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The distribution of trace precious metals in minerals and mineral products

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Abstract

DATA on the distribution of the precious metals (Au, Ag and the platinum-group elements Ru, Rh, Pd, Os, Ir, Pt) are rapidly accumulating as a consequence of the application of microbeam analytical techniques such as the electron microprobe, the proton microprobe, and the ion microprobe. The new data obtained with these techniques build on knowledge accumulated over the last 140 years using bulk analytical methods (e.g. spectrographic). The nature of the occurrence, the concentrations, and the variation in amounts of precious metals in minerals and mineral products are reviewed with comments as to the significance of the results with respect to industrial and environmental concerns. Future directions in mineral-specific analysis of trace precious-metal concentrations and applications outside of process mineralogy are discussed.

KEYWORDS: precious metals, Au, Ag, PGE, microbeam techniques, electron-, proton- and ion-microprobes, process mineralogy, mineral balances, mineral processing, extractive metallurgy, environment.

Introduction

IT is appropriate that this Hallimond lecture is concerned with the distribution of trace precious metals in minerals because the approach used depends upon a good understanding of ore mineralogy. Hallimond himself made important contributions to ore mineralogy through studies of the reflectance properties of minerals (Hallimond, 1956). It is interesting, moreover, to note that some exploration geologists are beginning to realize the importance of ore mineralogy. The statement by Canadian exploration geologists in a monograph on Archaean gold deposits is appropriate: '. . . it became obvious in the preparation of this paper that the available data on ore mineralogy and associated minerals were completely inadequate to assess their significance. While modern technology has rendered this research "old fashioned", it may provide critical information on ore paragenesis and have practical applications. This deficiency will be addressed by the authors, and hopefully by other researchers', Colvine *et al.* (1988). I hope to be able to demonstrate that effective application of modern technology depends on a good understanding of ore mineralogy.

In an important review of minor element concentrations in some sulphide minerals, Fleischer (1955) pointed out that investigation of the minor elements in sulphide ores in the previous 100 years was aimed at finding new elements and new sources of some of the rarer elements. He pointed out that the quality of data

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obtained from these *bulk* analyses had steadily improved over those 100 years, ranging from qualitative to semi-quantitative, to quantitative for most analyses in the previous 15 years. He concluded that the emphasis had also shifted, thus the aim of many of the recent investigations '. . . has been to obtain information about the processes of ore formation'. Fleischer also quoted from Gavelin and Gabrielson (1947) 'From a metallurgical point of view it is obviously of great importance to know the amount and distribution even of small concentrations of certain chemical elements that may be of importance for the refining processes and which influence the character of the substances to be extracted from the ore'. How perceptive of Gavelin and Gabrielson, especially because commercial ores in those days were usually coarser grained and richer in tenor when compared to current ores; in addition, environmental concerns did not receive the attention they do today.

What about the distribution of trace quantities of the precious metals, in particular, among different minerals? The precious metals are generally considered to include gold, silver and the six platinum-group elements (ruthenium, rhodium, palladium, osmium, iridium and platinum). These are well-known to occur as discrete metallic alloys and as minerals, in which the precious metal is an essential component. The author has been involved, for a number of years, in the application of several microbeam analytical techniques to determine trace quantities of precious metals in sulphides and oxides (Cabri and Laflamme, 1976, with the electron microprobe; McIntyre *et al.*, 1984, Chryssoulis *et al.*, 1987 and 1989*b* with the ion microprobe; Cabri *et al.*, 1984 and 1985 with the proton microprobe). These trace quantities constitute the so-called 'invisible precious metals'.

It was just five years ago, for example, that the author pointed out the importance of several new developments for *in situ* trace-element analysis for the precious metals (Cabri, 1987). However, is is only recently that the significance of sub-microscopic concentrations of precious metals is being demonstrated through the application of these powerful new microbeam analytical methods to produce mineralogical balances for ores containing different precious metals (Cabri and Laflamme, 1984; Chryssoulis and Surges, 1988; Chryssoulis and Cabri, 1990; Cabri, 1991).

Our understanding of the nature of the distribution of sub-microscopic precious metals, on the other hand, is not as far advanced as is our ability to measure their concentration at very low levels. For example, we do not always know whether microbeam analyses represent finely divided 'invisible' precious metal mineral grains *less* than 0.1 μm in diameter, colloidal-size particulates, clusters of less than about 100 atoms, or true solid solutions. Some information is available, in the case of gold, through use of bulk analytical techniques such as ^{197}Au Mössbauer spectroscopy (Wagner *et al.*, 1986) and use of relatively broad-beam spectroscopic methods such as X-Ray Photoelectron Spectroscopy (Chryssoulis, pers. commun., 1991). Being able to distinguish between, for example, gold in solid solution and colloidal-size gold is important when preconcentration by sulphide flotation is under consideration as part of a metallurgical flow-sheet, because solid solution will be restricted to one or few sulphides (e.g. arsenopyrite, pyrite), whereas colloidal-size gold can occur in several minerals, including gangue minerals (Chryssoulis, 1990).

Thus, the theme developed in this paper follows my interest in the precious metals, beginning with the first analyses of platinum-group minerals (PGM) by electron microprobe in Canada (Cabri and Traill, 1966). This first exposure to the PGM was accidental and arose out of my interests in phase relations in the Cu–Fe–S system (MacLean *et al.*, 1972; Cabri, 1973) and Cu-Fe sulphide mineralogy (Cabri and Hall, 1972; Cabri *et al.* 1973). I had received a sample of so-called 'cubic chalcopyrite' from Noril'sk (Cabri, 1967) which was eventually known as talnakhite (Cabri and Harris, 1971). The electron microprobe used in 1965–66, the first to be manufactured commercially in North America (1961), was a relatively primitive instrument in comparison to today's models (Harris, 1990a). That first introduction to the electron microprobe and to PGM made me realize that: (*a*) little was known about the PGM, and, (*b*) microbeam methods would play an increasingly important role in the analysis of precious metals.

Microbeam techniques

The author's principal interest in microbeam techniques in the early 1970s was in obtaining quantitative analyses of PGM in order to understand the platinum-group-element (PGE) distribution in terms of discrete PGM. Indeed, the use of the electron microprobe has contributed to an explosion in the number of new PGM species in the last 20 years (Cabri, 1980) and to a better understanding of PGM and PGE distributions (Cabri, 1981). The increase in the number of fully characterized PGM from 1748, the year attributed to the discovery of platinum, to 1990 is shown in Fig. 1. Quantitative analyses of PGM in

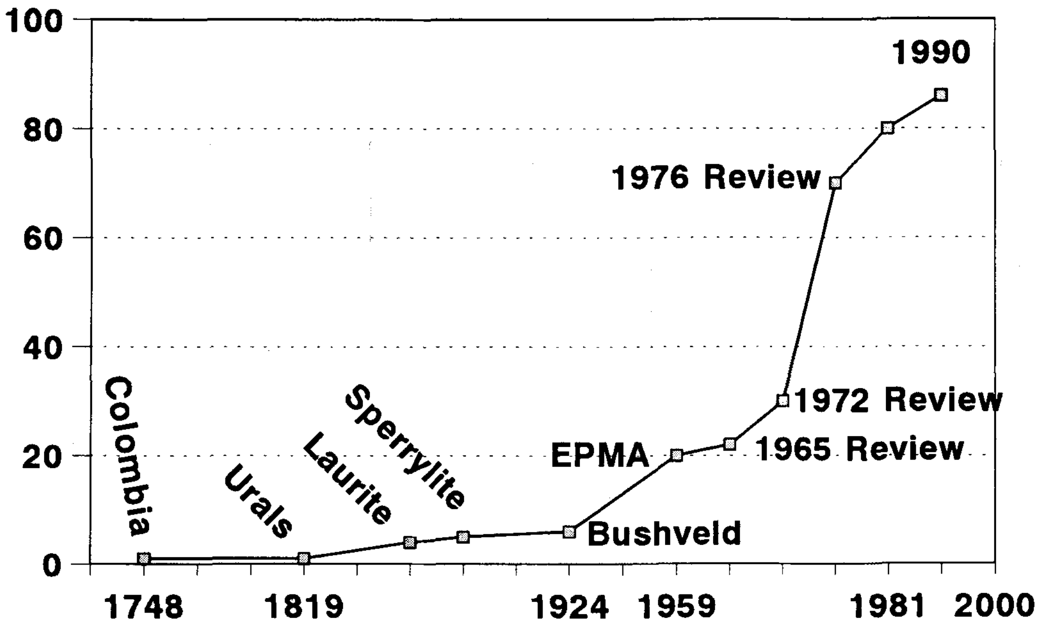

FIG. 1. Histogram, updated from Cabri (1980), showing the increase in PGM species, from the discovery of platinum in Columbia in 1748, to 1990. An additional estimated 200 unnamed PGM are not considered. EPMA refers to the first application of EPMA to analysis of PGM by Genkin (1959). 1965 Review is that of Wright and Fleischer (1965), 1972 Review is that of Cabri (1972) and 1976 Review is that of Cabri (1976).

the author's laboratory were done using synthetic standards and corrections to the microprobe data were applied mainly using EMPADR VII (Rucklidge and Gasparrini, 1969), but also using MAGIC IV of J.W. Colby.

Though quantitative analysis of PGM was the principal goal, it became apparent that some of the PGE must occur as trace constituents in the more common sulphides and sulpharsenides. Results were limited by the relatively high detection levels of the electron microprobes available; in those days a reasonable balance had to be achieved between stability and sensitivity for an acceptable counting period. Minimum detection levels were of the order of 300 ppm for Pd, 400 ppm for Pt, and 500 ppm for Rh. The early results, however, documented that sulpharsenides were carriers of PGE at concentrations above these detection levels in some Cu-Ni sulphide deposits in which PGE were a by-product, as for example, the Kanichee deposit, Ontario (Cabri, 1974) and the South Range deposits of the Sudbury irruptive (Cabri and Laflamme, 1976). On the other hand, the so-called sulphide-poor, PGE-dominant deposits such as those at Stillwater (Montana), Lac des Iles (Ontario), and Merensky reef (Transvaal) contain measurable concentrations of PGE in sulphides, particularly pentlandite (Cabri, 1981). Unfortunately, satisfactory PGE mineralogical balances could not be achieved for many deposits because of the relatively high detection levels by electron microprobe (Cabri and Laflamme, 1984). An invitation by Ahmed El Goresy to spend several weeks in 1982 at the Max-Planck-Institut für Kernphysik, Heidelberg, introduced me to what was then the world's only mineralogically dedicated proton microprobe.

Operating conditions on the Max-Planck-Institut's proton microprobe at that time were far from ideal, and the results obtained were a source of both great excitement, as well as frustration. It was very exciting to be able to easily achieve detection levels for many elements in the region of 10 ppm, and with a bit more effort, in the range of 2–10 ppm. Particularly interesting were the various tests done to verify the results for both accuracy and precision (Cabri *et al.*, 1984; Harris *et al.*, 1984; Remond *et al.*, 1987). Eventually, comparisons were made among results obtained with different proton microprobes and different computer programs (Campbell *et al.*, 1987). It was frustrating, on the other hand, not to be able to detect any PGE in Sudbury sulphides!

At about the same time, I was exploring other analytical methods for the determination of trace quantities of precious metals such as Secondary Ion Mass Spectrometry (SIMS), also known as the ion microprobe. The first studies relied on prior experience with the electron and proton microprobes, using synthetic standards for reference (e.g. Cabri *et al.*, 1985). Because silver was an important commodity in the early 1980s, I investigated silver distribution in galena and sphalerite by SIMS. The first published ion-microprobe study of ore minerals was based on synthetic standards: a series of Pb and Zn–Fe sulphides with varying silver contents (McIntyre *et al.*, 1984). The study demonstrated that the intensity ratios of the secondary ions of a major element were proportional, for the element of interest, to the concentration of a trace element in a specific matrix. It became apparent, however, that this approach to quantification was not suitable for ore minerals, primarily because of the effects of substitutions between major elements (e.g. Fe for Zn) on ion yields. Fortunately, this problem was successfully addressed by Chryssoulis *et al.* (1986) using ion implantation (after Leta and Morrison, 1980) to determine silver in sphalerite. An interesting development that arose from the investigations of the trace silver content of major sulphide minerals at Brunswick Mining and Smelting Corporation Limited concerned the different results from electron microprobe analyses done on ore mined in 1977 and that mined in 1985. The 1985 results (involving 700 spot analyses) showed clearly a single galena population with a median value of 0.074 wt.% Ag, (Laflamme and Cabri, 1986 *a,b*), which is about 10% less than the earlier result of 0.084 wt.% Ag, obtained with an older electron microprobe on 240 galena grains. The difference in results is significant when doing a mineralogical balance (e.g. Chryssoulis and Surges, 1988), but in this case one cannot be certain whether the variation is attributable to different instrumentation or to a change in ore.

The ion implantation technique has since been successfully applied to trace gold analyses (Chryssoulis *et al.*, 1987, 1989*b*), and is being tested on the PGE (Chryssoulis *et al.*, 1989*a*, 1991; Chryssoulis and Cabri, 1991). I look forward with a great deal of interest to talks by several speakers at this symposium because they will be presenting new data on trace precious-metal concentrations obtained by proton and ion microprobes [See *Abstracts of the Winter Conference*].

Trace precious metal database

The precious-metal database that is presented is derived largely from microbeam analytical data in the literature. Each precious metal is treated separately, with reference to analyses documented in the literature for identified deposits. Though there are, unfortunately, many analyses of material from unidentified sources recorded in the literature, it is felt that there are sufficient data on samples from identified sources to provide a realistic assessment of the concentration and range of values that may be expected in different minerals for different deposit-types. The trace-element data for different host 'common' minerals are presented in the form of tables for each precious metal.

Minor- to trace-element substitutions occur frequently in rarer minerals, which often are precious-metal minerals, but these minerals are not listed. Also, the deposits are not tabulated in terms of type, but are grouped only by country; further details for each locality may be found in the references. It should be noted that data are tabulated in ppmw (μg/g) as well as in wt.%. Abbreviations for minerals and analytical methods are given in Table 1.

Gold. According to Harris (1990*b*), there are only 26 valid gold-mineral species, 3 new gold minerals whose descriptions await publication, 2 doubtful species and 13 incompletely characterized, unnamed gold-containing compounds. The distribution of gold in ores had been somewhat controversial since the recognition of 'invisible gold' (e.g. Bürg, 1930), and reliable mineralogical balances for gold in many ores were not possible until recently (Chryssoulis and Cabri, 1990). The data presented in Table 2 indicate that gold may occur invisibly in many sulphide, sulpharsenide, and arsenide minerals. The greatest concentration is attained in arsenopyrite, followed by pyrite, löllingite, tetrahedrite, and chalcopyrite. The highest concentrations in pyrite were reported for a Columbian sample (up to 3000 ppmw) and from Villeranges, France, (up to 600 ppmw) by Marion *et al.* (1991*b*) using SIMS and EPMA, but with few analytical details. Additionally, 0.05–0.46% Au, occurring as Au-rich rims in pyrite from the Carlin-type Banqi deposit (Guizhou, China) was determined by EPMA; the gold occurs as submicroscopic native gold inclusions, as deduced from chemical dissolution tests (Mao, 1991). High concentrations obtained by EPMA of pyrite are 550–800 ppmw (Picot and Marcoux, 1987) and 488 ppmw (Swash, 1988), but few analytical details are provided; hence these high values should be

Table 1. Abbreviations used in subsequent tables and text

asp = arsenopyrite
bn = bornite
br = breithauptite
cp = chalcopyrite
cob = cobaltite
cb = cubanite
ga = galena
gf = gersdorffite
gd = godlevskite
lo = löllingite
ma = marcasite
mau = maucherite
mh = mooihoekite
mk = mackinawite
mt = magnetite
nc = nickeline
pn = pentlandite
po - pyrrhotite
py = pyrite
tet = tetrahedrite
tk = talnakhite
tr = troilite

AMS	Accelerator Mass Spectrometry
BSE	Back Scattered Electron
EPMA	Electron Probe Micro-Analysis
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
HRTEM	High Resolution Transmission Electron Microscopy
LIMS	Laser Ionization Mass Spectrometry
PIXE	Particle-Induced-X-Ray Emission
SEM	Scanning Electron Microscopy
STM	Scanning Tunneling Microscopy
SIMS	Secondary Ion Mass Spectrometry
SXRF	Synchrotron X-Ray Fluorescence
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

treated with caution. On the other hand, the high proportion of pyrite in many ore deposits often makes even low concentrations of gold in pyrite significant (e.g. <2 ppmw). Gold has also been reported in magnetite from a skarn deposit at Rossland, British Columbia (Wilson *et al.*, 1990) but more information is required for an evaluation of this type of trace-gold occurrence.

Whether the gold is structurally bound in every example listed in Table 2 is not known. Many of the analyses represent invisible colloidal-size gold, possibly smaller than 20 nm in diameter (Chryssoulis and Cabri, 1990; Mao, 1991). Detailed investigations using Mössbauer spectroscopy (e.g. Wagner *et al.*, 1986), EPMA and XRD (e.g. Johan *et al.*, 1989), SIMS–EPMA–HRTEM (Cabri *et al.*, 1989), hydrothermal synthesis (Wu and Delbove, 1989) and XPS analyses (Chryssoulis, in prep.) collectively indicate that in many cases the gold is bound in the arsenopyrite structure, probably as Au^{3+}. A Mössbauer spectrum of pyrite from Columbia, in which a large proportion of the gold is structurally bound was illustrated by Marion *et al.* (1991*b*).

Understanding the nature and distribution of invisible gold has been more of a concern to the process mineralogist and the metallurgist than to the exploration geologist. The exsolution of gold globules from pyrite (Bürg, 1935) and arsenopyrite (Dunn *et al.*, 1989) by heating at temperatures of 500–700°C was indirect evidence of the presence of invisible gold. It has long been postulated, however, before confirmation of the occurrence of invisible gold in sulphides, that certain epigenetic deposits contained gold-bearing arsenopyrite and pyrite during their formation in greenstone belts (e.g. Boyle, 1979). Subsequent recrystallization of sulphides during deformation and continued hydrothermal activity caused much of the gold, silver, antimony and other elements to be exsolved from the early sulphides, and redeposited in local dilatant zones such as fractures in quartz lenses, local tension fractures, and small faults in shear zones. It can therefore be expected that auriferous deposits (or parts of deposits) which had been subjected to less recrystallization may contain a greater proportion of invisible gold.

It is becoming apparent from the database that invisible gold occurs in a great variety of geological environments and throughout geological time, depending on the extent and nature of metamorphic events. For example, the polymetallic Olympias deposit (Greece), of Late Cretaceous to Tertiary age (Kalogeropoulos *et al.*, 1989) contains 5.5 g/t Au, most of which is invisible. A pyrite-rich concentrate containing 31.5 g/t Au had 43.8% of the Au in arsenopyrite (av. 49 ppmw), 31.5% in As-rich pyrite (av. 49 ppmw), and 15.7% in As-poor pyrite (av.

Table 2. Concentrations of gold determined in common minerals (ppmw and wt.%)

Deposit	asp	bn	cp	ga	lo	ma	mt	po	py	tet	Method	Ref.
Congress	1.7ppmw-1.3%					<0.25-0.5			<0.25-21.0		SIMS	7
Elmtree	0.4-912								0.9-107.8		SIMS	7
Elmtree	<300-500										EPMA	2
Elmtree									28-86		PIXE	3
Estrades	<0.3-170		<0.25-0.4	0.2-0.4		<0.25-4.1			<0.25-12.0		SIMS	7
Golden Pond	0.3-402								<0.25-4.1		SIMS	7
HW		0.2-1.6	<0.25-7.7	0.6-3.4					<0.25-2.8	<0.25-59	SIMS	7
Ketza River	1.3-46							<0.25-1.8			SIMS	7
Lara	1.9-22			<0.25-0.28					<0.25-3.4	<0.25-22.6	SIMS	4,7
Lupin					1.5-50						SIMS	5
Mobrun			0.15- 6.0						<0.25-5.6		SIMS	7
Opemiska			<0.5-20.0								SIMS	6
Rossland	2.01-3.58		0.011-0.095			0.049	0.003-0.170	0.006-0.068			AMS	15
Trout Lake	2.0-112								<0.25-6.8		SIMS	7
Windy Craggy									<0.25-2.7		SIMS	7
Le Châtelet	1.15%										EPMA	8
Massif Central	1.7%								500*		EPMA	12
Villeranges	1.52%										EPMA	12
Villeranges									24-600**		SIMS/EPMA	10
Griffin's Find	1.4-17				351-1087						SIMS	11
Lancefield	<40-405										PIXE	13
Pilbara	0.8-5				79-162						SIMS	11
Olympias	2.3-370								1.0-110		SIMS	7
Julcani									800*		EPMA	8
Luzon		<0.5	<0.5						<0.5-9.6		SIMS	1
Banqi (Guizhou)	0.15%								0.05%-0.46%		EPMA	9
Fairview	max. 2700								max. 488*		EPMA	14
Sheba	68-1900										SIMS	2,7
Sheba	<400-4400										EPMA	2
Overall range:	<0.3ppmw-1.7%	0.2-1.6	0.011-20.0	0.2-3.4	1.5-1087	0.05-4.1	0.003-0.17	0.006-1.8	<0.25-800?	<0.25-59		

*Anomalously high values are reported by EPMA, but with insufficient details; also values of 300-500 ppmw Au in berthierite and 500 ppmw in gudmundite.
**Anomalously high values reported by SIMS, confirmed by EPMA, see text for details.

References: 1. Cabri (unpublished); 2. Cabri et al. (1989); 3. Cabri et al. (1991); 4. Chryssoulis (1989); 5. Chryssoulis (1991); 6. Chryssoulis et al. (1987); 7. Cook and Chryssoulis (1990); 8. Johan et al. (1989); 9. Mao (1991); 10. Marion et al. (1991b); 11. Neumayr et al. (in prep.); 12. Picot and Marcoux (1987); 13. Sie et al. (1989); 14. Swash (1988); 15. Wilson et al. (1990).

3.4 ppmw) (Cabri and Chryssoulis, 1990). The Cambro-Ordovician gold-bearing As–Sb vein deposits of the Massif Central (France), such as Le Châtelet, Viges, and Villeranges, are known for their high contents of invisible gold in many sulphides, especially arsenopyrite (Picot and Marcoux, 1987). These authors suggested that gold was originally concentrated in early pyrrhotite (at concentrations up to 30 ppm) from which native gold later exsolved during alteration of the pyrrhotite to pyrite–marcasite. Picot and Marcoux also related the type of final gold mineralization to the type of fractures: in tight shear zones (e.g. Le Châtelet) the transformation of pyrrhotite to marcasite-pyrite occurred early, coevally with the deposition of arsenopyrite that attracted and retained the gold released from the pyrrhotite. Deposits which had large structural openings, (e.g. Le Bournieux) contain no arsenopyrite, and hence the gold is released from the pyrrhotite in the native form.

Archaean gold deposits and volcanogenic massive sulphide (VMS) deposits in the Canadian Shield generally contain smaller quantities of invisible gold than deposits in younger rocks. For example, at the Trout Lake VMS deposit (Manitoba), it was estimated that 93% of the gold occurs as Au–Ag–Hg alloys and that the balance occurs as invisible gold in pyrite (6%) and arsenopyrite (1%) (Healy and Petruk, 1990) Part of this study involved the tailings and showed that 26.7% of the gold was in pyrite, 8.9% in arsenopyrite, and 64.4% as minute inclusions <1.5 μm (Chryssoulis, 1989).

Silver. In contrast to the other precious metals, silver forms a large number of minerals: currently 131 species are recognised (Nickel and Nichols, 1991). There are, in addition, about 55 unnamed or incompletely characterized silver-bearing minerals, some of which may be new species. Besides native silver, acanthite, and other common silver minerals, it is well-known that silver occurs in solid solution, substituting for copper in many sulphide and sulphosalt minerals, and for gold or lead in telluride and selenide minerals (Thorpe *et al.*, 1976; Gasparrini, 1984). The significance of dilute solid solution of silver in common base metal minerals (e.g. bornite, chalcopyrite, galena, pyrite, pyrrhotite, sphalerite) is questioned by some. Gasparrini (1984), for example, opined that silver in solid solution in these minerals is not common (at concentrations within the detection limits of EPMA, which are given as 50–100 ppmw) and that '. . . a large proportion, if not all of the silver, occurs in discrete fine particles which are not visible at average magnifications of 100× to 200×'. There is no doubt that there are published analyses of common minerals in which the silver is erroneously ascribed to solid solution. The silver contents may be partly or principally accounted for by very fine grains of silver minerals, such as silver sulphosalts in galena (as discussed by Hall and Czamanske, 1972, Laflamme and Cabri, 1986*b*, Knights and Patterson, 1988, and Foord and Shawe, 1989).

The complexity of having coexisting solid-solution silver as well as very small inclusions of a silver sulphosalt is described by Sharp *et al.*, (1990) in a study using scanning tunnelling microscopy. They observed surface pits, 10–300 nm in diameter, on cleavage faces, interpreted as due to plucking of diaphorite inclusions during cleavage of the galena. Rod-shaped inclusions of diaphorite had previously been observed to occur in these samples by HRTEM images (Sharp and Buseck, 1989). Sharp *et al.* (1990) were also able to discern that the surface structure of galena has local distortions, which were interpreted to result from substitution of Ag^+ and Sb^{3+} for Pb^{2+}. In a related study (using EPMA, BSE imaging and HRTEM), Sharp and Buseck (1992) have shown that in galena from La Paz and Zacatecas (Mexico) there is coupled substitution of Ag and Sb for Pb, as well as rod-shaped inclusions of diaphorite (20 nm to 50μm long) and disk-shaped inclusions of frankeite. In other silver-rich galenas, however, there seems to be a better correlation between Ag and Bi than between Ag and Sb (Jambor and Laflamme, 1978; Chen and Petruk, 1980; Laflamme and Cabri, 1986*a*) as shown in Figs. 2 and 3. The highest reported silver value for galena (9.4 wt.% Ag) is part of an extensive solid solution between galena and ourayite from the Round Mountain–Manhattan area (Nevada), the apparent solid solution involves a coupling $2Pb^{2+} \rightleftharpoons Bi^{3+} + Ag^+$, with minor substitution of Sb for Bi (Foord *et al.*, 1988). Exchange between trace elements and Pb in galena is probably more complicated than simple coupled substitution, and more elements may be involved (e.g. Johan, 1988). For example, Micro-PIXE analyses of carefully characterised galena from the Blagodatskoye deposit, Transbaikal (Cabri *et al.*, in prep.) showed a variety of trace elements (in ppmw): 6542 Sb, 6050 Ag, 582 Sn and 52 Cd (bismuth could not be detected by EPMA, MDL 700 ppmw).

It is also apparent, however, that some careful studies document silver solid solution as a significant contribution to the silver mineralogical distribution of base-metal ores, whereas other careful studies indicate that the silver contribution from the common base-metal minerals is minor. For example, Chryssoulis and Surges

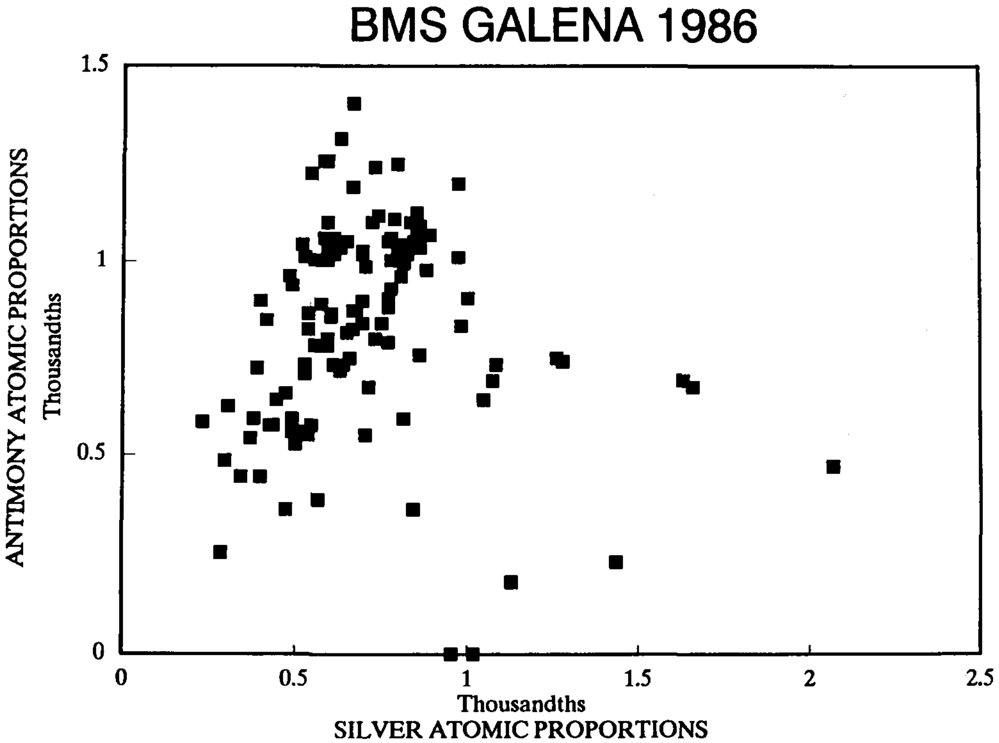

FIG. 2. Silver versus antimony by EPMA in galena from Brunswick No. 12 mine, New Brunswick (Laflamme and Cabri, 1986*b*).

(1988) concluded that 30% of the silver in the mill circuits at Brunswick Mining and Smelting Corporation, New Brunswick, occurs as solid solution in galena. This work was based on an average Ag concentration in galena of 740 ppmw, obtained by EPMA, with high silver values checked for minute inclusions at magnifications of over 3000× (Laflamme and Cabri, 1986*b*). A lesser contribution to the silver mineralogical balance was ascribed to sphalerite, chalcopyrite, and pyrite (totalling 7.5%) by ion-microprobe analyses, and the bulk of the silver was attributed to tetrahedrite, which contains from 0.1 to 36.5 wt.% Ag. In another example, approximately 60% of the silver in the 'A' ore at the Kidd Creek mine (2800L), Ontario, occurs as a solid solution in chalcopyrite, with an average of 183 ppmw obtained by Micro-PIXE analyses (Cabri, 1988*b*). Two separate studies of the silver distribution at Zacatecas (Mexico) arrived at exactly the same figures for the contribution of silver due to solid solution versus that due to silver mineral inclusions. Pearson *et al.* (1988) determined that the bulk of the silver was in solid solution in galena and calculated that 29% of the silver recovered from lead concentrates was due to silver mineral inclusions. Sharp and Buseck (1992) independently determined that 29% of the silver in Zacatecas galena is due to silver sulphosalt inclusions.

Bérubé *et al.* (1985) determined by EPMA that averages of 880 and 850 ppmw Ag occur in solid solution in chalcopyrite and galena, respectively, in tailings from the New Calumet mine (Quebec). By using these values, they were able to calculate that the bulk of the silver was lost as Ag-bearing tetrahedrite, rather than from the chalcopyrite and galena, which contained only 6% and 9% of the total silver in the tailings, respectively.

Thus, the author believes that the silver content of base-metal minerals, though usually well below 1 wt.% for individual minerals, is frequently a significant contributor to the silver mineralogical balance. This is especially true where the silver occurs in the more common base metal minerals. It is therefore essential to determine the silver mineralogical balance in order to understand the silver distribution, without any preconceived notions. Naturally, care must be taken with trace-element analyses, and selection of appropriate analytical techniques and methodologies has to be emphasized.

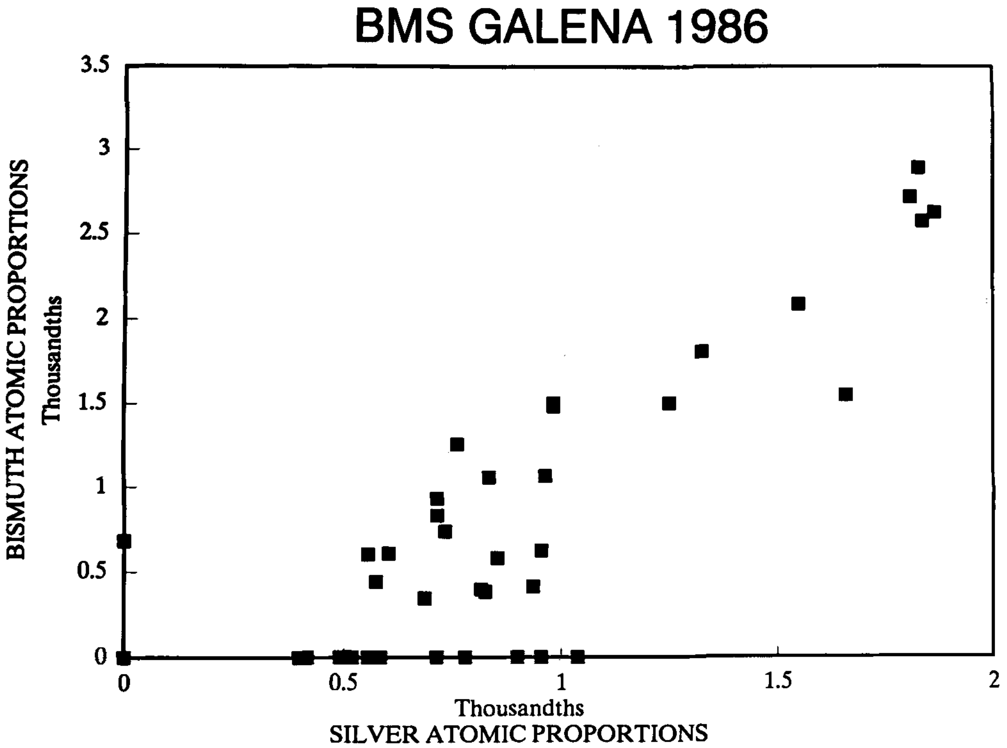

FIG. 3. Silver versus bismuth by EPMA in galena from Brunswick No. 12 mine, New Brunswick (Laflamme and Cabri, 1986*a*).

Palladium. Palladium is a component of most PGM, and it also attains the highest trace-element concentrations of all the PGE in common minerals (Cabri, 1991). The best-known concentrators of palladium are pentlandite (up to 4.6 wt.%), breithauptite (up to 18.9%), and the Co- and Ni-sulpharsenides (up to 5.5 wt.%), as shown in Table 3. Also listed in the Table is a 'pentlandite' from Stillwater that contains 8.6–12.1 wt.% Pd. Because this mineral contains approximately one atom of Pd, it can be thought of as a new mineral, analogous to argentopentlandite. Other common sulphides, such as chalcopyrite and pyrrhotite, seem to carry trace quantities of palladium, but the database is insufficient for quantitative assessment at this time. Palladium concentrations as high as 2920 ppmw in mackinawite are reported by Czamanske *et al.* (1992). Maximum values reported for Pd in pentlandite (in ppmw) are: J-M reef (46000), Platreef (20000), Lac des Iles (6500), Medvezhy Creek (2540), Great Dyke (1990), Penikat (1800), Merensky reef (1164). It should be noted, however, that some of these values represent anomalously high concentrations, e.g. the value for Platreef pentlandite (Kinloch, 1982). In marked contrast, some sulphide-rich Ni–Cu deposits containing PGE as by-products such as Sudbury and Kambalda, probably contain less than 2ppmw Pd in pentlandite. These sulphide-rich deposits, however, have high concentrations of palladium in arsenides and sulpharsenides (up to several wt.%).

The palladium concentration in sulphide minerals seems to be related to, or controlled by the geological environment. It is interesting to note that the sulphide-poor PGE-dominant deposits as well as some of the sulphide-rich Noril'sk Cu–Ni ores contain variable, but significant quantities of Pd in pentlandite. Kinloch and Peyerl (1990) suggest that the variations in PGE solid solution in base-metal sulphides in the Bushveld deposits are due to genetic factors. They postulate that so-called normal volatile-*bearing* Merensky reef has low PGE in solid solution in pentlandite and pyrrhotite because there was sufficient time between liquidus and solidus for crystallization of the PGM. In contrast, in the abnormal volatile-*enriched* Merensky reef the liquidus temperature was lowered, result-

Table 3. Concentrations of palladium determined in common minerals (ppmw and wt.%)

Deposit/product	br	cp	cob	cb	gf	mau	mk	nc	pn	po	tk	Method	Ref.
Clarabelle mill			av. 0.05%		av. 0.05%							EPMA	6
Copper Cliff mill			0.28%		0.16%	0.09%						EPMA	5
Copper Cliff South					<0.03%-0.14%	<0.03%-1.84%		<0.03%-0.05%				EPMA	3
Crean Hill			<0.03%-0.09%		<0.03%-0.31%							EPMA	3
Creighton					<0.03%-0.13%							EPMA	3
Falconbridge					<0.03%-0.05%							EPMA	3
Frood					0.24%							EPMA	3
Inco concentrates		<2.1							<1.8	<1.2		PIXE	8
Victoria			<0.03%-0.74%		<0.03%-1.95%							EPMA	3
Cuthbert									16			PIXE	14
Lac des Iles									0.02-0.54%			EPMA	4
Namew Lake									<8-16			PIXE	14
Pipe						<0.03%-0.07%						EPMA	5
Rathbun		<15-23(a)										PIXE	1
Rottenstone									<8-17			PIXE	14
Rottenstone									<13-20(a)			PIXE	1
Wellgreen		<5-9							<5-34	<5-5.6		PIXE	7
Wellgreen									<8-17			PIXE	14
Wellgreen(b)	<0.03-18.9%											EPMA	7
J-M reef(c)									0.18%-1.36%			PIXE	8
J-M reef									0.2%-3.3%			EPMA	18
J-M reef(d)									1.4%-4.6%			EPMA	12
J-M reef(d)									8.6%-12.1%(e)			EPMA	12
J-M reef(d)		<5-9							1748-2210	43-47		PIXE	1
Merensky reef(f)									<0.03%-0.05%			EPMA	5
Merensky reef(g)									932-983			PIXE	2
Merensky reef(h)									<8-455			PIXE	14
Merensky reef(i)		16-17							1102-1164	<5		PIXE	1
Merensky reef(j)		<7							289-320			PIXE	1
Merensky reef(k)		<7-12(a)							8-527	<6		PIXE	1
Merensky reef									24-320			PIXE	17
Platreef(l)									2.0%			EPMA	10
Wedza-Mimosa									max. 0.19%			EPMA	15
Penikat									<600-0.18%			EPMA	1
Acoje									<11-148			PIXE	13
Kambalda								16-1110				PIXE	16
Komsomolsky									134-254			PIXE	9
Medvezhy Creek		<6-35		<5-50			310-2920		203-2540	<4.5-11		PIXE	9
Oktyabr'sky(m)		<6-96		<5-142			7-115		<5-402	<5-6	<8-38(a)	PIXE	9
Kupferschiefer			(n)		(n)							EPMA	11
Overall range:	<0.03-18.9%	<2.1-96	<0.03%-0.74%	<5-142	<0.03%-1.95%	<0.03%-1.84%	7-2920	16-1110	<2ppmw-4.6%	<1-47	<8-38		

Notes: (a) single analysis >MDL; (b) Also ullmannite <0.03-0.09%; (c) West Fork adit; (d) Minneapolis adit; (e) see text for discussion; (f) Rustenburg; (g) regional pothole reef, Spitzkop; (h) Western Platinum; (i) pothole reef, NW; (j) normal reef, NW; (k) normal reef, NNW; (l) Zwartfontein; (m) Also bn 19 ppmw, gd <6-19 ppmw, mh <6-25; (n) up to 5.5 wt.% Pd is reported in "Co- and Ni-arsenides".

References: 1. Cabri (unpublished); 2. Cabri (1988a); 3. Cabri and Laflamme (1976); 4. Cabri and Laflamme (1979); 5. Cabri and Laflamme (1981); 6. Cabri and Laflamme (1984); 7. Cabri *et al.* (1991); 8. Cabri *et al.* (1984); 9. Czamanske *et al.* (1992); 10. Kinloch (1982); 11. Kucha (1991); 12. Laflamme (unpublished); 13. Orberger and Traxel (1991); 14. Paktunc *et al.* (1990); 15. Prendergast (1990); 16. Ryan *et al.* (1990); 17. Sie *et al.* (1990); 18. Todd *et al.* (1982).

ing in a compressed time-frame for crystallization of PGM, thus allowing much more of the PGE to remain trapped as solid solutions in the base-metal sulphides (except for Pt which formed eutectic textures of Pt-Fe alloys with the sulphides). PIXE data (Table 3) for pentlandite from pothole reef compared to that for normal reef appear to support the suggestion of Kinloch and Peyerl (1990).

The ores of the Noril'sk area, which vary from massive sulphide ore bodies to veins to disseminations, may shown high concentrations of numerous trace elements and a wide diversity of PGM (Genkin, 1968, 1991). The extent of solid solutions of PGE in Noril'sk ores is being reinvestigated (e.g. Chryssoulis *et al.*, 1991*a*; Czamanske *et al.*, 1991, 1992), and it had been estimated that the majority of the PGE accumulated as solid solutions in the main ore-forming iron-nickel sulphides (Genkin, 1991). Czamanske *et al.* (1992) show that correlation between palladium in pentlandite and the Ni/Fe ratio in pentlandite may be largely an artifact of considering mixed sample populations; there is also no correlation between palladium concentration in pentlandite and the bulk palladium content of the ore. For the Oktyabr'sky orebody, they show that pyrrhotite-bearing ores containing 10–39 ppmw Pd have 68–284 ppmw Pd in pentlandite, whereas in pyrrhotite-free ores containing 77–149 ppmw Pd, a maximum of 14 ppmw Pd is present in pentlandite. These authors postulate that differences in crystallization history account for the variation in the palladium content of pentlandite.

The precious-metal-bearing Kupferschieffer deposits, which contain a concentration of heavy metals at the base of a black shale unit, have been studied by EPMA and Micro-PIXE (Pryzbylowicz *et al.*, 1990; Kucha, 1991). It is reported that optically inclusion-free areas of thucolite contain from <110 to 1000 ppmw Pd, apparently associated with As concentrations. The exact siting of the Pd in this unusual geochemical setting requires further investigation.

Rhodium and ruthenium. The databases for rhodium (Table 4) and for ruthenium (Table 5) show a distribution similar to that of palladium, except for the expectedly smaller concentrations. High concentrations occur in Co- and Ni-sulpharsenides (up to 10.5 and 3.7 wt%, respectively, for rhodium; up to 3.3. and 2.1 wt.%, respectively, for ruthenium) and in pentlandite (up to 866 ppmw for rhodium and 79 ppmw for ruthenium). Whereas palladium concentrations in pentlandite from pothole Merensky reef ore are higher than those for normal Merensky reef ore, the opposite is found for the highest rhodium and ruthenium values. Troilite in the Merensky reef contains up to 65 ppmw Ru, but the database is limited for this occurrence, and is also limited for

Table 4. Concentrations of rhodium determined in common minerals (ppmw and wt.%)

Deposit	cp	cob	gf	pn	po	tr	Method	Ref.
Clarabelle mill		av.225					EPMA	5
Copper Cliff mill		<0.05%-2.4%	<0.05%-3.3%				EPMA	4
Crean Hill		<0.05%-1.5%	<0.05%-1.53%				EPMA	3
Creighton							EPMA	3
Falconbridge							EPMA	3
Frood		<0.05%-0.58%					EPMA	3
Inco concentrates	<1.9			<1.6	<3.0		PIXE	8
Namew Lake				<5-8			PIXE	12
Pipe		<0.05%-7.2%					EPMA	4
Rottenstone	<13-17(a)						PIXE	1
Wellgreen	<5-10	up to 2.7%		<4-12			PIXE/EPMA	6
J-M reef				<14-86			PIXE	8
J-M reef (b)	<5			351-685	<6		PIXE	1
Merensky reef(c)				250-266		<9	PIXE	2
Merensky reef(d)	<6			21-361	<5-10		PIXE	1
Merensky reef(e)	<6-7(a)			7-55			PIXE	1
Merensky reef(f)	<7-24(a)			<6-866	<6-13(a)		PIXE	1
Merensky reef				19-708			PIXE	13
Volspruit pyroxenite				27-41			PIXE	12
Bushveld anorthosite				<5-6			PIXE	12
UG-2				<5-12			PIXE	12
Pechenga		0.45%-10.5%	3.7%				EPMA	10
Komsomolsky	<5			<5-10(a)	<4		PIXE	9
Medvezhy Creek	<5			<5-30	<4-12(g)		PIXE	9
Oktyabr'sky	<5			<5	<4		PIXE	9
Lower Tagil'sk				4.0%(h)			EPMA	11
Yubdo				13.2%-14.1%(h)			EPMA	7
Overall range:	<2-24	<0.05%-10.5%	<0.05%-3.7%	<2-866	<3-13	<9		

Notes: (a) Single analysis >MDL; (b) Minneapolis adit; (c) regional pothole reef, Spitzkop; (d) pothole reef, NW; (e) normal reef, NW; (f) normal reef, NNW; (g) monoclinic pyrrhotite; (h) see text for discussion.

References: 1. Cabri (unpublished); 2. Cabri (1988a); 3. Cabri and Laflamme (1976); 4. Cabri and Laflamme (1981); 5. Cabri and Laflamme (1984); 6. Cabri and Laflamme (1991); 7. Cabri et al. (1981); 8. Cabri et al. (1984); 9. Czamanske et al. (1992); 10. Distler and Laputina (1979); 11. Genkin et al. (1974); 12. Paktunc et al. (1990); 13. Sie et al. (1990).

Table 5. Concentrations of ruthenium determined in common minerals (ppmw and wt.%)

Deposit	cp	cob	gf	pn	po	tr	Method	Ref.
Rottenstone					<9-15(a)		PIXE	1
Wellgreen	<5-10			<5-13			PIXE	3
J-M reef (b)				<14-47			PIXE	4
J-M reef (c)	<5			50-79	<6		PIXE	1
Merensky reef(d)						<10-65	PIXE	2
Merensky reef(e)	<5			<7	<5-25		PIXE	1
Merensky reef(f)	<6			<5-22			PIXE	1
Merensky reef(g)	<6-19(a)			7-28	6-7		PIXE	1
Merensky reef				~5	8-12		PIXE	9
Pechenga		1.65%-3.3%	2.1%				EPMA	6
Lower Tagil'sk				9.6%(b)			EPMA	7
Komsomolsky	<5			<5	<4		PIXE	5
Medvezhy Creek	<5			<5-14	<4		PIXE	5
Oktyabr'sky	<5			<5	<4-21(h)		PIXE	5
Overall range:	<5-19	1.65%-3.3%	to 2.1%	<5-79	<4-25	<10-65		

Notes: (a) Single analysis >MDL; (b) see text for discussion; (c) Minneapolis adit; (d) regional pothole reef, Spitzkop; (e) pothole reef, NW; (f) normal reef, NW; (g) normal reef, NNW; (h) Hexagonal pyrrhotite

References: 1. Cabri (unpublished); 2. Cabri (1988a); 3. Cabri and Laflamme (1991); 4. Cabri et al. (1984); 5. Czamanske et al. (1992); 6. Distler and Laputina (1979); 7. Genkin et al. (1974); 8. Paktunc et al. (1990); 9. Sie et al. (1990).

rhodium and ruthenium analyses in pentlandite. Although it is, therefore, premature to draw conclusions from these relationships, these data are in agreement with the general conclusions of mineralogists studying the Bushveld ores (e.g. Peyerl, 1983) that virtually all the rhodium in the Merensky reef occurs in solid solution within base-metal sulphides.

Czamanske *et al.* (1992) found that droplet ore in picritic–taxitic gabbrodolerite at the Medvezhy Creek deposit in the Noril'sk I instrusion contains Rh (<5–28 ppmw) and Ru (11–12 ppmw) in pentlandite, and 11–12 ppmw Rh in monoclinic pyrrhotite. They ascribed this contrast to other Noril'sk-area ores as due to more rapid quenching of this ore type. Chryssoulis *et al.* (1991*a*) reported orally that certain Noril'sk pyrrhotite grains from massive and disseminated ores contain 2 ppmw rhodium. Genkin (1991) concluded that nearly all of the rhodium and ruthenium in the Noril'sk deposits occurs in solid solution in pentlandite and pyrrhotite. Cabri and Laflamme (1984) concluded that 60–80% of the rhodium in a sample from the Clarabelle primary mill (Sudbury) occurs in solid solution in sulpharsenides, 20–30% in hollingworthite, and 5% as a solid solution in sperrylite. There is no doubt that future SIMS analyses of Sudbury pentlandite and pyrrhotite will enable better mineralogical balances to be calculated for rhodium.

High rhodium and ruthenium concentrations found in rare 'pentlandites' from Alaskan-type deposits such as Lower Tagil'sk (Genkin *et al.*, 1974) and Yubdo (Cabri *et al.*, 1981) probably represent a rhodium or rhodium-bearing ruthenian analogue of argentopentlandite, respectively. Genkin *et al.* (1974) proposed that these (Ru, Rh)-rich 'pentlandites' were formed during serpentinization, with the PGE derived from primary PGM which were subjected to hydrothermal metamorphism. Interestingly, these minerals, which are known in association only with Alaskan-type ultramafics, contain no palladium. This contrasts with the common occurrence of

Table 6. Concentrations of platinum determined in common minerals (ppmw and wt.%)

Deposit	cob	gf	mau	mt	nc	pn	po	Method	Ref.
Clarabelle mill	av. 330	av. 330						EPMA	3
Copper Cliff mill		to 0.15%						EPMA	2
Copper Cliff South					<0.04%-0.08%			EPMA	1
Crean Hill	<0.04%-0.19%							EPMA	1
Frood		<0.04%-0.25%						EPMA	1
Pipe	max. 0.20%							EPMA	2
Pechenga	0.91%							EPMA	6
Noril'sk						<0.05-2.0	<0.1-2.0	SIMS	5
Yubdo				to 0.34%		<0.04%-1.9%(a)		EPMA	4
Duluth Complex (b)			0.06%-0.13%		0.11%			EPMA	7
Overall range:	<0.04%-0.91%	<0.04%-0.25%	0.06%-0.13%	to 0.34%	<0.04%-0.11%	<0.05ppmw-1.9%	<0.1-2.0		

Notes: (a) see text for details; (b) massive sulphide samples.

References: 1. Cabri and Laflamme (1976); 2. Cabri and Laflamme (1981); 3. Cabri and Laflamme (1984); 4. Cabri et al. (1981); 5. Chryssoulis et al. (1991a); 6. *Distler and Laputina* (1979); 7. Iwasaki et al. (1983).

Table 7. Concentrations of iridium and osmium determined in common minerals (wt.%)

Deposit	cob(Ir)	cob(Os)	gf(Ir)	gf(Os)	Method	Ref.
Copper Cliff mill	0.26%				EPMA	1
Pipe	0.19%				EPMA	1
Pechenga	5.8%	0.15%-3.2%	0.23%	9.6%	EPMA	2
Overall range:	0.19%-5.8%	0.15%-3.25%	0.23%	9.6%		

References: 1. Cabri and Laflamme (1981); 2. Distler and Laputina (1979)

palladium, with subordinate quantities of rhodium and ruthenium, in pentlandite associated with sulphide-poor, PGE-dominant deposits and some Noril'sk ores (Table 3).

Platinum. The database for trace platinum is not well-developed (Table 6). The Co- and Ni-sulpharsenides and arsenides in sulphide-rich Cu-Ni deposits such as Sudbury and Pechenga, as well as in the Duluth complex, contain some platinum but in much lower concentrations than palladium or rhodium. The relatively high platinum content listed under pentlandite (Table 6) is for the possibly new rhodium-bearing, ruthenian equivalent of argentopentlandite. Platinum was reported to be present in magnetite (Cabri *et al.*, 1981), but more work is necessary to verify this type of occurrence because the magnetite is closely associated with Pt–Fe alloys. New data on platinum in pyrrhotite and pentlandite for some Noril'sk samples were reported orally by Chryssoulis *et al.* (1991*a*). Pyrrhotite in disseminated ores contains from about 0.3 to 2 ppmw Pt, whereas pyrrhotite from massive ores has less than 0.1 ppmw Pt. Similarly, pentlandite in disseminated ores has 0.2 to 2 ppmw Pt, whereas pentlandite in massive ores contains less than 0.05 ppmw Pt.

Iridium and osmium. Very little is known about the mineralogy of iridium and osmium. They form well-known alloys with each other and with other PGE (Harris and Cabri, 1991), but only a few other minerals, such as irarsite and erlichmanite, are known. Iridium and osmium have been reported to occur in sulpharsenides from Pechenga and Sudbury (Table 7), but the distribution and concentration of these elements in common minerals can only be inferred from bulk assays.

Industrial products and environmental considerations

The distribution of trace precious metals in industrial products may be discussed in terms of three principal types of products, categorized according to the treatment that they receive, i.e. mineral dressing, extractive metallurgy, or manufacturing. A brief survey of the first two categories follows.

Mineral dressing products. The products of mineral dressing range widely in type, coming from anywhere in a mill circuit, but it is often the trailings that are the focus of study. The distribution of trace precious metals in mineral-dressing products is currently undergoing a revival, and quantitative mineral balances are possible because of the application of sensitive microbeam analytical techniques. For many gold-bearing ores, the concern is with sulphide refractory ores; i.e. ores which are not readily treated by conventional milling and cyanide extraction techniques. Examples of the trace gold distribution in tailings are those from the Trout Lake deposit (Manitoba) and the Olympias deposit (Greece), both mentioned previously. For Olympias, knowledge of the gold distribution and contrasts in concentrations of gold in As-rich and As-poor pyrite may be relevant to a grinding strategy of maximum exposure of the As- and Au-rich areas for selective dissolution or oxidation.

As discussed above, it is not always possible to distinguish between precious metals that are in solid solution or, say, those that occur as minute colloidal-size particles. It is interesting to note that Haycock (1937) concluded that, 'As regards actual milling practice, it may be of little significance whether sub-microscopic gold is merely very finely divided, colloidal, or in solid solution, because . . . the lower limit of visible gold falls below the lower limit of . . . cyanidation'. Though this statement is true, and in principle also applies to silver and the PGE, there are circumstances where this information is important. For example, preconcentrated gold-bearing concentrates may have the gold restricted to one or more sulphides such as arsenopyrite and pyrite, whereas colloidal-size gold can occur in several minerals, including gangue minerals (Chryssoulis, 1990). The positive correlation observed between gold and arsenic in gold-bearing pyrite (Chryssoulis and Cabri, 1990) may be an important consideration both for environmental and economic reasons.

A summary of research into the silver carriers at the Brunswick massive sulphide deposit (New Brunswick) is given in Cabri (1988*b*) and Chryssoulis and Surges (1988). Though some galena is an important silver carrier, great care must be taken to discern between areas containing fine sulphosalt inclusions (e.g. diaphorite) and inclusion-free areas of galena (Laflamme and Cabri, 1986*a,b*; Sharp and Buseck, 1992).

Data for the PGE in sulpharsenides and arsenides from mills in the Sudbury area are given in Tables 3, 4, 6 and 7. The distribution of rhodium is perhaps less-well understood in ores such as those at Sudbury (Kerr and Kipkie, 1985). There is no doubt, however, that the occurrence of rhodium in sulpharsenides and the close association of these sulpharsenides with rare rhodium minerals, together with the high frequency of these minerals as small inclusions in pyrrhotite, is a matter of concern (Cabri and Laflamme, 1984). On the one hand, sulphur abatement requires reduction of pyrrhotite in concentrates, but on the other hand, the high price of rhodium makes maximum recovery highly desirable.

Extractive metallurgy products. Refractory sulphide-rich gold-bearing ores have traditionally been treated by oxidative roasting of flotation concentrates (as a single- or two-stage process, depending on arsenic content) to produce a porous calcine that is more amenable to cyanidation (Demopoulos and Papangelakis, 1989). The process involves the topochemical breakdown of arsenopyrite and pyrite by gaseous diffusion of As and S to produce pyrrhotite (Swash and Ellis, 1986). The pyrrhotite then recrystallizes, diffusion becomes grain-boundary controlled, and further oxidation of the pyrrhotite may produce magnetite and hematite. Though oxidative roasting is a well established technology, it is considered less attractive than aqueous oxidation processes due to environmental concerns and demand for increasingly higher recoveries. The latter may be affected adversely by changes in roaster temperature and feed composition, which may result in incomplete gold liberation. Each metallurgical product, however, requires separate study. For example, most of the unleachable gold in the cyanide-leach residue from a particular calcine was determined by SIMS analyses to be contained within roasted pyrrhotite (67 ppmw), with only part of the gold occurring locked within iron-oxide particles (Chryssoulis, 1990). The location of As- and Au-rich zones on pyrite grain margins in some deposits is also of interest to metallurgical engineers. In a study done mainly on refractory ore from the Kalgoorlie region, it was found by SEM examination that only the smallest gold grains were trapped within iron-oxide minerals, representing an insignificant loss (Dunn *et al.*, 1989). On the other hand, these authors concluded that the coarser gold grains, especially those derived from the alteration of primary tellurides, may be the source of gold losses because they require longer leaching times for total dissolution.

In yet a different product, a matte (140 g/t Au) produced by smelting of a gold ore was examined by ^{197}Au Mössbauer spectroscopy. The spectra were interpreted as indicating that most of the gold was chemically bound in troilite (Wagner *et al.*, 1988). The only SIMS data on smelting products is a qualitative SIMS line scan showing gold distribution across phases in a PGE-bearing matte (Lindsay and Sellschop, 1988).

There is still research being done in testing new approaches to roasting to make the process less environmentally damaging, but most of the current work on refractory gold-extraction technologies involves hydrometallurgical methods (Demopoulos and Papangelakis, 1989). These new approaches are chiefly aqueous-oxidation routes: chemical oxidation, biochemical oxidation, and pressure oxidation. Little quantitative data are currently available on the trace distribution in products from such processes.

Smelting of copper-sulphide concentrates and pyrometallurgical treatment of copper scrap produces the bulk of the world's copper. In both cases, many impurities report to the copper anodes. PIXE and SIMS analyses of several copper anodes indicated low levels of gold which ranged between 61 ppmw (PIXE) and 7–16 ppmw (SIMS), demonstrating that the bulk of the gold is in solid solution in the copper (Chen and Dutrizac, 1991).

Besides the classic vein and disseminated silver deposits, much of the world's silver is recovered from base-metal ores that, typically, yield copper, lead, and zinc concentrates, or combinations thereof. Silver recovery from copper concentrates is usually very good, probably because most of the silver collects in the smelter matte and hence in the copper anodes. Chen and Dutrizac (1990) concluded that >95% of the silver occurs in a solid solution in copper anodes, based on EPMA with values ranging from 0.03–%0.44 wt.%. Good silver recovery is also possible from lead concentrate treated by conventional pyrometallurgical technology. However, in-plant hygiene problems associated with lead-bearing dusts and fines produced during conventional pyrometallurgical processing have provided an impetus for research into hydrometallurgical methods for treating lead concentrates. The research has met with mixed success, in part because silver recovery is very erratic (0–100%).

Silver losses from zinc concentrates are also very erratic and can be 100%, depending on the extractive process used. Over 80% of the world's primary zinc production is based on the electrolytic process, and this technology continues to expand at the expense of older, less efficient zinc processes (Temple, 1985). As zinc concentrates treated by the roast-leach-electrolysis process commonly contain 0–300 g/t Ag, the silver can be a valuable by-product of zinc processing (Dutrizac and Chen, 1990). A study of roaster products from the Kidd Creek Division of Falconbridge (Ontario) showed a complex silver mineralogy and distribution (Dutrizac and Chen, 1990). The bulk of the silver occurs as <0.5 μm grains of silver metal, but silver is also an important constituent of an abundant lead silicate phase (up to 1.37 wt.% Ag).

The recovery of PGE after milling of nickel-copper ores is largely done through pyrometallurgical–hydrometallurgical refining technologies, usually by first concentrating the PGE in magnetic alloys. The recovery of PGE in Canadian nickel/copper smelters is generally greater than 95% (Cabri *et al.*, 1988), and similarly high recoveries are typical world-wide. The newly operating process employed for Stillwater (Montana) Pd-Pt ore, electric furnace smelting followed by upgrading with oxygen-blown converting, gives recoveries of better than 99% (Hodges *et al.*, 1991). South African practice on treatment of PGE-dominant ores is to produce a matte containing all of the metals and subject it to pressure leaching and refining, again with high recoveries. There may, therefore, be little incentive to study the distribution of trace Pt and Pd in such operations, especially as the bulk of the PGE losses (which may be substantial) are thought to occur during mineral-dressing operations (Newman, 1973). Neverthelesss, tracking the more elusive PGE such as Rh and Ir in smelting, converting, or treatment of leach residues may prove profitable. Little is known about SIMS analyses of matte samples, except that Lindsay (1988) states that the Ni-poor matrix of Ni–Fe alloys inhibits the ionization of most of the PGE.

Conclusions and future directions

The trace-precious-metal database is growing rapidly, and it is now possible to predetermine the most likely carriers of several of these metals. Much more data must be gathered, as more minerals from more deposit types are studied quantitatively, possibly changing our understanding of the relative importance of gold- and silver-carrier minerals for different geological environments. Carriers for platinum and rhodium will be better understood and mineralogical balances for these elements will be achieved. All this accumulation of data will have implications for our understanding of the mineral chemistry (e.g. by HRTEM and STM) with possible spin-offs for mineral processing and environmental science through advances in surface chemistry. By providing better mineralogical balances for precious metals, the process mineralogist will be able to play a greater and earlier role in the design and implementation of processing flow-sheets.

Microbeam techniques capable of providing quantitative analyses of all the precious metals at trace levels are attracting wide interest, especially in process mineralogy, because of the practical applications. It seems likely that greater interest will be shown by the exploration and economic geology fraternity as the potential of reliable mineral-specific analyses at the ppmw and ppbw levels becomes appreciated. As was noted by Colvine *et al.* (1988) 'The absence of systematic studies of these mineralogical associations of gold is an obvious deficiency in the documenation of gold deposits. Much of the problem . . . is the lack of precise, detailed mineralogical studies completed within mine environments. Without an adequate data base, it is impossible to evaluate if such mineral associations are of fundamental significance to understanding how Archean lode gold deposits formed'. The application of the proton microprobe to diamond exploration is one example of the application of microbeam analyses of trace elements to mineral exploration (Griffin *et al.*, 1990) as is the non-destructive aspect of Micro-PIXE analyses of fluid inclusions during the study of hydrothermal deposits (Anderson *et al.*, 1989; Halden *et al.*, 1991). Likewise, the potential for studies of magmatic ore deposits through large mineral-specific, trace-element data bases, including the precious metals, has its attractions (Czamanske *et al.*, 1992). It can also be envisaged that the combination of trace precious-metal analyses by SIMS may be done on the same mineral grains that provide stable-isotope data, with obvious possibilities for new insight in understanding hydrothermal deposits.

The complementarity of these methods must always be kept in mind. Competition between different research groups will continue and it is those who apply the data who will make the final decisions on analytical methods. Price and availability are important considerations, but equally important is the reliability of the analyses coupled with an understanding of the ore mineralogy. Data will increase from research groups with access to more unique trace-element techniques such as AMS and SXRF. Some newer methods will be explored to solve particular problems involving trace elements that cannot be done with methods mentioned above, or that can be done more cheaply. Some of these methods will depend on laser applications such as LIMS (e.g. Chryssoulis *et al.* 1991*b*) or other commercially available configurations such as laser ablation ICP-MS (e.g. Broadhead *et al.*, 1990; Jackson *et al.*, 1990) which has attracted considerable interest due to the rapidity of analyses.

The use of scanning techniques for imaging trace elements is also bound to have a dramatic impact on future directions. Visual representation, combined with the quantitative documentation of the trace-precious-metal distribution, is very attractive. For SIMS, imaging with a resistive-anode encoder shows substantial promise (Elphick *et al.*, 1991; Marion *et al.*, 1991*a*). Similarly, the scanning-proton microprobe offers much (e.g. Campbell *et al.,* 1991). Each competing method will have to be carefully evaluated, mineral by mineral, with attention given to accuracy, precision and a clear understanding as to what each analysis represents. The future potential is indeed great.

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