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COMPUTER SIMULATION OF THE FRACTIONATION OF OLIVINE AND SULFIDE FROM MAFIC AND ULTRAMAFIC MAGMAS

J.M. DUKE
Geological Survey of Canada, 601 Booth Street, Ottawa Ontario K1A 0E8

ABSTRACT

The effect of fractionating variable proportions of olivine and molten sulfide from peridotitic komatiite and ocean-ridge basalt magmas is investigated with the computer model of Duke & Naldrett (1978). Significant differences in the chemical trends of chalcophile elements are predicted in sulfide-saturated as compared with sulfide-undersaturated systems if the molecular olivine/sulfide ratio is less than about 100. The trends of Ni and Co are more sensitive to the olivine/sulfide ratio in the ultramafic compositional range than in basalts. The compositions of magmatic sulfides are expected to be quite variable depending upon the stage during differentiation at which sulfide segregation occurs and upon the relative proportions of sulfide and silicate material.

SOMMAIRE

On étudie sur ordinateur, au moyen du modèle de Duke & Naldrett (1978), le fractionnement de mélanges, en proportions diverses, d'olivine et de sulfures fondus à partir de deux magmas, l'un komatiitique (péridotitique), l'autre basaltique tel d'une ride médio-océanique. On peut prévoir d'importantes différences d'allure, dans la variation chimique des éléments chalcophiles, entre systèmes saturés et sous-saturés (en sulfures), lorsque le rapport molaire olivine:sulfures est inférieur à ~ 100. La variation du Ni ou du Co est plus sensible à la valeur de ce rapport dans le domaine des compositions ultramafiques que dans celui des compositions basaltiques. On prévoit aussi des compositions différentes pour les sulfures magmatiques selon (1) le stade de la différenciation auquel a lieu leur ségrégation et (2) les proportions relatives des sulfures et silicates.

(Traduit par la Rédaction)

INTRODUCTION

Magmatic sulfide ores exhibit a range of compositions, such that those of ultramafic association are generally richer in nickel and poorer in copper than those hosted by mafic rocks. In part, this compositional variation reflects the relative concentrations of the metals in the magmas from which the ores segregated. Recent experimental investigations of the distribution of chalcophile elements between sulfide and silicate melts provide a basis for the quantitative prediction of the composition of molten sulfide in equilibrium with a given magma, and *vice versa* (MacLean & Shimazaki 1976, Rajamani & Naldrett 1978). Duke & Naldrett (1978) incorporated these and other experimental data in a computer program that calculates the compositional trends of silicate liquid, olivine and sulfide melt during fractionation of mafic or ultramafic magma. The numerical model was used to simulate the low-pressure differentiation of a typical peridotitic komatiite liquid; it was found that significantly different chalcophile-element trends are to be expected as a result of fractionation of sulfide-saturated compared with sulfide-undersaturated magma.

An outline of the calculation procedure was given by Duke & Naldrett (1978). The computer program subtracts an olivine increment of specified size from the given starting liquid composition. The composition of the olivine and derivative silicate liquid are calculated using empirical expressions for partition coefficients. The computation is reiterated for as many increments as desired, using the derivative liquid composition from one step as the starting composition for the subsequent step; if the increment size is sufficiently small, perfect fractional crystallization of olivine is simulated. If the starting liquid for any step is just saturated with sulfide, subtraction of an increment of olivine will result in removal of an amount of sulfide directly proportional to the sulfide solubility, and the sulfide content of the derivative liquid is maintained just at the saturation point. The sulfide solubility is expected to decrease with ongoing olivine fractionation in natural systems as the liquid becomes less mafic and the temperature drops (see also Czamanske & Moore 1977, p. 598) and the ratio of olivine to sul-

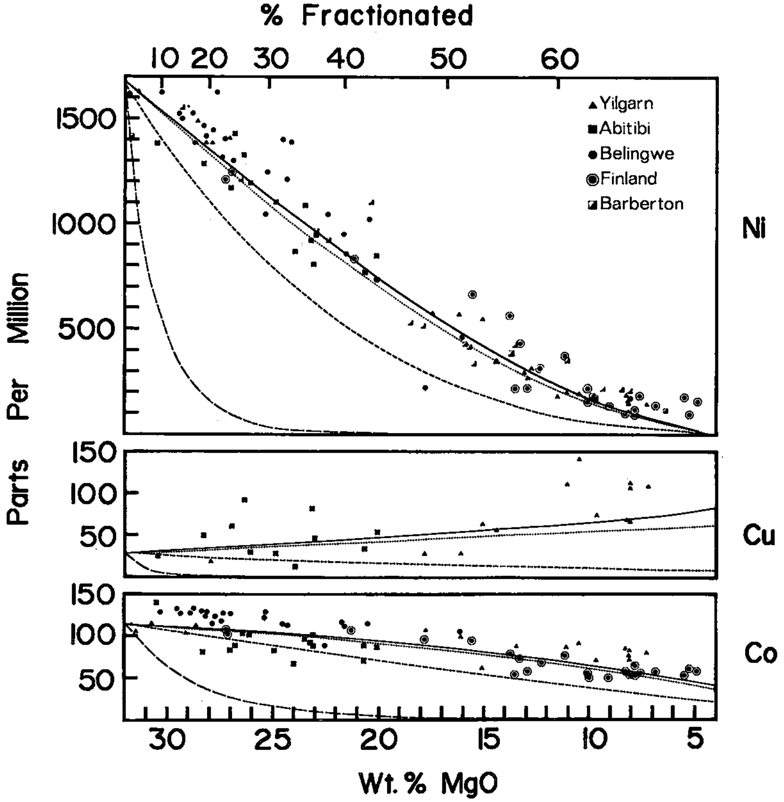

FIG. 1. Concentrations of chalcophile elements in derivative silicate liquids as a function of the MgO concentration in the liquid for the model komatiite system for sulfide-free fractionation (solid lines) and olivine/sulfide ratios of 1000 (dotted line), 100 (short deshed lines) and 10 (long dashed lines). The points are published analyses of natural komatiite lavas.

fide fractionating increases as a result. Accordingly, in the komatiite system modeled by Duke & Naldrett (1978), sulfide solubility was assumed to decrease as the MgO content of the liquid decreased; the molecular ratio of olivine to sulfide being removed changes from 37.5 when the liquid contained 30 wt. % MgO, 41.5 when it contained 20 wt. % MgO and 48.5 when it contained 10 wt. % MgO. Because the magnitude and variability of sulfide solubility in natural magmas are imperfectly understood, it is interesting to consider the extent to which the chemical trends in derivative sulfide and silicate liquids are influenced by the relative proportions of olivine and sulfide being fractionated. The present paper, which should be read in conjunction with Duke & Naldrett (1978), describes the results of model calculations in which the molecular olivine/sulfide ratio is fixed at values of 10, 100 and 1000 for two starting liquid compositions, a peridotitic komatiite and a mid-ocean-ridge basalt.

RESULTS

Model komatiite system

The calculated variation of Ni, Cu and Co with MgO concentration in the derivative silicate liquids in the model komatiite system is illustrated in Figure 1. Note that the initial liquid composition (Table 1) has slightly higher Ni and Co concentrations than that employed by Duke & Naldrett (1978). The differences between the sulfide-suturated and sulfide-undersaturated trends are negligible when the olivine/sulfide ratio is on the order of 1000, but become noticeable at lower ratios. When considered in relation to typical analytical uncertainties, it is likely that a sulfide-saturated trend would not be recognized in a suite of natural samples unless the ratio of olivine to sulfide fractionated had been less than about 100. The copper-enrichment trend characteristic of sulfide-undersaturated fractionation becomes a depletion trend if the molecular olivine/

sulfide ratio is less than about 175.

The compositions of some natural liquid-equivalent komatiites from the Yilgarn Block of Western Australia (Naldrett & Turner 1977, Nesbitt & Sun 1976), the Abitibi greenstone belt of the Canadian Shield (Nesbitt & Sun 1976, Duke, unpublished data), the Belingwe greenstone belt of Rhodesia (Nisbet *et al.* 1977), the Barberton Mountainland of South Africa (Cawthorn & McIver 1977) and the Kuhmo, Suomossalmi and Tipasjarvi greenstone belts of Finland (Jahn *et al.*, in press) are plotted in Figure 1. Much of the variation in chalcophile-element concentrations among these samples could apparently have resulted from fractional crystallization of olivine from rather similar parent magmas. There is little to suggest that these magmas were, in general, saturated with sulfide. It is noteworthy that even within a given suite, certain groups of samples of similar MgO content have rather wider ranges of concentrations of nickel and copper than might be expected to result from analytical uncertainties

TABLE 1. INITIAL LIQUID COMPOSITIONS USED IN CALCULATIONS

	KOMATIITE	OCEAN RIDGE BASALT
SiO_2	45.50	49.17
TiO_2	0.25	0.82
Al_2O_3	5.60	15.58
FeO	10.40	8.82
MnO	0.20	0.15
MgO	32.00	11.40
CaO	5.55	12.01
Na_2O	0.35	1.87
K_2O	0.00	0.11
Ni	1685 ppm	267 ppm
Co	116 ppm	52 ppm
Cu	30 ppm	82 ppm

Project FAMOUS sample 525-5-2, analysis from Langmuir et al. (1977).

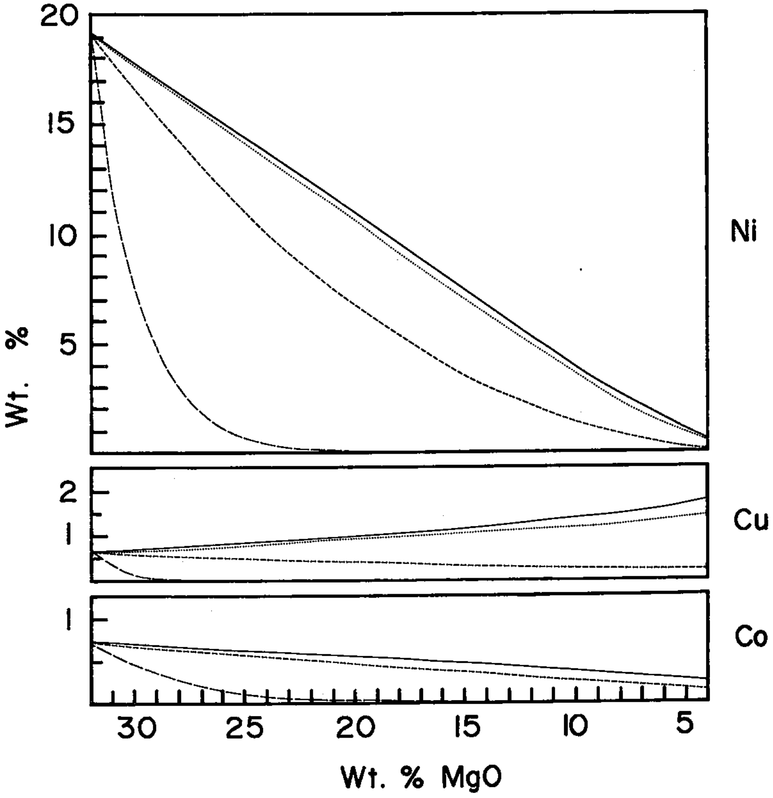

FIG. 2. Compositions of initial (solid lines) and subsequent sulfides in the komatiite system with olivine/sulfide ratios of 1000 (dotted line), 100 (short dashed lines) and 10 (long dashed lines). Trend for ratio of 1000 coincides with initial trend in the case of cobalt.

alone. Owing, for example, to alteration or cumulus enrichment, some samples are probably not representative of liquid compositions. On the other hand, it is possible that the compositional diversity of the komatiite magma series does not result from the operation of a single petrogenetic process.

The relationship between the calculated composition of sulfide melt and silicate liquid is illustrated in Figures 2 and 3. Two types of sulfide chemical trends were recognized by Duke & Naldrett (1978). The *initial* trend describes the composition of the first sulfide increment to exsolve from the silicate liquid at the point during the fractional crystallization of olivine at which the silicate liquid first becomes sulfide-saturated. The initial trend plotted in Figure 2 is analogous to the sulfide trends calculated by MacLean & Shimazaki (1976, Fig. 6) and by Rajamani & Naldrett (1977, Fig. 5). The *subsequent* sulfide trend gives the composition of sulfide melt segregated from a silicate liquid of given MgO content where both olivine and sulfide have already been fractionated from the liquid. The subsequent sulfide trends mirror the respective trends in the silicate liquid for the fractionation of various proportions of molten sulfide. Removal of a relatively large proportion of sulfide results in rapid depletion of the subsequent sulfides in nickel and copper and could ultimately yield essentially 'barren' magmatic sulfides. If the olivine/sulfide ratio is high, on the other hand, the subsequent sulfide compositions do not

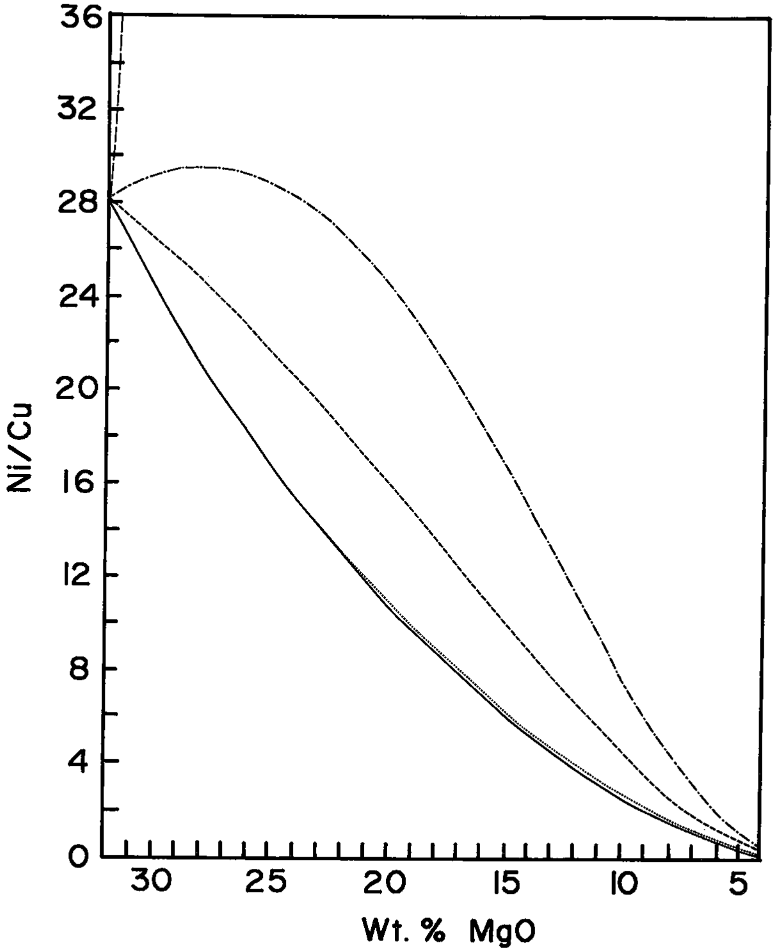

FIG. 3. Ni/Cu ratios of initial sulfides (solid line) and subsequent sulfides in the komatiite system with olivine/sulfide ratios of 1000 (dotted line), 100 (short dashed lines), 50 (dot dashed line) and 10 (long dashed lines).

deviate significantly from the initial trend. The Ni/Cu ratio of the subsequent sulfides is very dependent on the relative proportions of fractionating olivine and sulfide. The Ni/Cu ratio decreases steadily with ongoing differentiation so long as the olivine/sulfide ratio exceeds about 75, but if greater proportions of sulfide are removed, the Ni/Cu ratio increases and goes through a maximum.

The limited data available suggest that magmatic sulfide ores associated with peridotitic komatiites are rather variable in composition. Concentration ranges of 6.5 to 22.4 wt. % nickel and 0.38 to 1.2 wt. % copper have been quoted (*e.g.*, Naldrett & Cabri 1976, Table 6; Duke & Naldrett 1978, Table 3) and Ni/Cu ratios generally exceed 10. Model calculations show that the sulfide composition is very sensitive to the relative amount of sulfide and the composition of the magma, and so the diversity of natural ore composition is perhaps not surprising.

Mid-ocean-ridge basalt system

Model calculations have been carried out using an initial liquid composition corresponding to one of the most magnesium-rich basalts from the Project FAMOUS area of the Mid-Atlantic Ridge (Table 1). This was selected as an example of fractionation in a basaltic system because there are abundant compositional data available for silicate glasses (*i.e.*, silicate liquids) and for sulfide globules of magmatic origin from the MORB rocks. The calculated trends for Ni, Cu and Co in the silicate liquids are illustrated in Figure 4. The distinctions between sulfide-undersaturated and -saturated trends are analogous to those observed in the model komatiite liquid trends. Note however that the removal of a given proportion of sulfide has a less marked effect in the mafic liquids than in the ultramafic compositional range. This reflects the much greater difference in the relative magnitudes of the sulfide/liquid and olivine/liquid partition coefficients in the ultramafic as compared with the basaltic system. For example, according to the assumptions of Duke & Naldrett (1978), the olivine/liquid partition coefficient for nickel is 2.0 where the liquid contains 32 wt. % MgO and 9.5 where the liquid contains 10 wt. % MgO; the corresponding sulfide/liquid coefficients are 115 and 285 (partition coefficients are expressed in weight fraction terms here). Thus the bulk partition coefficients (*i.e.*, the weighted average of olivine/liquid and sulfide/liquid coefficients) for the fractionation of a 100:1 olivine–sulfide mixture is 3.1 for the 32 wt. % MgO liquid and 12.2 for the 10 wt. % MgO liquid; these values correspond to increases of 56% and 29%, respectively, over the partition coefficients for the fractionation of olivine alone.

The compositions of olivine basalts from the FAMOUS area have been plotted in Figure 4. Only samples in which olivine is the only significant phenocryst phase are plotted as these are most likely to reflect olivine control. The FAMOUS lavas are compositionally variable, with the lavas from the centre of the rift valley tending to be more primitive than those collected from the flanks (Bryan & Moore 1977). Low-pressure fractionation of olivine or plagioclase (or both), in some instances accompanied by clinopyroxene, may account for much of the compositional variation among these rocks (*e.g.*,

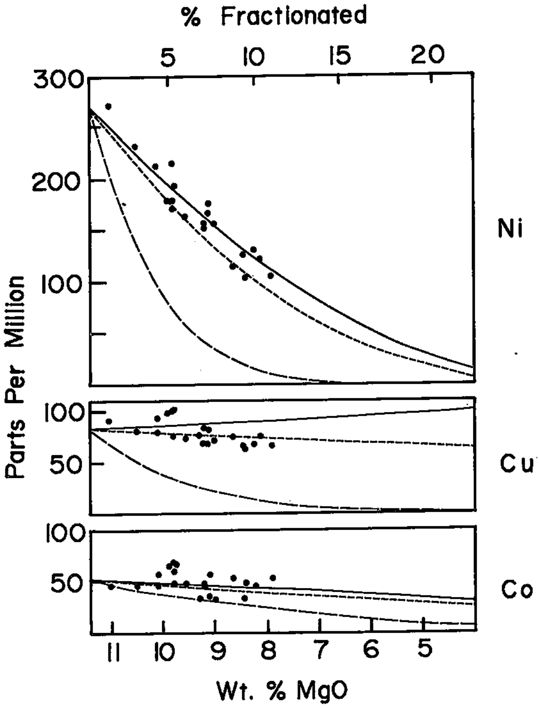

FIG. 4. Concentrations of chalcophile elements in derivative silicate liquids for the MORB model system as a function of the MgO concentration in the liquid for sulfide-undersaturated fractionation (solid lines) and olivine/sulfide ratios of 100 (short dashed lines) and 10 (long dashed lines). The trends for an olivine/sulfide ratio of 1000 do not differ significantly from the undersaturated trends. The points are published analyses of natural olivine basalts.

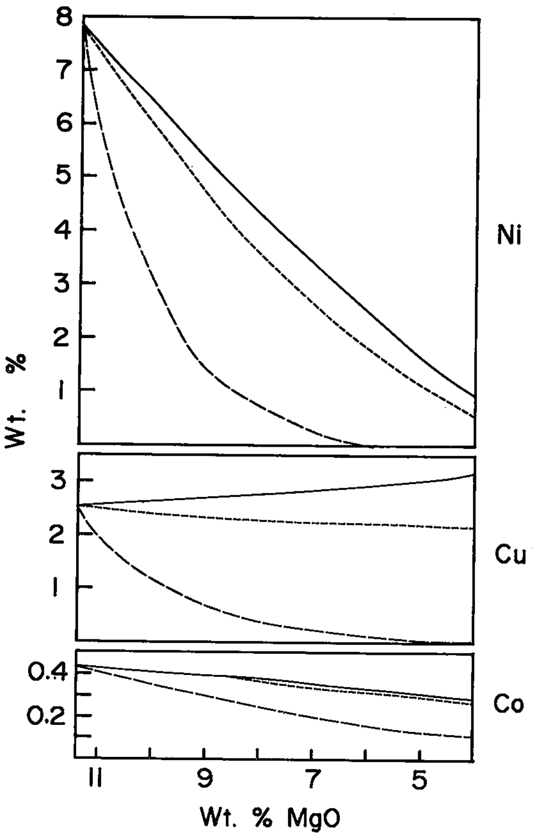

FIG. 5. Compositions of initial (solid lines) and subsequent sulfides in the MORB system with olivine/sulfide ratios of 100 (short dashed lines) and 10 (long dashed lines). The trend for subsequent sulfides where the olivine/sulfide ratio is 1000 does not differ significantly from the initial trend.

Bryan & Moore 1977, Flower *et al.* 1977) although some have questioned this conclusion (Langmuir *et al.* 1977). From material balance calculations, Czamanske & Moore (1977) concluded that Cu, Ni, Fe and S had been removed from the FAMOUS magmas by the fractionation of molten sulfide. The results of the computer modeling are generally consistent with differentiation involving the fractionation of olivine and a small amount of sulfide. The analytical points are somewhat scattered in relation to the model curves but the copper plot in particular suggests an olivine/sulfide ratio on the order of 100.

The calculated variation of molten sulfide composition with magmatic differentiation is illustrated in Figures 5 and 6. The relationships between initial and subsequent sulfide trends are analogous to those discussed above for the komatiite system. An interesting contrast between the ultramafic and basaltic systems is observed in the Ni/Cu ratios. Whereas the Ni/Cu ratio in the ultramafic system is very sensitive to the relative amounts of fractionating olivine and sulfide, such is not the case in the basaltic system. This is because it has been assumed that the sulfide/silicate-liquid partition coefficient of nickel increases as the liquid becomes less ultramafic and temperature decreases, whereas that of copper remains constant (Rajamani & Naldrett 1978, Duke & Naldrett 1978). Thus the partition coefficient of nickel is much lower than that of copper in the ultramafic compositions, of similar magnitude in the olivine basalt compositional range and greater in the less magnesian liquids. Accordingly, decreasing the olivine/sulfide ratio increases Ni/Cu in the subsequent sulfides in the ultramafic compositions but decreases Ni/Cu in subsequent sulfides that separate from basaltic liquids.

The compositions of magmatic sulfide globules from some of the FAMOUS basalts have been determined by Czamanske & Moore (1977) and are summarized in Table 2 together with those of magmatic sulfides from some other ocean-floor rocks (Mathez & Yeats 1976, Mac-

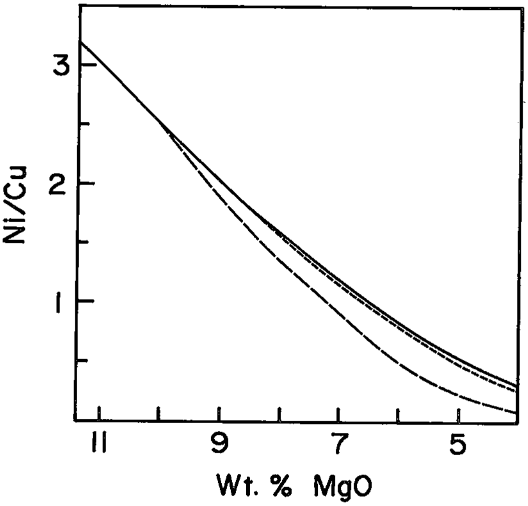

FIG. 6. Ni/Cu ratios of initial (solid line) and subsequent sulfides in the MORB system with olivine/sulfide ratios of 100 (short dashed lines) and 10 (long dashed lines). The trend for subsequent sulfides where the olivine/sulfide ratio is 1000 does not differ significantly from the initial trend.

Lean 1977). Although the Ni/Cu ratios of the model sulfides are similar to those in the natural samples, the nickel and particularly the copper concentrations are significantly lower in the model compositions. Czamanske & Moore noted that the comparison of sulfide globule and silicate glass compositions implied sulfide/silicate partition coefficients of 370 to 770 for nickel and 1010 to 1210 for copper (coefficients calculated on weight fraction basis). These are higher than the values used in the model by factors of about 1½ to 3 and 4 to 5, respectively. This discrepancy indicates that either the experimentally determined partition coefficients are not applicable to this system, or that the natural sulfide-globule compositions do not reflect magmatic equilibrium with their host liquids (*i.e.*, glasses).

TABLE 2. COMPOSITIONS OF MAGMATIC SULFIDE GLOBULES FROM OCEAN-FLOOR ROCKS

Rock Type	n	Ni (wt.%)	Cu (wt.%)	Reference
Primitive olivine & picritic basalts	13	13.3	9.4	Czamanske & Moore (1977)
Plagioclase-olivine-pyroxene basalts	20	5.9	8.8	
Aphyric & plagioclase-rich basalts	6	8.2	8.0	
Ocean-floor tholeiite	1	8.3	4.1	Mathez & Yeats (1976)
Ocean floor tholeiite	1	6.9	8.9	
Ocean-floor tholeiite	1	7.8	6.6	
Basalt	91	2.8	7.2	MacLean (1977)
Gabbro	15	5.8	5.6	
Peridotite	12	26.0	7.8	

CONCLUSION

The crystallization of olivine from sulfide-saturated mafic or ultramafic magma is expected to cause exsolution of molten sulfide from the silicate liquid. The amount of sulfide to exsolve per unit olivine crystallized will be proportional to the sulfide solubility. As the solubility will normally decrease with ongoing differentiation, the ratio of olivine to sulfide fractionating will increase. The relative proportions of olivine and sulfide subtracted from the liquid can have a profound effect on the chemical trends of chalcophile elements in the subsequently formed silicate and sulfide phases. The present calculations suggest that olivine/sulfide ratios on the order of 100 or less are required to produce trends that differ significantly from those resulting from the fractionation of olivine alone (*i.e.*, significant relative to uncertainties in the analyses of natural rocks). The trends in ultramafic systems are more sensitive to this ratio than are the trends in mafic systems.

The elemental trends of spinifex-textured peridotites and other liquid-equivalent komatiitic rocks from several localities are consistent with differentiation due to the fractional crystallization of olivine. If these magmas were in general sulfide-saturated, the ratio of olivine to sulfide fractionated was probably considerably greater than 100. The concentrations of chalcophile elements in olivine-basalt glasses from the FAMOUS area of the Mid-Atlantic ridge are indicative of cofractionation of olivine and sulfide in a ratio of the order of 100. The compositions of sulfide ores associated with peridotitic komatiites are in general agreement with the model sulfide compositions. On the other hand, there is a serious discrepancy between the calculated and observed compositions of magmatic sulfide blebs in the MORB basalts which warrants further investigation.

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