Supp/Appendix 1 – Calculation protocol for MgO-FeO parent magma estimates

The process of estimating MgO and FeO contents of parent magmas to intrusions requires multiple steps:

1) Correction of FeO for sulfide content and FeO/Fe$_2$O$_3$ ratio
2) Use of Molar ratio variation diagrams, , to extract subsets of samples approximating pure olivine-liquid mixtures;
3) Use of different molar ratio plots to extract composition of the olivine component;
4) Use of a combination of FeO vs MgO plots with known Fe/Mg distribution coefficients between olivine and liquid to calculate the liquid component composition in equilibrium with that olivine.

This method has been used in number of studies, starting with (Chai and Naldrett 1992) most recently (Taranovic *et al.* 2022) for the host intrusions to the Nova-Bollinger deposits.

FeO-Fe2O3 correction

Conventionally, Fe is split between the divalent and trivalent oxides on the assumption that ten percent of the Fe is present as Fe3+ (Fe2O3). However, this assumption is valid only for liquids. Fo an olivine adcumulate, all of the Fe in rock is in olivine and will all be FeO. We therefore use a sliding scale as follows: pre adcumulate, FeO/(total Fe)= 1, mesocumulate =0.97, orthocumulate = 0.95, non-cumulate = 0.9. If it is not possible to make this assessment reliably, assume that all the cumulates are orthocumulates and use the value 0.95. A more complex (but probably unnecessary) correction is described in Supp Appendix 2.

Correcting Fe for sulfide-associated Fe.

The Fe content of the sulfide can be estimated assuming stoichiometry of the sulfide fraction, following the widely-used "sulfide norm" procedure, with all Cu assumed to be present in chalcopyrite. The method depends on an assumed value of the molar ratio S/[Fe+Ni], henceforth abbreviated as SM. In most magmatic sulfides, SM is between 1 and 1.3, corresponding to the typical pyrrhotite – pentlandite – chalcopyrite assemblage with minor pyrite, but we can usually assume a value of 1. (All Cu is still assumed to be in chalcopyrite, with S/[Cu+Fe]=1). Under these assumptions, the following equation applies:

Fe(sul)={(S/32)-(Cu/63.5)*(1/SM)-(Ni-Nisil)/58.7}*55.8   [3]

Where Fesul = Fe associated with sulfide, S, Cu and Ni are raw whole rock values, Nisil is the estimated content of background silicate Ni and SM is the molar ratio S/[Fe+Ni] in the sulfide assemblage. Silicate Ni is best obtained by determining the intercept on the Ni access of a linear regression on a plot of Ni vs. S. Total silicate FeO* in the rock is then obtained by difference:

$$FeO^* = FeO(total) - 1.29 \times Fe(sul)$$

Where FeO total is the total Fe content in the rock expressed as FeO.

All values are in weight %. This calculation then gives an approximation of the weight % sulfide component in the rock. It should be noted that the precision of this correction becomes progressively worse as the sulfide content increases, but this method is reasonably reliable for S contents of <5%. A more detailed analysis of error propagation can be found in Supp Appendix 2.

Identifying olivine cumulates - Pearce Element Ratio plots

Molar ratio variation diagrams, also sometimes referred to as Pearce Element Ratio plots (Pearce 1968), use molar ratios of elemental components of cumulus minerals to excluded elements not present in those minerals. A full explanation of the principles behind these plots is given by (Stanley and Russell 1989) and details of the calculation are given in the appendix. An example of application of the most useful of these plots is shown in Figure 15, using a large body of data from the Fraser Zone of the Albany Fraser Orogen in Western Australia. The molar ratio of SiO_2 to the excluded component TiO2 is plotted against the molar ratio of [MgO + FeO*] to TiO_2. Where FeO* refers to the sulfide and ferric-iron corrected FeO as outlined above. Accumulation of olivine to form olivine cumulates generates a data array with a slope of 0.5, corresponding to the stoichiometric mineral formula of olivine; accumulation of orthopyroxene alone gives a slope of 1, and accumulation of cotectic proportions of 40% pyroxene and 60% plagioclase (cumulate norite or gabbronorite) gives a slope of about 2. This plot very clearly discriminates ultramafic and mafic cumulates. The Fraser Zone rocks define a distinct olivine trend, (Taranovic et al., 2021), a distinct cotectic norite or gabbronorite trend, a mixed olivine-orthopyroxene trend mainly defined by the more orthocumulate rocks of the ore-hosting Lower Intrusion, and steeper trends defined by country rock mafic paragneisses and amphibolites.
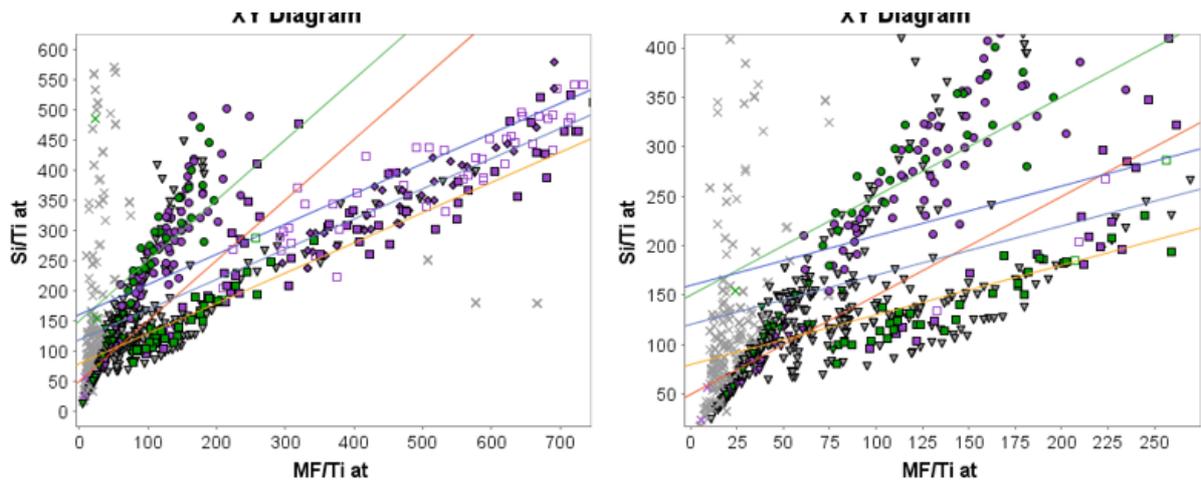
Figure 1 PER plots. Coloured data points are from the host intrusions to the Nova-Bollinger deposit.

Once a suite of olivine-only cumulates has been identified, trends of MgO vs FeO* within this suite can be inverted to give estimates of the MgO and FeO* contents of the average magma from which they crystallised. The process involves regressing FeO* on MgO and projecting the regression line to intersect radiating lines from the origin of constant FeO*/MgO ratio, where the target ratio is that of the melt in equilibrium with the average olivine composition. The latter is represented by the intersection of the regression line with the composition line for pure olivine determined from stoichiometry. Alternatively, the average cumulus olivine composition for the trend can be obtained from a regression of molar Fe/Ti vs Mg/Ti (Fig supp xA), then the olivine-liquid mixing line obtained by projecting a line between this olivine and the average orthocumulate whole rock composition. The (large) uncertainty in this graphical calculation can be determined by estimating the likely uncertainty in the regression estimates; visual inspection is generally the best method. An example of such an stimate is given in Fig supp xB.
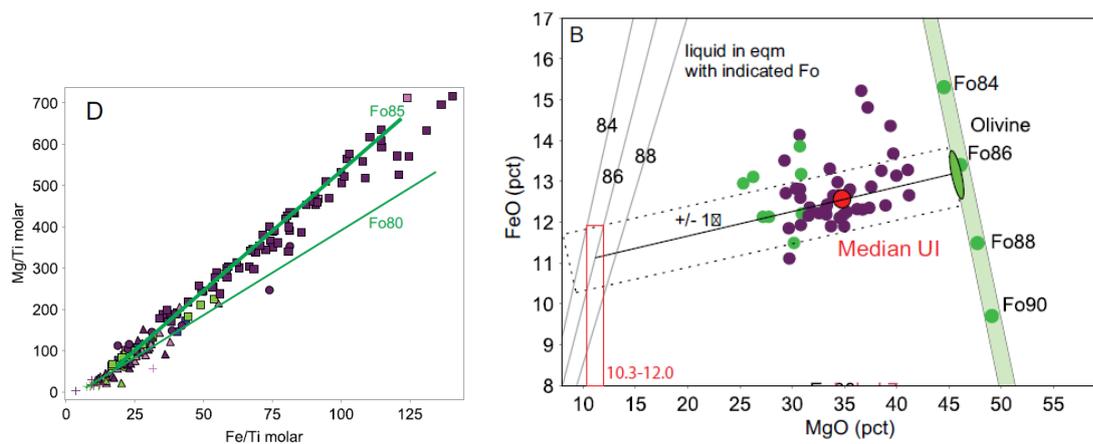
A more complex calculation can be performed using a spreadsheet associated with this resource, name.xls. This starts with an average orthocumulate composition, and subtracts olivine of the estimated average Fo content in various proportions until the calculated KDFeMg

molar(Fe/Mg)(liquid)/(molar(Fe/Mg)olivine) reaches the accepted equilibrium value of 0.30. The calculation

This method has the advantage of yielding a full major element composition estimate for the liquid component, but is also subject to significant propagation of errors.

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Volatile-free and sulfide-free normalisation of whole-rock analyses of komatiites and mafic-ultramafic cumulate rocks, and estimation of disseminated sulfide tenors.

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Supplementary Appendix 2 associated with **Lithogeochemistry in exploration for intrusion-hosted magmatic Ni-Cu-Co deposits**

(manuscript submitted to GEEA, May 2022).

1. INTRODUCTION

Ultramafic rocks, particularly komatiitic olivine cumulate rocks, are highly susceptible to addition of volatile components during alteration. Komatiites and ultramafic cumulates are universally hydrated or carbonated (or both), resulting in "Loss on Ignition" values commonly about 10 weight %, and in some cases of talc carbonate alteration in excess of 20 weight %. In most cases, it appears that alteration proceeds largely by addition of water with or without CO_2, and that the relative proportions of the major components MgO, SiO_2, Al_2O_3, TiO_2 and FeO, and minor and trace components such as Ni, Cr, V and Zr, remain relatively unchanged during the process (refs). Interpretation of whole rock geochemical data on komatiites therefore requires a consistent process of normalising the whole-rock analysis to

100% volatile free, and it is desirable to have a consistent methodology so that results from different studies can be compared.

The methods presented here were originally developed specifically for komatiites, but most are equally applicable to any mafic or ultramafic rock.

A number of authors have suggested that komatiites had primary water contents of the order of several percent, whereas the method described here assumes that they were initially entirely "dry". Regardless of the validity of the "wet komatiite" hypothesis, and given that it is impossibly to directly assess the primary water content of an altered rock, it is necessary to standardise, and the simplest process is to normalise to a completely volatile-free analysis.

Komatiitic rocks commonly contain a component of what was originally magmatic sulfide liquid. It is desirable to be able to calculate the primary silicate composition of the rock by "extracting" this sulfide component, and vice versa. In the case of S-rich rocks, it is also possible in principle to extract the composition of the sulfide component of the rock, which is very useful in studies of (or exploration for) magmatic sulfide deposits.

There are a number of different ways of doing these calculations, and a number of peculiarities of komatiite petrology and geochemistry which require a customised approach. In the interests of standardisation, this contribution describes a consistent methodology which takes these peculiarities into account. The algorithms described have been incorporated into an Excel spreadsheet, components of which are described in detail below, and which can be obtained from the author on request (or available on the journal's website).

The methodology is designed specifically for komatiites, but is potentially applicable to all ultramafic rocks and picrites, although some adjustments may be necessary.

2. FERROUS-FERRIC IRON RATIOS

Primary magmatic ferrous:ferric iron ratios can never be determined in altered komatiites, and it is necessary to adopt consistent assumptions in calculating them. By convention, and with some experimental justification, the whole rock ratio of ferric iron to ferrous iron is usually taken to be 1:10 in mafic lavas, and this convention is extended to komatiites. In the case of komatiites, however, the picture is complicated by the fact that lithologies range up to almost completely pure olivine adcumulates, where the primary ferric iron content was presumably close to zero. It is therefore necessary to introduce a ramp function into the calculation procedure, where the molar ratio $Fe_2O_3/[FeO+Fe_2O_3]$ varies from 0.1 in rocks assumed to represent liquids to 0 in pure adcumulates (Fig. 1). This is approximated in the calculation by assuming a linear variation in the ratio from 0.1 at 25% MgO to 0 at 50% MgO; constant values of 0.1 or 0 are assumed respectively below and above this range. The calculation is completed in a single column in the spreadsheet using multiplication by Boolean expressions, as follows:

$Fe_2O_3/[FeO+Fe_2O_3]$ =(MgO<50)*(MgO>25)*(0.1-0.1*(MgO-25)/25) + (MgO<25)*0.1   [1]

after a first-pass correction of all major element components to 100% H_2O- and CO_2-free. In komatiitic basalt suites such as those of the Cape Smith Belt or the Thompson Belt the MgO values of either end of the "ramp" should be lower, around 16% and 48%, corresponding to the maximum MgO content of likely parent magma, and the minimum MgO content of the corresponding pure olivine. For cumulates derived

from mafic magmas, the ramp should be set at lower values: 10 and 40% MgO are

recommended.
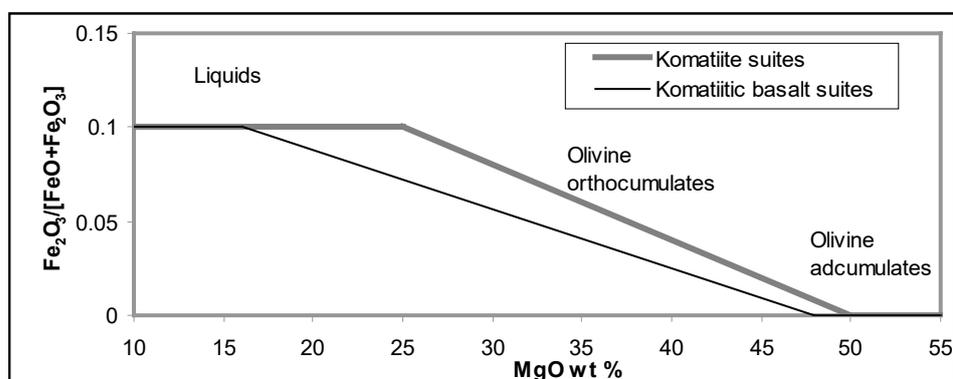
Figure 1. The variation in Fe₂O₃/[FeO+Fe₂O₃] (mol ratio) assumed for komatiite

suites, and komatiitic basalt suites, based on a value of 0.1 in liquid and 0 in pure

olivine.

3. TREATMENT OF THE SULFIDE COMPONENT

Estimation of sulfide tenors in disseminated ores, and correction of whole rock Fe for

Fe associated with sulfide, are necessary for the rigorous correction of whole rock

data.

The sulfide component of komatiitic rocks contains essentially all of the S and Cu in

the rock, and an unknown proportion of the whole rock Ni and Fe. The sulfide

component is now represented by a variety of different sulfide assemblages, most

commonly pyrrhotite – pentlandite – chalcopyrite with or without pyrite, and less

commonly including other phases such as millerite, polydimite and vaesite (figure 2).

It is theoretically possible to calculate the primary silicate composition of the rock by

"extracting" this sulfide component, and also to determine the composition of the

sulfide component. This cannot be done with rigorous accuracy, but a good

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approximation can be made using some simplifying assumptions. This contribution presents a modification of the procedure described by Naldrett (2004, page 15).
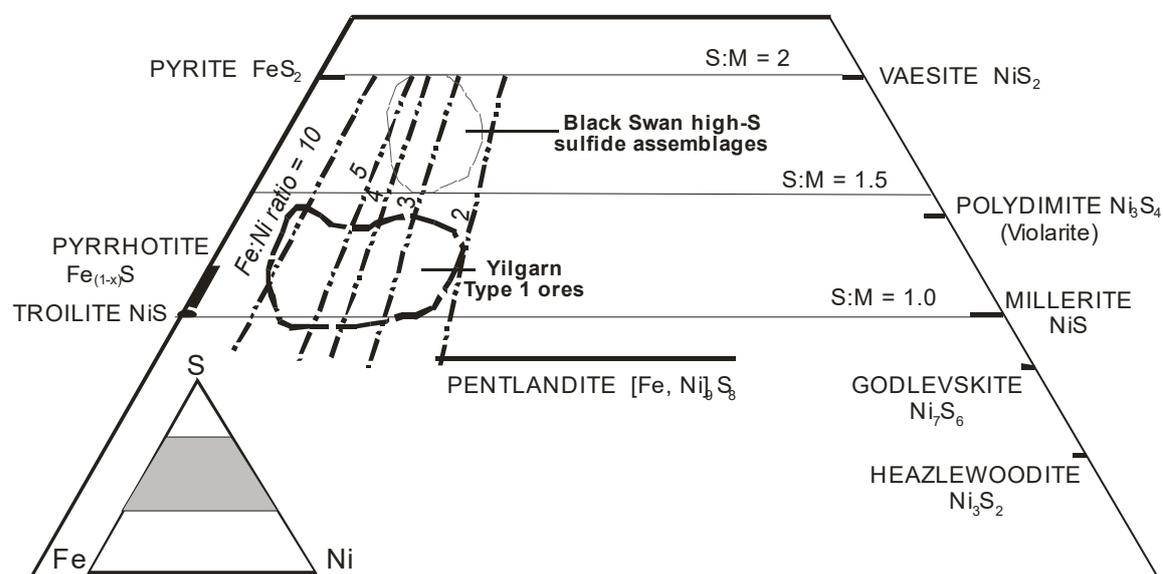
Figure 2. Central section of the Fe-Ni-S system, showing the phases most commonly found within komatiite hosted sulfides. S:M is the molar ratio of S to Fe+Ni, Fe:Ni is the molar ratio of Fe to Ni. Dashed fields show the range of variation of massive sulfide ores hosted by komatiites in the Yilgarn Craton, data from, , , corrected for S and Fe in chalcopyrite. Black Swan field shows compositional range of sulfides associated with talc-carbonates at Black Swan, Western Australia.

Two different methodologies are necessary to minimise uncertainties; one where the nickel content of the rock is primarily within silicates, and the other where sulfides are the dominant reservoir of nickel. In the first case, it is most reliable to estimate the nickel content of the sulfide phase, and then calculate that of the silicate component; in the second, the calculation is done the other way around, by first estimating the silicate Ni component of the rock.

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3.1. Method 1, sulfide-rich rocks – Ni predominantly in sulfide.

This case applies to rocks with S contents in excess of around 1-2%. The methodology here is to make an assumption regarding the original silicate Ni content of the rock, based on the observed strong correlation between Ni and MgO in komatiite suites. This correlation gives rise to the following approximation:

$$Ni_{sil}=(\{[MgO*100/siltotal]>10\}*\{[MgO*100/siltotal]-10\}*90)*(siltotal/100) \qquad [2]$$

Where "siltotal" is the volatile-free total of non sulfide, non-volatile components in the raw analysis: SiO_2, Al_2O_3, TiO_2, total Fe as FeO, MnO, MgO, CaO, K_2O, Na_2O and Cr_2O_3.

The whole-rock Ni in the sulfide component of the rock is then obtained from the whole rock value by difference. The Fe content of the sulfide can now be estimated assuming stoichiometry of the sulfide fraction, following the widely-used "sulfide norm" procedure, with all Cu assumed to be present in chalcopyrite. The method depends on an assumed value of the molar ratio S/[Fe+Ni], henceforth abbreviated as SM. In most magmatic sulfides, SM is between 1 and 1.3, corresponding to the typical pyrrhotite – pentlandite – chalcopyrite assemblage with minor pyrite (Figure 2). In some cases, such as Black Swan in Western Australia sulfide assemblages are much more S-rich, ranging up to pyrite-vaesite assemblages with SM close to 2 (Figure 2). To allow for this, the calculation permits user definition of SM in the sulfide assemblage for each sample, with the typical value being 1. (All Cu is still assumed to be in chalcopyrite, with S/[Cu+Fe]=1). Under these assumptions, the following equation applies:

$$Fe_{sul}=\{(S/32)-(Cu/63.5)*(1/SM)-(Ni-Ni_{sil})/58.7\}*55.8 \qquad [3]$$

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Where Fe_{sul} = Fe associated with sulfide, S, Cu and Ni are raw whole rock values, and SM is the molar ratio S/[Fe+Ni] in the sulfide assemblage. Total silicate Fe in the rock is then obtained by difference. All values are in weight %. This calculation then gives an approximation of the weight % sulfide component in the rock.

3.2. Method 2, sulfide poor rocks – Ni predominantly in silicate

In this circumstance, the Ni content of the sulfide component is essentially indeterminate, and a better estimate of the total sulfide mode is obtained by assuming a value for the Fe/Ni ratio in the sulfide component. A user-defined value other than unity for S/[Fe+Ni] can also be used, as in the previous situation. The following equations now apply:

$$Fe_{sul}=(1/SM)*((FN/(1+FN))*S/32)*55.8 \qquad\qquad [4]$$

and

$$Ni_{sul}=(1/SM)*(1/FN)*S/32)*58.7 \qquad\qquad [5]$$

Where FN = molar Fe/Ni in sulfide, and Ni_{sul} and Fe_{sul} are weight % Ni and Fe in the rock associated with sulfide. Natural values of FN in komatiite hosted sulfides are best estimated from compositions of type 1 massive sulfide ores (Figures 2, 3). A value of 3 for FN is a good approximation for most komatiite-hosted disseminated sulfides. The sulfide mode is relatively insensitive to this variable, however, owing to the similarity in atomic numbers of Fe and Ni.

3.3. Error propagation and uncertainty

The uncertainties in the method can be assessed through some sample calculations. Table 1 shows the results of the two calculation methods on two pairs of different

samples with different S contents, two with a typical monosulfide assemblage, and

two Black Swan samples with dominantly disulfide FeNiS assemblages, and shows

the sensitivity of the results to assumed values of FN and SM.

A second estimate of precision of the calculated sulfide mode, and Ni tenor of 100%

sulfide, was made using method 1 (sulfide-rich rocks) only. Three samples were

processed, allowing a randomised uncertainty of +/- 50% in the assumed Ni-in-

silicate background, combined with randomised values for SM (sulfur:metal ratio in

sulfide) between 1 and 1.5, over 100 repetitions of the calculation. The results of this

simulation are shown in Figure 4.
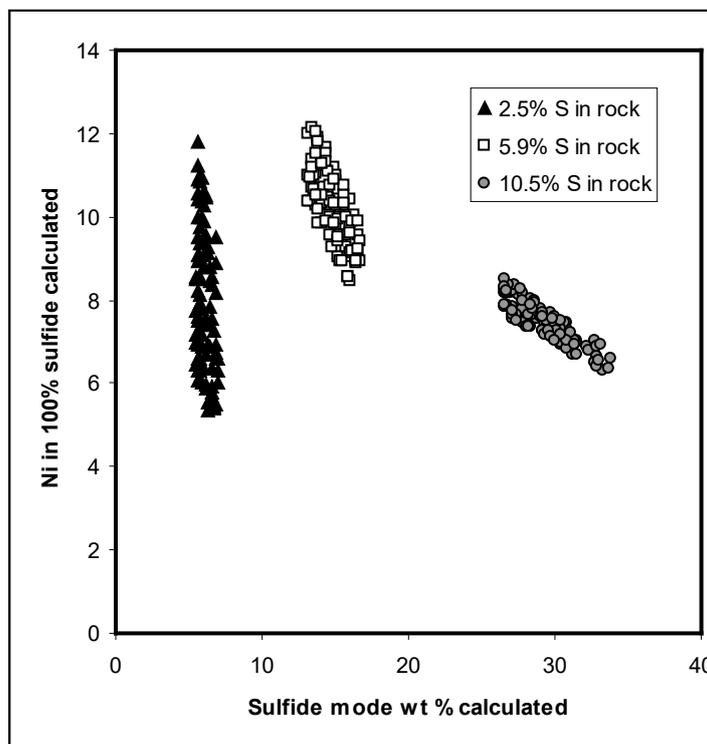
Figure 4. Estimate of uncertainty in sulfide mode and Ni tenor of 100% sulfide in

three different samples of given S content, based on randomised variation of SM

(sulfur:metal ratio in sulfide) between 1 and 1.5, and in Ni content of silicate

component (plus or minus 50% of calculated value). Data points for each sample

represent the results of 100 randomised combinations of input variables.

Sulfide Ni tenor can never be reliably estimated in rocks with S contents much below 2%, and is subject to large uncertainties for S contents up to 5%. However, if the silicate Ni content can be determined independently, either by direct analysis or from the intercept on a Ni vs S plot for a given group of samples, then a much better estimate can be made.

Even in the case of more S-rich rocks, it is evident from these results that the calculated composition of the sulfide phase is still assumption-dependent. The sulfide Ni tenor (i.e. the concentration of Ni in 100% sulfide) is relatively robust in rocks with 5% S or more, and is much more reliable if the sulfide mineralogy (and hence SM) is known.

The total sulfide mode is a relatively robust estimate, even in S-poor rocks, and is relatively insensitive to the assumed FN value. The main uncertainty is due to uncertainty in the SM value. In most cases of rocks with pyrrhotite-pentlandite assemblages, it is safe to assume an SM value close to 1. An uncertainty of 25% in this value gives rise to an uncertainty of about 15-20% in the calculated sulfide mode.

In the absence of partial analyses of the sulfide and silicate analyses, these two alternative methods give reliable approximations of the total modal percentage of sulfide in the rock. Using this value, a calculation can be made of the volatile-free, sulfide-free whole rock composition.

4. SUMMARY OF THE RECALCULATION METHOD

The overall method employed in the normalisation process (and encoded in the spreadsheet associated with this paper – available from the author or on the website of the journal) is summarised as follows:

1) compute a rough initial 100% volatile-free normalisation of all major element components including Ni, Cu and S.

2) compute an approximate composition and mode of the sulfide fraction, by either of the two methods described, depending on the S content, consistent with a reasonable result for the silicate and sulfide Fe concentration.

3) Compute a volatile and sulfide free renormalisation to 100% total for the silicate component of the rock, splitting silicate Fe into FeO and Fe_2O_3 as described above, and excluding the calculated sulfide-associated Ni, Fe, Cu and S.

4) Compute an H_2O-CO_2-free normalisation for the rock incorporating the sulfide-hosted Fe, Ni, S and Cu.

Obviously erroneous assumptions can give rise to obviously unreasonable estimates in sensitive results such as Ni tenor in sulfide in S-poor rocks, and silicate Fe in S-rich rocks. Ideally, a trial and error method should be used, guided by mineralogy where possible, to derive sensible ranges of user-defined assumptions for a suite of rocks. If this is done, then the compositions of both the silicate and sulfide components of moderately S-rich rocks can be estimated with a useful degree of precision, and this is potentially of value in assessing komatiites for Ni mineralisation potential.

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