Lorentzian lines (Friedl, 1993). For the widths of the Lorentzian components, the natural line width of 1.89 mm/s was used.

The samples used in the Mössbauer experiments were concentrates containing >95 percent arsenopyrite grains. Rather smaller than optimum amounts (between 0.5 and 2 g) of these concentrates were available and the absorbers therefore had to be made with areas between 0.25 and 1 cm² only, instead of the usual areas of 2 to 4 cm². The small absorber area reduced the count rate, but resulted in an absorber thickness of about 2 g/cm², which was acceptable but still less than the optimum thickness of about 4 g/cm².