Mr. President, Ladies and Gentlemen:

INTRODUCTION

I remember well the first MAC Presidential Address that I heard, by the late Dr. Hans Frohberg, in 1967. A mining engineer, trained at the famous Mining Akademie Freiberg, "where mineralogy for more than 200 years has been treated as a very important subject in the training of mining students", he wondered at the general lack of interest in mineralogy among North American mining engineers and geologists, especially since minerals provide their bread and butter. Dr. Frohberg impressed the audience with his examples of missed opportunities when economically important minerals were not recognized during expensive programs of exploration (e.g., the Eldorado mine on Great Bear Lake and the renowned Flat River tungsten deposit, N.W.T.). As a contrast, he cited the example of Dr. Dick Hutchinson who was curious about some minerals that originally has been logged as quartz-feldspar, and which proved on re-examination to be pollucite at the now famous Bernic Lake deposit, Manitoba (Frohberg 1967). I hope that, were he present today, he would appreciate the thrust of my talk, which concerns itself with the significance of learning more about the distribution of precious metals in common minerals such as pyrite, for example.

Regretfully, nineteen years later, I can only echo Dr. Frohberg's dismay at the current lack of appreciation of the usefulness of mineralogy. Today, moreover, we have available the most marvellous analytical tools, often used on a routine basis. Unfortunately, these are sometimes applied, in my estimation, without a proper understanding and sufficient knowledge of the minerals being analyzed! Sophisticated mineral analyses, without competent mineralogical input and guidance, are fraught with pitfalls, and the results could well prove to be misleading.

TRENDS IN THE MINERALOGY OF Precious Metals

Certain aspects of mineralogical science, like other areas of human endeavor, are influenced by "fashionable ideas" or by changing trends of thought as acceptance of a new discovery becomes influential. For example, ideas on the distribution of the platinum-group elements (PGE) were influenced for several decades by statements such as

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*President of the Mineralogical Association of Canada, 1984 and 1985.
that made by the renowned microscopist Schneiderhohn in summarizing his work on various ores from the Merensky Reef. He reported (in Wagner 1929) that he could not find "so much as a trace of a platinum or palladium mineral under the microscope, notwithstanding that a large number of excellent polished sections were submitted to the closest scrutiny, using the highest powers of magnification with oil-immersion objectives". It was not until the late fifties that early application of the electron microprobe to PGE-bearing ores (Noril'sk, Bushveld) began a new trend, one that resulted in suggestions that the bulk of the PGE occur as discrete platinum-group minerals (PGM) rather than dispersed as solid solutions (Stumpfl 1962, Cabri 1974, Cabri & Laflamme 1976). This view was, no doubt, reinforced by the steep increase in rate of discovery and characterization of new PGM that began in 1959 (Cabri 1980).

A personal experience concerning a mineralogical investigation that I performed on hand samples from a Pb-Zn prospect in 1973 is also relevant. The mineralogy was very simple: coarse-grained sphalerite, galena and pyrite associated with quartz and calcite. Routine electron-microprobe analyses of the sphalerite gave its Fe and Cd contents, and I predicted that exploitation of the deposit should not encounter any beneficiation problems. Whereas that proved correct, I did not appreciate, in 1973, that only some of the silver would be present in solid solution in galena and therefore report to the lead concentrate. This assumption proved costly because the metallurgical treatment of the concentrates results in large annual losses of silver. For example, mill feed in this particular mine in 1984 contained over 34,000 kg Ag (or 1 million oz). About 16% of this Ag was lost to tailings, and only 48% recovered from refinery products, i.e., probably something like 12,400 kg Ag (360,000 oz), annually, is held in solid solution in the sphalerite and thus is lost because metallurgical treatment is not designed for Ag recovery from Zn concentrates. This unrecovered silver is worth about $U.S. 1.9 million annually, taking silver at $5.00/oz.

Thus, mineralogists in the sixties and seventies were influenced by the capabilities of the electron microprobe in providing identifications and analyses of precious-metal minerals and of precious-metal-containing minerals. The detection of trace quantities of precious metals with the electron microprobe, however, was difficult, and detection levels were relatively high. Consequently, when accounting for the distribution of precious metals, one had to depend on the ambiguous results derived from bulk analyses. Today, we see a trend to a more balanced view on precious-metal distribution, a trend that is aided by several new in situ trace-element analytical techniques.

The Precious Metals

Traditionally, precious metals comprise gold, silver and the six platinum-group elements (Pt, Pd, Rh, Ir, Ru and Os). Their principal similarity is that they are generally of economic interest even when present in concentrations as low as a few grams per tonne (g/t) or parts per million (ppm). It is also relevant to consider a broader definition of "precious" metal due to the demand for certain elements. For example, gallium and germanium are commonly produced as by-products, but current high prices and predicted future demand have resulted in the opening of a new type of mine - a gallium-germanium mine (Dutrizac et al. 1986). A second aspect of the precious metals, and one I believe not to be widely appreciated, is that they can occur in three ways, if defined from a practical point of view. The first, and best known, manner of occurrence, is as discrete minerals of gold, silver or the PGE, ranging from the native alloys to a variety of minerals in which these elements are an essential and major constituent. The second way is what I refer to as the precious-metal-containing minerals, i.e., minerals containing nonessential quantities of precious metal(s), but more than about 1 wt.%. The third way, and one I believe not to be widely appreciated or understood, refers to the precious-metal-bearing minerals, i.e., those with concentrations generally less than about 1 wt.% of the precious metal(s). The subdivision between the last two is not arbitrary, but was proposed, in the case of silver, to denote the approximate threshold in concentration where one departs from routine analytical methods to employ more specialized methods and instrumentation (Cabri et al. 1984b).

Current Mineral-Processing and Metallurgical Practice

Mineral processing transforms mined ore into concentrates or other products suitable for subsequent metallurgical treatment designed to extract the desired metal. Flow sheets developed for any ore are based on knowledge of the mineralogy, past practice on similar ores, and on bench and pilot-plant testwork. The mineral-dressing engineer's principal concern is to liberate valuable minerals from the gangue; thus knowledge of mineral associations, grain sizes and textures is important to him. The type of concentrate produced is guided by the metallurgical processes to follow. If a proportion of the precious metals is held within a mineral, either as very fine microscopic or submicroscopic inclusions, or in the form of a solid solution, the precious metals cannot be liberated by grinding. Hence the distinction between, say, almost submicroscopic inclusions and a solid solution, is widely regarded to be academic among mineral processors. On the other hand, there
are other reasons for looking into this problem more deeply.

Let us look at the situation for gold. In 1984 losses of gold to tailings from Canadian mines, exclusive of placer mining, totalled over 14,000 kg (or about 446,000 troy oz), which is currently worth nearly U.S. $157 million (at $340/oz). This amount was divided nearly equally between primary gold producers and the by- and co-product producers. In addition, average gold losses to tails for all Canadian gold producers in 1984 were 17%. The lowest-grade Canadian gold ore mined and processed in 1984 was of the order of 3.4 g/t (0.1 oz/ton). Thus, if we assign a hypothetical 17% gold loss to tails, then the concentration of gold in the tailings is 0.578 g/t. Let's assume, further, that 20% of the gold in the tailings (0.116 g/t) is dispersed and that 80% occurs within a particular mineral that is normally rejected, say pyrite. Therefore, if we assume a not unusual proportion of 10% pyrite in the tailings, then 90% of the tails grade 0.116 g/t Au and the remaining 10% is pyrite with a concentration of 4.736 g/t Au, i.e., 40% richer than the original "ore"!

There are examples where detailed mineralogical investigations, combined with bulk chemistry of mineral separates, will provide a strong case for allocation of the "invisible" or unaccounted gold to different minerals. Consider, for example, the gold distribution in Porgera ore (Henley & Steveson 1979). In that particular case, direct cyanidation could extract only about 40% of the gold (present as native gold), and the bulk of the remaining gold (52.6% of the total) was thought to occur in a submicroscopic form in pyrite. The results, derived by inference, were successfully applied in this case, as the pyrite is now roasted. In another example, Hausen (1983) demonstrated that gold could not be observed in the fine-grained pyritiferous Carlin deposit and concluded that it occurs either in solid solution in pyrite or as inclusions smaller than 0.02 micrometres (200 Å). Hausen was able to demonstrate that whereas the oxidized ores at Carlin were amenable to simple cyanidation, the more refractory ores could be successfully treated by several processes of aqueous oxidation that were dependent on the porous nature of the fine-grained sphaleroidal pyrite (1 – 10 micrometres) because it had a large accessible surface-area. The coarser euhedral and denser pyrite (10 – 100 micrometres), however, is less easily oxidized and hence is considered very refractory. Hausen's conclusions were supported by some preliminary electron-microprobe results on Carlin pyrite and arsenopyrite (Wells & Mullens 1973). However, even experienced mineralogists remain sceptical that solid solution of gold in minerals is possible (Gasparini 1983), and it is therefore essential to prove more directly whether "invisible" gold occurs as submicroscopic inclusions or as a form of solid solution. If one or the other were proven, a data base of the various gold-bearing minerals for different deposits would be a valuable starting-point. Eventually, this base could be expanded to precise determinations of the nature of the distribution of gold within specific mineral species. Detailed mineralogical data on the gold content of all the gold-bearing minerals would permit the mineral-dressing engineer to consider the economics of concentrating minerals, otherwise rejected, for separate metallurgical treatment. This type of information, together with more detailed knowledge of the distribution of gold within a particular mineral, would be extremely valuable to the metallurgical engineer; he would then be in a better position to research and develop extractive methods for specific types of deposit, especially where roasting (with its usual sulfur and arsenic contaminations) is not suitable or economical.

A similar situation exists in the case of silver. A comparison of silver losses to tailings from Canadian mines between 1980 and 1984 reveals large and increasing losses over the four years, from 310,000 kg (10 million troy oz) to about 500,000 kg (16 million troy oz, worth U.S. $80 million today). To these quantities may be added the silver content of Canadian zinc concentrates, 140,000 kg in 1980 (or 4.5 million troy oz) and 163,000 kg in 1984 (or 5.2 million troy oz, worth U.S. $26 million), since a large proportion of this silver is in many instances not recovered. It is relevant to look at the mineral processing of silver-bearing base-metal ores where, typically, copper, lead and zinc concentrates (or combinations thereof) are produced. Silver recovery from copper concentrates is usually very good, and this is also true for lead concentrates where conventional pyrometallurgical technology is applied. However, in-plant hygiene problems associated with lead-bearing dusts and fines produced during conventional pyrometallurgical processing have resulted in research into hydrometallurgical methods for treating lead concentrates. These approaches have met with mixed success 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 (e.g., the jarosite conversion process: Dutrizac & Chen 1984).

It is, therefore, essential to characterize fully the silver distribution in such ores – not an easy task. Silver mineralogy, in contrast to gold mineralogy, is much more complex, owing to the large number of silver minerals (native silver, acanthite, freibergite, silver sulfosalts, etc.), silver-containing minerals (tetrahedrite, tennantite, etc.) and silver-bearing minerals. Detailed studies on the distribution of silver in New Brunswick ores and zinc concentrates at CANDRE, over a number of years (Jambor & Laflamme 1978, Chen & Petruk 1980, Petruk & Schnarr 1981), have either shown that a large propor-
tion of the distribution of silver is unknown or suggested different hosts for the unknown fraction by making different assumptions. It is, nevertheless, crucial to determine more precisely where all the silver is located; whereas these particular cited studies were competently done detailed investigations, none had access to a trace-analytical technique with greater sensitivity than the electron microprobe.

There are those, such as Henley & Steveson (1979), who stated when discussing the distribution of silver that chalcopyrite, galena, sphalerite and pyrite are known to commonly contain silver in solid solution. At the time that was written, this statement had not been substantiated by direct analyses, except for galena. It is only recently, as new trace-element techniques have been developed, that it has been possible to demonstrate by proton-microprobe analyses (Cabri et al. 1985a) and by the ion microprobe (Chryssoulis et al. 1985) that chalcopyrite, sphalerite and pyrite are indeed important carriers of silver. However, much more research is required to determine the nature of the silver content and to obtain a scientific understanding of the submicroscopic distribution of the precious metals.

The fact that nearly all the silver and half the gold lost to tailings occur mainly at mines where these precious metals are by-products is an additional reason why industry should be particularly interested in improving recoveries. Most of these mines are base-metal producers and, in view of the current depression in base-metal prices, with no obvious significant improvements in the short term, the situation appears to be a classic case for demand-driven research directed toward increasing recoveries of the precious metals. Higher precious-metal recoveries would allow Canada's base-metal mines to maintain continuous operations and to have longer productive years in spite of low base-metal prices; this would, in general, help create and maintain a healthier mining industry. This is especially relevant because much publicity has been given, in Canada, to "demand-driven" research, i.e., research undertaken in response to a clearly defined need (cf. the "Wright report", 1984). The need to know more about precious-metal mineralogy is easily demonstrated by enquiring into the current rate of metal recovery in the mining industry and the losses to tailings.

There are two aspects to reversing in an effective manner the trend of increasing precious-metal losses. The first is the need to know precisely where the precious metals are located in an ore; this is where the experienced mineralogist is most important. Secondly, we need to maintain good communications with the metallurgical industry so that metallurgists may be fully apprised of newly discovered mineralogical complexities in the pattern of distribution of the precious metals. In this way, traditional trends in metallurgical research may, in turn, be redirected at developing new processes based on modern mineralogical data. It is also true, of course, that other factors might influence the decision, but at least the decision made will be based on sound mineralogical data and not on ignorance.

**NEW DEVELOPMENTS FOR IN SITU TRACE-ELEMENT ANALYSIS**

I will briefly mention some of the exciting new techniques being developed and applied to the *in situ* analysis of trace quantities of precious metals in minerals. I will be extremely brief and just refer to those techniques with which I am most familiar. I suggest that those seeking more details on these and other new techniques attend the Special Session on Current Developments in Microanalysis Applied to Mineralogy and Geochemistry tomorrow morning.

The first of these techniques has become the workhorse of mineralogical microanalysis, i.e., the electron microprobe. Improvements in electronics and higher-quality diffracting crystals have reduced detection limits to as low as 25 to 50 ppm for some elements (Bence & Holzworth 1986). For the precious metals in sulfide matrices, however, we have to live with detection levels on the order of 200 ppm for silver, palladium and gold (L.a.). Advances in quantitative image-analysis by using backscattered-electron images obtained with a SEM will permit fairly accurate determination of the distribution of major elements (Reid *et al.* 1984, Petruk 1986). The distribution of the minor elements, such as those found in silver-containing minerals, may also be eventually obtained. This type of mineral analysis can be combined with detailed trace-element microanalyses obtainable by one of several methods; no one method is ideal for all elements in all matrices.

The proton microprobe (Micro-PIXE) has been successfully applied for the detection and quantitative measurement of concentrations of elements from Zn (Z = 30) to Sn (Z = 50). In particular, detection levels have been reported down to about 7 ppm for silver, 1.2-3 ppm for palladium, 1.6-3 ppm for rhodium and 14 ppm for ruthenium (Cabri *et al.* 1984a, 1985a). Where possible, results have been compared to those obtained with the electron microprobe. In the case of palladium in pentlandite, for example, comparisons were within ± 7% (Cabri *et al.* 1984a). More recently, trace analyses of chalcopyrite grains using two completely different proton microprobes were most encouraging, as most had ratios that fall to 1.18 ± 0.13 for silver and 1.07 ± 0.11 for indium (Campbell *et al.* 1987).

The ion microprobe (SIMS) has been used to determine the concentration of silver in sphalerite and galena to levels of about 5 ppm using synthetic standards (McIntyre *et al.* 1984). The method has been...
refined by Chryssoulis et al. (1985, 1986) by using an ion-implantation technique for standards. The results of Chryssoulis et al. on the silver distribution in ore samples from Brunswick Mining and Smelting Corp. Ltd. have direct implications on metal recoveries. The ion-implantation approach to quantitative SIMS analyses is also being applied, with promising results, to gold analyses. We believe that this technique will result in a sensitivity of less than 1 ppm Au in a pyrite matrix, something extremely useful when considering the levels of concentration that are currently economically interesting, as discussed earlier. This method can be particularly powerful, as the ion beam slowly sputters a few ångströms at a time, thus providing analytical data in depth.

The last of the new techniques that I will briefly mention is synchrotron X-ray-fluorescence (SXRF) microanalysis, in which minimum detection-levels of 300 – 500 ppb (Fe to Zr) have been reported for silicate minerals and 3 – 5 ppm for sulfide minerals (Se to Ag) (Rivers et al. 1986, Cabri et al. 1985b). This technique is still under development; the aim is to have the current 30–50 micrometre spot size reduced to about 1 micrometre.

THE CHALLENGE

We need to address the problem related to the elusive "invisible" portion of precious-metal distributions. We must also bear in mind, however, that minerals from different deposits must each be examined in detail because, as expressed by Bajon et al. (1982), "... each ore seems to have its own personality." Not only do we need to document representative and statistically credible precious-metal concentrations in many minerals, but we need to determine the exact reason for their "invisibility". Are they in the form of discrete submicroscopic particles or do they occur as a dilute solid-solution? If the presence of discrete particles is the answer, of what kind are they? Are they metallic alloys or are they precious-metal salts within fluid inclusions? If solid solution is the answer, what type of solid solution is it? How is it formed? How is the host mineral best treated in order to release the precious metal?

Because the problems I’ve highlighted relate to very low concentrations, we are somewhat limited in the approaches that can be brought to bear to solve the questions (e.g., we cannot use XRD, Mössbauer, NMR techniques, etc.). We have to rely mainly on in situ microanalytical methods of trace-element analysis and on our background knowledge, particularly of mineralogy. Most of the minerals of interest are sulfides, opaque to transmitted light.

We have, to date, analyzed a great many samples of sphalerite with the proton microprobe. These samples come from several deposits, but most are from the Kidd Creek and Brunswick No. 12 deposits. Spot analyses of two or more areas within single grains,
or of several grains from the same sample, show remarkable reproducibility at the ppm level for elements such as silver and indium. Analyses of Kidd Creek sphalerite, for example, have a reproducibility of ± 6.8% at a concentration of 300 ppm Ag; for In the reproducibility is ± 6% for low values (33 ppm) and drops to ± 1% for higher concentrations (2000 ppm). On the other hand, the relatively unmetamorphosed and locally silver-rich sphalerite from the Nanisivik (N.W.T.) deposit demonstrates a heterogeneity that is very interesting, as it appears to be correlated with the iron content (Fig. 1).

Once we have solved some of these problems and applied the data to a few deposits, we shall need to go one step further. We will then have to demonstrate the significance of our findings to the metallurgical engineers – hopefully not as formidable a task as solving the problems of precious-metal distributions.

**CONCLUDING REMARKS**

When I graduated from the University of the Witwatersrand with a B.Sc. (Hons.) in 1955, I knew little about mineralogical analytical techniques, except for some microscopy. The next four years of geological field-work for the mining industry in humid African jungles and arid deserts distanced me even further from advances in mineralogical analytical techniques. For example, I was introduced to the XRD and XRF techniques only after arrival at McGill University – no electron microprobe in those days! Whereas it is important to appreciate how far we have advanced in this short period, it must be remembered that the microscope remains at the heart of all our investigations. Without a proper understanding and use of the microscope and microscopic methods, the most sophisticated investigation is for naught. Let us hope that this message will be noted and remembered!

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