## GUIDELINES FOR THE CALCULATION AND USE OF SULPHIDE METAL CONTENTS IN RESEARCH AND MINERAL EXPLORATION

A. Kerr Mineral Deposits Section

### ABSTRACT

The metal contents of samples of magmatic sulphide mineralization are generally correlated with their sulphide contents, because the metal content of bulk sulphides remains approximately constant in this environment. Sulphide metal contents provide valuable information in mineral exploration and research, and are readily calculated if the mass fraction of sulphides is known. The latter is most simply calculated from the measured sulphur content using an assumed sulphur content of 35.7% S for a typical pyrrhotite–chalcopyrite–pentlandite mixture. There appears to be little advantage in accounting for the individual sulphide minerals in the sample. For samples containing > 10% S, calculations are very robust, but lower sulphur contents generally demand at least some correction for metals contained in nonsulphide minerals. These can become significant below 5% S, and/or in olivine-rich samples. Corrections can readily be performed by simple mass-balance calculations, using concentration data from unmineralized host rocks.

Significant uncertainties are introduced by analytical errors for sulphur and metals, which are commonly measured from separate sample aliquots. The combined errors in calculated sulphide metal contents will generally exceed  $\pm 10\%$ , but get larger at low S contents. Caution must generally be used in the treatment of data from samples containing < 2.5% S, especially for the PGE. Application of the method in simple grade-potential assessment is easy, but research-oriented studies involving sulphide-poor samples are more problematic. Invalid correction of data for nonsulphide-hosted metals can lead to false negative or positive correlations between metal contents and sulphide content, which itself could be linked to geological parameters, such as depth within an intrusive body. There are also several valid geological reasons for such correlations, but data of this type require careful assessment to separate true variation from artifacts. Propagated analytical uncertainties are largest in sulphide-poor samples, for which corrections may also be required. These potential inaccuracies must be borne in mind whenever data from different localities or mineralization types are compared and contrasted. Simple charts allow assessment of the reliability of data in various situations, and spreadsheet programs were developed for easy recalculation of data.

#### **INTRODUCTION**

In magmatic sulphide deposits, such as Voisey's Bay, ore-metal concentrations are typically strongly correlated with the sulphide content of samples. In many producing deposits, such as those of the Sudbury area, face samples are rarely assayed, because visual estimates of the amounts of sulphide content suffice for grade-control purposes. This correlation reflects the fact that essentially all base metals and platinum-group-elements (PGE) are contained in sulphide minerals, and that the bulk sulphide fraction shows a narrow range of values for these elements, within a given deposit. This parameter is called the sulphide metal content or tenor; in this article the first term is preferred, because "tenor" can also refer to the proportion of sulphides within an ore sample. Calculated sulphide metal contents represent a grade projection for material consisting of 100 percent sulphides, and thus provide an upper limit for undiscovered massive sulphide deposits on a given property. However, they provide no inference as to the actual existence of such deposits! Sulphide metal contents also permit the examination of subtler variations in metal contents and metal ratios from a more academic perspective (e.g., Lightfoot et al., 2001a, b). Perhaps the most useful application of calculated sulphide metal contents is in comparing and classifying magmatic sulphide mineralization, by removing "noise" linked to variations in sulphide content. The procedure is quite common in exploration, and increasingly popular in research applications, although there are few formal descriptions and evaluations of it. This article outlines the procedure and provides some guidelines for the use of such calculations in different types of studies. For a more detailed discussion, readers are referred to a forthcoming article in Exploration and Mining Geology (Kerr, in press).

### SUMMARY OF CALCULATION METHODS

#### BASIC PRINCIPLES

In a typical sample of magmatic sulphide mineralization, virtually all of the base metals and PGE reside in the sulphides. Nickel and Co are generally in pentlandite, and Cu in chalcopyrite, but all the metals were originally dispersed in a high-temperature sulphide mineral termed Monosulphide Solid Solution (MSS), which converted to pyrrhotite, pentlandite and chalcopyrite as it cooled. PGE may be hosted in chalcopyrite or pentlandite, but they may also occur in a wide variety of rarer sulphide, telluride and arsenide minerals. The main sulphide minerals have similar sulphur contents, i.e., 33.3% (pentlandite), 34.9% (chalcopyrite) and 36.5% (pure FeS - i.e., troilite; natural pyrrhotite will be more S-rich, as it is metal-deficient). If all metals are in sulphide minerals, the sulphide metal contents can readily be derived from the whole-rock analysis, providing that the mass fraction of sulphides is known. The latter can be derived by dividing the sulphur content of the sample by the assumed sulphur content of a rock consisting purely of sulphides. As the dominant sulphide mineral is usually pyrrhotite, a common approach is to assume a value of 36.5% S for pure sulphides. The sulphide metal content is then obtained by dividing the whole-rock metal content by the mass fraction of sulphides. For example, if a sample contains 4000 ppm Ni, and 7.3% sulphur, the mass fraction of sulphides is 0.2 (i.e., 7.3 / 36.5), and the sulphide metal content is 20 000 ppm (i.e., 4000 / 0.2), or 2% Ni.

All calculations involve this basic method, which is simplistic, because some metals can reside in silicates, and the sulphides include more than one mineral. The procedure is also commonly an extrapolation because the samples may actually contain only small amounts of sulphides. Extrapolations are prone to error propagation, and there are several potential sources of errors, which also need to be considered in interpreting data.

# CALCULATING THE MASS FRACTION OF SULPHIDES

Methods for calculating the mass fraction of sulphides differ only in the assignment of an assumed sulphur content for pure sulphides. There are essentially two approaches, i.e., to use an arbitrary value (as outlined above), or to endeavour to account for the sulphide minerals individually.

In previous articles (e.g., Kerr, 1999), the author assigned a value of 35% S for pure sulphides. This is an underestimate, as pyrrhotite (>36.5% S) is generally the dominant sulphide. This choice was deliberately made to ensure that estimates of sulphide metal contents remain conservative. Naldrett *et al.* (2000) and Li *et al.* (2001) summa-

rize the more complex methods. In these, Ni and Co are combined, and assigned to pentlandite. The latter is assumed to have a combined (Ni+Co) content of 36%, typical of material from Sudbury. The sulphur required to make pentlandite is then subtracted from the total sulphur content. Copper is then assigned to chalcopyrite, and the total sulphur content is again corrected. The remaining sulphur is then assigned to pyrrhotite, using either the ideal FeS formula (Naldrett *et al.*, 2000) or Fe<sub>7</sub>S<sub>8</sub> (Li *et al.*, 2001). The sulphur content of a rock containing 100 percent sulphides is then readily calculated from the proportions of the three sulphide minerals and their ideal sulphur contents. This method also results in a slight underestimate if "ideal" FeS is used, but it may result in an overestimate, if Fe<sub>7</sub>S<sub>8</sub> is used.

Calculations suggest that differences between these methods are trivial. Typically, the differences in calculated sulphide metal contents are less than 0.1 wt%, and are insensitive to Ni/Cu variations, except at very low sulphide contents. A close fit to the method of Naldrett *et al.* (2000) was obtained by using a slightly revised value of 35.7% for 100% sulphides. Compared to the uncertainties introduced by analytical errors, and those involved in correction for nonsulphide-hosted metals, such differences are negligible. There thus appears to be no advantage in the more complex approach.

# CORRECTIONS FOR METALS IN NONSULPHIDE MINERALS

There are instances where essentially all metals reside in sulphide minerals, as for example in discordant sulphide mineralization hosted by monomineralic anorthosites. However, in most cases, some metals will reside in silicate minerals such as olivine and pyroxene, and perhaps also in iron oxides. In particular, olivine-bearing rocks are likely to contain significant silicate-hosted Ni. Under some circumstances, corrections must be made for these metals.

Mass-balance equations dictate that :

$$X_{WR} = (X_{sulph} * M_{sulph}) + (X_{other} * M_{other})$$
(1)

where X indicates the concentrations (in whole-rock, sulphides, and other minerals, respectively) and M indicates the relevant mass-fractions of each. Rearrangement of equation (1) shows that the *true* sulphide metal content is given by :

$$X_{sulph} = [X_{WR} - (X_{other} * M_{other})] / M_{sulph}$$
(2)

Thus, corrected sulphide metal contents are readily obtained if the concentration in bulk nonsulphides is known, because  $M_{other}$  is given simply by [1 -  $M_{sulph}$ ]. Sulphide metal contents used in previous articles (e.g., Kerr, 1999; Kerr and Smith, 2000) were corrected via this method, using values for X<sub>other</sub> based upon analytical data from unmineralized host rocks of analogous composition. If such data are unavailable, an arbitrary value can be substituted.

Nonsulphide metal corrections suggested by Naldrett et al. (2000) use essentially the same method, but account only for Ni in olivines. The calculation of the Ni content of olivine is based on the observation that Ni/Fe<sub>(olivine)</sub> = (Ni/Fe(sulphide) / 25) in samples from Voisey's Bay, in which the olivines are believed to have reequilibrated with sulphide liquid (Li and Naldrett, 1999). Assuming an olivine composition of Fo<sub>65</sub>, the Ni content of coexisting olivines (Xolivine), is obtained from the uncorrected sulphide metal content. The method also requires an estimated value for the modal proportion of olivine (Molivine) in the nonsulphide portion of the sample, from which the bulk nonsulphide Ni content is derived for use in equation (2). Calculations show that the magnitudes of corrections using this method resem ble those from the simpler method, providing that the modal proportion of olivine lies in the range of 20 to 40%. However, the magnitude of corrections increases at higher sulphide metal contents, whereas it remains essentially fixed in the first method.

It is evident from equation (1) that the contribution of sulphides to the whole-rock metal contents will be overwhelming if  $M_{sulph}$  is significant because the concentrations in sulphides will generally be at least two orders of magnitude greater than in the bulk nonsulphides. In rocks that contain large amounts of sulphide and in which sulphide metal contents are high, the contribution of metal from sulphides is so overwhelming that any correction is unnecessary (*see below*). At low sulphide contents (or if sulphide metal contents are low), the first method has several advantages, in addition to being simpler to calculate. First, it requires no assumptions about olivine contents, compositions or Fe/Ni partitioning effects. Second, it is more readily adaptable to local circumstances.

# THE IMPORTANCE OF NONSULPHIDE METAL CORRECTIONS

Nonsulphide metal corrections are inversely correlated with the mass fraction of sulphides, and become most significant as  $M_{sulph}$  approaches 0. They are also inversely correlated with the ratio between the metal contents of sulphides and nonsulphides ( $X_{sulph}/X_{other}$ ), and become less significant at high sulphide metal contents.

These relationships are best illustrated by graphing the required correction (here expressed as a negative percentage



**Figure 1.** Curves expressing the magnitude of corrections for metals contained in nonsulphide minerals as a function of the amount of sulphur, and the ratio between the uncorrected sulphide metal content ( $X_{sulph}$ ) and the estimated bulk nonsulphide metal content ( $X_{other}$ ). Typical relative values for  $X_{sulph}/X_{other}$  for the Voisey's Bay deposit in Labrador are also indicated. See text for further explanation.

of the uncorrected sulphide metal content) and the ratio  $X_{sulph}/X_{other}$  (where  $X_{sulph}$  is the uncorrected sulphide metal content). Figure 1 shows several curves for variable amounts of sulphur in a sample, ranging from 0.1% to 30%. If the estimated value of  $X_{sulph}/X_{other}$  for a given sample does not intersect the appropriate sulphur content curve, the correction exceeds –100 percent, and the procedure is meaningless. This outcome may indicate that sulphides are metal-free, but it more likely reflects overestimates of  $X_{other}$ . At low S contents, corrections may be very significant unless the sulphides are very metal-rich. Conversely, at high sulphide contents, corrections are insignificant unless the sulphides are very metal-poor. The graph in Figure 1 is useful in indicating whether or not nonsulphide metal corrections are needed in a given situation.

Figure 1 also shows that the interpretation of data from sulphide-poor rocks that contain metal-bearing nonsulphide phases could be difficult. In the absence of correction, there will be an apparent inverse relationship between sulphide metal contents and the amount of sulphide, even if the true sulphide metal content is constant. Conversely, overly conservative corrections for sulphide-poor samples could lead to false patterns in which corrected sulphide metal contents are positively correlated with sulphur abundance. Sulphide metal contents and sulphur abundance have been noted to be inversely correlated (e.g., Barnes *et al.*, 1997; Kerr, *in* 

*press*), but viable geological explanations exist for such patterns. When dealing with sulphide-poor rocks, the sulphur content of samples, and the precision of such data, must be closely monitored. Also, reliable "background" data from sulphide-free samples should routinely be acquired, so that corrections are as accurate as possible.

The magnitude of required corrections will also vary for different elements. In unmineralized mafic rocks, Ni and Co commonly have similar abundances, but magmatic sulphide deposits have much higher Ni/Co ratios, and the ratio  $X_{sulph}/X_{other}$  will generally be an order of magnitude greater for Ni than for Co. Calculated sulphide Co contents from S-deficient samples are thus unreliable, and other methods of estimating this parameter should be used. Sulphide Cu contents are the least sensitive to corrections, but this advantage is balanced by more intrinsic "geological" variation, mostly due to fractionation during crystallization of sulphide liquids (e.g., Barnes *et al.*, 1997).

### ERRORS IN CALCULATED SULPHIDE METAL CONTENTS

The results of any calculation are only as accurate or reliable as the input data. In the case of sulphide metal content calculations, input errors come from analyses of metals, and analyses of sulphur content. Furthermore, base metals, PGE's and sulphur are generally analysed using different techniques, from discrete aliquots of the original sample. Thus, sample heterogeneity may also be an important consideration. As outlined above, nonsulphide metal corrections become important at low sulphur contents, or when metal concentrations are low, or when both situations apply. Thus, all of these potential problems converge at low sulphur contents and low concentrations.

Precision for sulphur analyses (Leco furnace method) was investigated for within-batch duplicates at a single laboratory and sample splits analyzed at two different laboratories. Within-batch duplicates are precise to  $\pm 4\%$  or better at all concentrations, but inter-laboratory precision is worse, and at low S concentrations precision is as poor as  $\pm 10$  to 15%. Some samples containing > 20% S also exhibit poor precision, suggesting that sample heterogeneity plays a role. Given that sulphur analyses almost always involve an aliquot separate from that used for metals, this suggests precision of  $\pm 5\%$  at all levels, degrading to  $\pm 10\%$  below about 2.5% S, and perhaps further degrading below 1% S.

Precision for base metals at the Department of Mines and Energy (ICP-ES method) was assessed from almost 300 duplicate analyses undertaken between 1996 and 1998 (Finch, 1998; unpublished data). Average precision for all data ranges from  $\pm$  5% for Ni to  $\pm$  6.5% for Cu. This improves significantly at intermediate values typical of weakly mineralized samples, ranging from  $\pm 2.9\%$  for Co (> 50 ppm) to  $\pm 4.6\%$  for Cu (> 100 ppm), but degrades again above 1000 ppm. Thus, conservative estimates of precision for base metals are around  $\pm 5\%$  to  $\pm 6\%$ .

Kerr (2002) recently presented results from a survey of the PGE contents of Labrador magmatic sulphides, using fire assay/ICP-ES analysis. Data from duplicate analyses (separate sample splits) indicates that analytical precision is poor below 100 ppb, likely worse than  $\pm$  10%, with very significant degradation approaching detection limits. Above 100 ppb, an appropriate conservative estimate of precision is at least  $\pm$  10%. Reanalysis of anomalous PGE values for verification purposes at a different laboratory resulted in differences in PGE contents of up to 50%, suggesting that sample heterogeneity and/or "nugget effects" from discrete Ptand Pd-rich mineral phases are also a potential problem (Kerr, 2002).

The combined effects of analytical uncertainties for sulphur and metals upon calculated sulphide metal contents are illustrated in Figure 2. This relates precision in metal analysis to total combined uncertainties, with a series of lines indicating variation in the precision of sulphur analysis. This assumes that errors in metal contents and sulphur contents are inversely correlated, which is unlikely, so these lines are conservative estimates, but they are large. For example, precision of  $\pm$  10% for both sets of input data yield combined uncertainties of +22.2% and -18.2% (mean 20.2%) in calculated sulphide metal contents. If the precision of sulphur analysis improves to  $\pm$  2%, these drop to +12.2% and -11.8% respectively (Figure 2a). The positive error is always greater than the negative error because it involves greater extrapolation, and the imbalance between the two grows with increasing uncertainty. The absolute magnitudes of errors can be quite high. For example, in a sample containing 1000 ppm Ni and 1% S, the total potential uncertainty in sulphide Ni content is 1.4% Ni, which is clearly significant in economic terms. Uncertainties in sulphide metal contents that are corrected for nonsulphide metals are greater than for uncorrected values, although this difference diminishes with increasing sulphur and metal contents. There are of course also uncertainties involved in the correction procedure itself, but these are more difficult to quantify.

Figure 2b is useful as a general guide to the assessment of potential total uncertainty as a function of analytical precision for metals and sulphur. Under most circumstances, uncertainties of  $\pm$  12% or so should be expected. The potential uncertainties are greatest below 1% S, where precision degrades, or if the analyses of metals are imprecise, as they may be for PGE. Combined uncertainties of  $\pm$  40% are entirely possible under these circumstances, and caution



**Figure 2.** Illustration of compound errors in the calculation of sulphide metal contents. (a) Positive (overestimate) and negative (underestimate) errors due to analytical uncertainties for metals ranging from  $\pm 0\%$  to  $\pm 20\%$ , with analytical uncertainties of  $\pm 2\%$  and  $\pm 10\%$  for sulphur. (b) Average combined uncertainties related to analytical precision for metals and sulphur. Note that labels on the lines indicate analytical precision for sulphur.

must be used in recalculation of any PGE data at low sulphide contents. There are also other reasons to be wary of calculated sulphide PGE contents. The uncertainties implied by Figure 2 must be borne in mind whenever data from different areas or mineralization types are compared and contrasted.

### SUMMARY AND CONCLUSIONS

A comparison of techniques for calculation and correction of data to obtain sulphide metal contents shows no great advantage for complex methods over simple ones, and the latter are thus recommended in most situations. In mineral exploration, where the prime objective is to assess the grades of potential massive sulphides, analytical uncertainties and corrections for nonsulphide-hosted metals are generally unimportant. Corrections are likely to be trivial unless the sulphides are metal-poor, in which case the accuracy of the results is largely irrelevant, because all grade predictions will be poor. However, overcorrection must be avoided, preferably by the acquisition of "control data" from unmineralized host rocks. Analytical errors can be a significant problem if the samples are poor in sulphides.

The treatment of data from sulphide-poor silicate rocks is inherently more complex. Correction for nonsulphidehosted metals, and propagated analytical uncertainties, may become very significant. All these problems converge below 5% S, and may become critical below about 2.5% S. For base metals, the calculation of sulphide metal contents from samples containing < 1% S is not recommended, unless the host rocks can be shown to be devoid of metals, and nonsulphide metal correction will generally be required below about 5% S. Correction is best approached through massbalance calculations, using input data from unmineralized samples. It must always be remembered that undercorrection can cause false trends where metal contents are negatively correlated with the amount of sulphide, and overcorrection can generate false positive correlations. As the amount of sulphide may also vary systematically (e.g., increasing toward the base of a magmatic body) such trends may be assigned unwarranted geological significance. The distinction of true geological variation from this artificial variation is perhaps the most difficult challenge in the interpretation of data from sulphide-poor rocks.

Sulphur and metals are commonly analyzed from separate aliquots, often at different laboratories, and sample heterogeneity may affect precision for all. Precision for sulphur degrades below about 5% S, where nonsulphide metal corrections become significant, and this adds to total uncertainty at these levels. Base metals exhibit reasonable precision (around  $\pm 6\%$ ) in the range typical of most silicate-dominated rocks. Typical exploration-quality PGE data exhibit poor precision unless sulphides are PGE-enriched, and the recalculation of such data from sulphide-poor samples is unwise. For base metals, total combined errors in calculated sulphide metal contents above 5% S are likely to be at least  $\pm 10\%$ , and these will be worse at lower sulphur contents. These propagated analytical errors must be considered whenever sulphide metal contents are used to characterize different "types" of mineralization, as subtle differences may be more apparent than real. Sulphide PGE contents encounter a further problem, because there is no guarantee that they are hosted by common sulphides, or even by sulphides at all. In rocks that have low S contents, such calculations may be very misleading.

To summarize, calculated sulphide metal contents have unquestioned value in the evaluation and study of magmatic sulphide deposits, and should be an important part of any exploration program. Calculations are generally robust, but results must be interpreted with knowledge of potential problems, particularly in samples that are sulphide-poor. These complications certainly do not preclude the use of the method, and there are valid geological reasons for many variations in sulphide metal contents described in the literature. Figures 1 and 2 provide guidelines for assessment of correction problems and analytical error, and should prove useful in assessing data of this type.

### SPREADSHEETS FOR EASY CALCULATION

The calculations involved in obtaining sulphide metal contents are not complicated, but they are undeniably tedious. Spreadsheet programs were developed for the calculation and correction methods discussed in this article, and are available as an open file (Kerr, 2003). The spreadsheets are available in Lotus 1-2-3 and Microsoft Excel versions, and include documentation and help screens. A separate spreadsheet is provided for the more complex method of Naldrett et al. (2000). The spreadsheets are not designed for the processing of large amounts of data, and present individual records in column-format, rather than row-format, because this makes it easier to compare uncorrected and corrected data. However, they can easily be modified by users to suit their specifications. The relevant open file can be obtained on diskette or by e-mail from the Geological Survey, Geoscience Publications and Information Section (www.geosurv.gov.nf.ca)

### ACKNOWLEDGMENTS

This article was prompted largely by conversations with exploration geologists in Labrador concerning such calculations. Chris Finch of the Department of Mines and Energy laboratory is thanked for providing data on analytical precision and accuracy. Don James and Baxter Kean are thanked for their comments on the initial version of this article.

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