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THE DISTRIBUTION OF NICKEL AND IRON BETWEEN OLIVINE AND MAGMATIC SULFIDES IN SOME NATURAL ASSEMBLAGES

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ABSTRACT

The distribution of nickel and iron between olivine and bulk sulfide has been determined in four nickel–copper–PGE (platinum-group-element) sulfide deposits. The mean distribution-coefficient $[K_{D(\text{Ni-Fe})}^{Sulf/Oliv}]$ is 5.0 ± 1.7 in the Katahdin deposit (Maine), 8.3 ± 3.1 in the Moxie pluton (Maine), 10.8 ± 2.3 in the Dumont deposit (Quebec), and 11.4 ± 4.8 in the Platinum Reef of the Stillwater complex (Montana). The weight of the evidence from this and previous studies of natural assemblages, as well as various direct and indirect experimental determinations, indicates that the distribution coefficient to be expected from the equilibration of olivine and molten sulfide under *normal* magmatic conditions will be in the range of 5 to 20, and most likely in the low part of the range.

Keywords: nickel, iron, distribution coefficient, natural assemblages, olivine, sulfide melt.

SOMMAIRE

On a déterminé la distribution du nickel et du fer entre l'olivine et l'ensemble des sulfures dans quatre gîtes de sulfures de nickel, cuivre et éléments du groupe du platine. Le coefficient de distribution moyen $[K_{D(\text{Ni-Fe})}^{Sulf/Oliv}]$ est de 5.0 ± 1.7 dans le gîte Katahdin (Maine), 8.3 ± 3.1 dans le pluton Moxie (Maine), 10.8 ± 2.3 dans le gîte Dumont (Québec) et 11.4 ± 4.8 dans le banc platinifère du complexe de Stillwater (Montana). Dans l'ensemble, ces déterminations, les résultats antérieurs obtenus sur assemblages naturels, et diverse déterminations expérimentales directes et indirectes indiquent qu'on peut prévoir, pour l'équilibre entre l'olivine et le bain sulfuré dans des conditions magmatiques normales, une valeur de K_D située entre 5 et 20, probablement vers la limite inférieure.

(Traduit par la Rédaction)

Mots-clés: nickel, fer, coefficient de distribution, assemblages naturels, olivine, bain sulfuré.

INTRODUCTION

Sulfide deposits that contain nickel, copper, cobalt and platinum-group elements occur in association with mafic and ultramafic rocks, and have been interpreted as having formed by the separation and accumulation of an immiscible sulfide liquid from silicate parent-magma (Vogt 1918, Scholtz 1937, Hawley 1962, Naldrett 1979, 1981). The composition of the sulfide liquid that separates from a given magma is controlled by the bulk composition of the system, the relative proportions of sulfide liquid, silicate magma and crystalline phases such as olivine, and the exchange equilibria governing the distribution of chalcophile elements among the various phases (MacLean & Shimazaki 1976, Duke & Naldrett 1978, Campbell & Naldrett 1979, Duke 1979). Some of the relevant exchange-equilibria have been studied experimentally, but there are a number of ambiguities in the resulting data (MacLean & Shimazaki 1976, Rajamani & Naldrett 1978, Medvedev & Almukhamedov 1978, Fleet *et al.* 1977, 1981, Boctor 1981, 1982). In particular, a controversy has arisen over the distribution of nickel and iron between olivine and molten sulfide, expressed by the distribution coefficient

$$[K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}] = \frac{(X_{\text{NiS}}^{\text{Sulf}})\,(X_{\text{FeSi}_{0.5}\text{O}_2}^{\text{Oliv}})}{(X_{\text{FeS}}^{\text{Sulf}})\,(X_{\text{NiSi}_{0.5}\text{O}_2}^{\text{Oliv}})} \qquad (1)$$

in which X_i^A is the mole fraction of component i in phase A. Values of the distribution coefficient determined directly and indirectly in experiments and deduced from natural assemblages range from less than 5 to more than 60. Opinions regarding the "correct" value of the distribution coefficient have been used as a basis to question or support the validity of the magmatic segregation hypothesis for the origin of Ni–Cu–PGE sulfide ores (*e.g.*, Fleet 1979, Naldrett 1979). Our purpose in this paper is to present data on the distribution coefficient in several natural assemblages in which we consider the geological evidence for a magmatic origin for the sulfides to be conclusive. Our data are derived from sulfide deposits associated with four different intrusive bodies that represent a range in composition of the parent magma and in petrological environments: the sulfide-bearing Moxie and Katahdin gabbros in Maine, the platinum reef of the Stillwater complex, Montana, and the dunite-hosted Dumont deposit in northwestern Quebec.

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GEOLOGY OF THE MAINE, STILLWATER AND DUMONT OCCURRENCES

The Moxie and Katahdin occurrences

The Moxie pluton is a large mafic intrusive body in central Maine, emplaced during the Acadian orogeny (Devonian). The Katahdin gabbro is a small mafic pluton that occurs to the southeast of the Moxie pluton and is probably genetically related to it. Both intrusive bodies were formed by the injection of variably fractionated magmas into irregular magma chambers and feeder zones (Thompson 1982). The southern half of the Moxie pluton hosts three small accumulations of sulfide: Black Narrows (BL), Burnt Nubble (BN) and Big Indian Pond (BIP). The sulfide assemblages in these occurrences are depleted in Ni and Cu relative to typical accumulations of magmatic sulfide in mafic rocks. The Katahdin gabbroic pluton hosts an enormous body of pyrrhotite (KI), whose overlying limonitic gossan was once exploited for iron ore. These sulfides also have a low tenor of Ni and Cu. Despite the unusual composition of the sulfide, there is sufficient evidence to indicate the magmatic origin of these accumulations, and their composition may be explained by magmatic processes (Thompson & Naldrett, in press).

The BL accumulation contains disseminated sulfide interstitial to cumulus olivine, whereas the BN and BIP sulfides are hosted by olivine–plagioclase cumulates. Olivine in the BL accumulation is Fo_{83-84}, as compared with Fo_{73-79} in the BN and BIP occurrences. A typical texture illustrating sulfide interstitial to olivine at BIP is shown in Figure 1. The KI body is largely massive (>75%) pyrrhotite containing euhedral olivine (Fo_{80}), plagioclase and rare chromite. The concentration mechanism of this mass of sulfide remains ambiguous, but its association with magmatic silicate minerals and the igneous textures support its magmatic origin (Thompson 1982). Minor secondary alteration is present at all the Maine sulfide occurrences but is only significant at the BL locality, where serpentinization and chloritization of olivine–plagioclase cumulates are relatively common. Alteration of this kind may change the composition of primary sulfides (Eckstrand 1975, Groves & Keays 1979) but is considered to be quantitatively insignificant in this case (Thompson & Naldrett, in press).

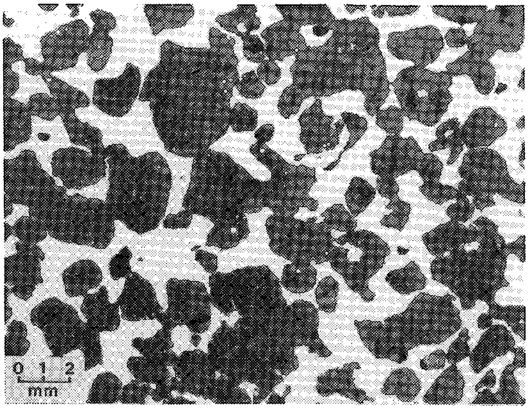

FIG. 1. Sulfide net-texture, Big Indian Pond occurrence, Moxie pluton. Magmatic sulfide is interstitial to cumulus olivine (dark grey). Reflected light.

The Stillwater platinum–palladium horizon

The Stillwater complex in Montana contains stratiform sulfide accumulations at a number of stratigraphic levels, the most economically significant being the platinum-rich zone or reef (Conn 1979, Bow *et al.* 1982). The reef occurs within the lower Banded Zone of the complex (McCallum *et al.* 1980), 400 m above the first appearance of cumulus plagioclase. It consists of a 1 to 2 m thick, laterally continuous layer of plagioclase and olivine cumulates containing 1–2% sulfides that are extremely platinum-rich. The sulfides occur as composite blebs of pyrrhotite – pentlandite – chalcopyrite – PGE minerals, interstitial to cumulus minerals and enclosed in intercumulus pyroxene (Bow *et al.* 1982). A typical texture is illustrated in Figure 2. The stratigraphic continuity of the reef and the textural relationship of sulfides to cumulus and intercumulus minerals leave no doubt as to a magmatic origin.

The Dumont deposit

The Dumont intrusive complex is a layered sill of Archean age occurring in the Abitibi greenstone belt in the Superior Province of the Canadian Shield. The sill is believed to have formed by the differentiation of a parent magma of peridotitic komatiite composition and comprises a lower Ultramafic Zone and an upper Mafic Zone. The Ultramafic Zone has been subdivided into three units, which are, from the base upward, the Lower Peridotite Subzone, the Dunite Subzone and the Upper Peridotite Subzone (Duke 1980). An extensive zone of disseminated sulfides occurs within the central part of the Dunite Subzone; the strict conformity of the sulfide-enriched horizons with the primary modal and cryptic layering is strong evidence for the magmatic origin of the mineralization (Duke 1982). The external morphology of the disseminated sulfide grains is also indicative of a magmatic origin, as illustrated in Figure 3 (see also Eckstrand 1975). The ultramafic rocks are variably serpentinized, but the primary textures are usually pseudomorphously preserved. The mineralogy and texture of serpentine are indicative of type-3 serpentinization (Wicks & Whittaker 1977), *i.e.*, that oc-

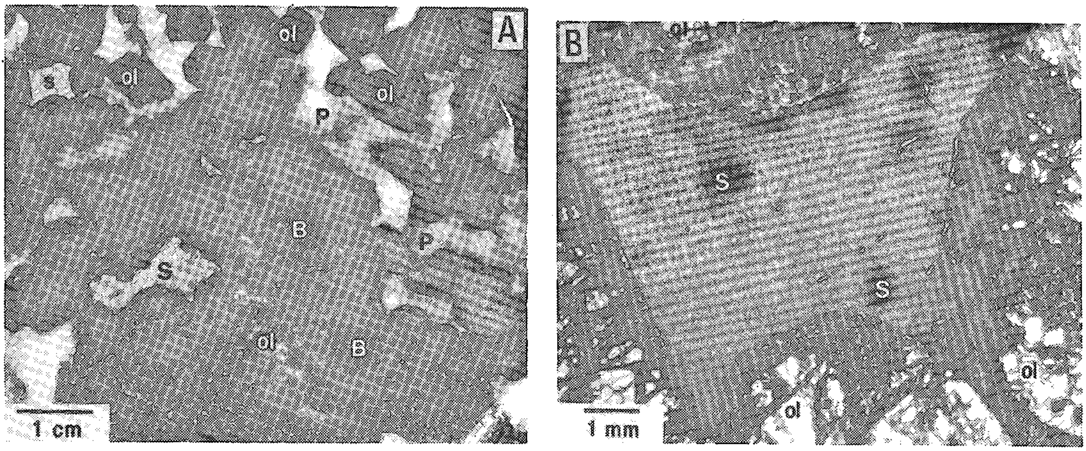

FIG. 2. Olivine–plagioclase cumulate, PGE reef, Stillwater complex. A. PGE-rich sulfide blebs (S) occur within intercumulus pyroxene (B) and interstitial to cumulus olivine (ol) and plagioclase (P). Incident light. B. Magmatic sulfide occurring interstitially to cumulus olivine. Transmitted light.

curred in a regime of falling or constant temperature without significant shearing or nucleation of antigorite. The effects of regional metamorphism are negligible. Prior to alteration, the mineralized dunite typically comprised more than 95% cumulus olivine, less than 3% cumulus sulfide and less than 2% intercumulus chromite and clinopyroxene. The fact that the bulk composition of unmineralized dunite very closely matches that of the contained relict olivine indicates that the olivine has retained its primary composition. However, the modal and bulk chemical compositions of the sulfide fraction have changed during serpentinization (Eckstrand 1975, Duke, in press). The grains of magmatic sulfide are polymineralic, and consist of pentlandite + magnetite ± awaruite ± heazlewoodite ± native copper. The assemblage pentlandite + magnetite + awaruite is the most common. The distribution coefficients given below are therefore not equilibrium values, inasmuch as they are calculated using compositions of primary olivine and of the secondary sulfides. There is, however, good evidence to support the contention that serpentinization has led to an increase in the Ni/Fe ratio of the sulfide fraction, such that the calculated distribution-coefficients are somewhat greater than the primary values.

ANALYTICAL TECHNIQUES

Olivine compositions

The distribution coefficients for the Maine and Stillwater samples were determined by the same methods. The major-element concentrations in olivine were determined by energy-dispersion techniques on the University of Toronto ARL microprobe using a modified version of the PESTRIPS (Statham 1975) reduction procedure. The method provided satisfactory accuracy and precision, better than 1 mole % forsterite overall. The Ni content of the olivine was determined by the wavelength-dispersion technique with a graphical method of reduction applied from a series of appropriate standards (Thompson 1982). The errors introduced by this reduction technique are insignificant at the concentration levels of interest. The extremely low Ni content of olivine from the Maine occurrences presented problems, and the low instrumental precision is the major source of errors in the determination of K_D. Olivine in the Stillwater rocks contains much higher levels of Ni; the variation in individual samples is thought to be due to inhomogeneities. Olivine in contact with

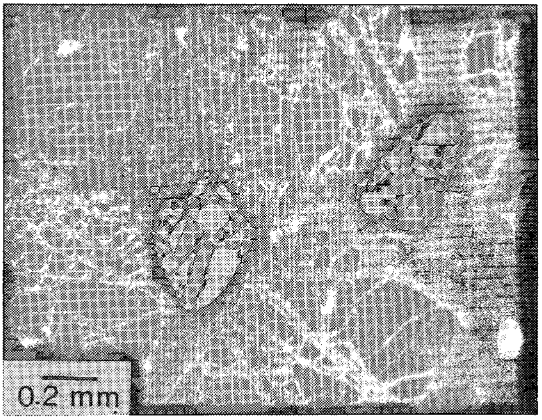

FIG. 3. Olivine–sulfide cumulate, Dunite subzone, Dumont intrusive complex. The primary magmatic morphology of the sulfide grain is preserved but the mineral assemblage, pentlandite + magnetite, results from secondary alteration. The olivine is partly altered to serpentine + brucite + magnetite. Reflected light.

sulfide was analyzed wherever possible in order to obtain the best possible approach to equilibrium. Olivine compositions from the four Maine sulfide localities and the Stillwater PGE reef are shown in Table 1.

The composition of the Dumont olivine was determined using a MAC electron microprobe at the Geological Survey of Canada. The concentrations of SiO_2, FeO, MnO, MgO and CaO were measured with the instrument operated in the energy-dispersion

TABLE 1. COMPOSITION OF OLIVINE FROM MOXIE, KATAHDIN AND STILLWATER

MOXIE PLUTON

SAMPLE	BL2		BL10B-1		BL10B-2		79BN1		79BN-7	
Analyses	6		2		2		6		6	
SiO_2	40.29	(0.14)	40.77	(0.02)	40.19	(0.14)	38.75	(0.15)	38.13	(0.31)
FeO	15.58	(0.82)	14.40	(0.55)	16.37	(0.08)	19.05	(0.41)	24.71	(0.33)
MnO	0.15	(0.06)	0.17	(0.01)	0.20	(0.04)	0.22	(0.04)	0.33	(0.03)
MgO	43.92	(0.52)	44.81	(0.16)	43.33	(0.01)	40.97	(0.33)	36.96	(0.71)
NiO	0.090	(0.007)	0.074	(0.003)	0.080	(0.004)	0.020	(0.014)	0.022	(0.015)
TOTAL	100.03		100.22		100.17		99.01		100.15	
Fo	83.4	(0.9)	84.7	(0.4)	82.5	(0.1)	79.3	(0.5)	72.8	(0.7)

SAMPLE	79M112		79BI3		79BI23		79BI27-1		79BI27-2	
Analyses	8		8		6		4		4	
SiO_2	38.37	(0.20)	38.56	(0.41)	38.48	(0.19)	38.47	(0.30)	37.89	(0.25)
FeO	22.69	(0.48)	24.32	(0.26)	23.97	(0.38)	22.22	(0.28)	24.96	(0.01)
MnO	0.27	(0.03)	0.32	(0.03)	0.34	(0.02)	0.29	(0.06)	0.28	(0.04)
MgO	38.46	(0.17)	37.09	(0.06)	37.74	(0.43)	39.09	(0.01)	36.24	(0.28)
NiO	0.044	(0.018)	0.022	(0.009)	0.032	(0.008)	0.023	(0.006)	0.043	(0.013)
TOTAL	99.83		100.31		100.56		100.09		99.41	
Fo	75.2	(0.4)	73.1	(0.2)	73.7	(0.5)	75.8	(0.3)	72.1	(0.1)

KATAHDIN

SAMPLE	78KT50		78KT60		78KT62		E2	
Analyses	2		6		6		2	
SiO_2	39.65	(0.30)	39.10	(0.41)	39.79	(0.37)	39.08	(0.21)
FeO	19.04	(0.18)	21.22	(0.29)	18.56	(0.27)	23.18	(0.35)
MnO	0.32	(0.02)	0.25	(0.03)	0.28	(0.04)	0.39	(0.06)
MgO	41.53	(0.04)	39.49	(0.47)	41.48	(0.46)	37.85	(0.18)
NiO	0.009	(0.004)	0.020	(0.008)	0.016	(0.009)	0.014	(0.004)
TOTAL	100.55		100.08		100.13		100.51	
Fo	79.9	(0.1)	76.8	(0.4)	80.1	(0.3)	74.5	(0.2)

STILLWATER

SAMPLE	346		4W-C2A		4W-C3		4W-D2B		12E-L1	
Analyses	2		4		8		5		4	
SiO_2	38.54	(0.51)	38.59	(0.52)	39.53	(0.48)	38.68	(0.44)	39.54	(0.51)
FeO	20.23	(0.48)	25.92	(0.53)	19.04	(0.21)	22.53	(0.15)	19.17	(0.19)
MgO	41.83	(0.36)	35.50	(0.42)	40.90	(0.41)	39.45	(0.25)	41.00	(0.36)
NiO	0.382	(0.018)	0.498	(0.014)	0.560	(0.018)	0.473	(0.014)	0.395	(0.011)
TOTAL	100.98		100.51		100.03		101.13		100.10	
Fo	78.3		70.8		79.4		76.1		79.2	

SAMPLE	12E-M1		12W-B1		8E-K3		8E-K3A	
Analyses	4		4		6		3	
SiO_2	39.45	(0.46)	38.23	(0.43)	38.83	(0.24)	38.46	(0.21)
FeO	21.09	(0.32)	24.03	(0.36)	24.78	(0.40)	25.09	(0.15)
MgO	39.59	(0.20)	37.08	(0.18)	36.21	(0.43)	36.53	(0.19)
NiO	0.339	(0.011)	0.421	(0.057)	0.438	(0.019)	0.422	(0.013)
TOTAL	100.47		99.76		100.26		100.50	
Fo	77.0		73.4		72.4		72.2	

All concentrations in weight percent; Fo = mole percent forsterite.

TABLE 2. COMPOSITION OF SULFIDE FROM MOXIE, KATAHDIN AND STILLWATER

	BL		BN		BIP		KI		STILLWATER	
Ni	1.87	(0.41)	0.44	(0.04)	0.84	(0.08)	0.21	(0.004)	9.3	(0.45)
Cu	0.72	(0.22)	0.32	(0.07)	0.65	(0.11)	0.10	(0.003)	6.9	(0.46)
Co	0.22	(0.04)	0.13	(0.01)	0.16	(0.01)	0.18	(0.004)	–	
NiS/FeS	0.0303	(0.0125)	0.0069	(0.0012)	0.0133	(0.0026)	0.0033	(0.0001)	0.180	(0.01)

mode, and the concentration of NiO was determined using wavelength-dispersion analysis. A large number of analyses of olivine from sulfide-free dunites from Dumont have been carried out; the excellent agreement between these results and the whole-rock compositions confirms the accuracy of the method. The low standard deviations associated with the average analyses reported in Table 3 (see below) reflect the extreme homogeneity of the olivine at Dumont.

Sulfide compositions

The direct analysis of the sulfide fraction in a sulfide-bearing rock presents major problems. Direct-leaching techniques (Davis 1972, Lynch 1971, Czamanske & Ingamells 1970, Karapetyan 1968) were investigated for individual samples from the Maine deposits, but were unsuccessful owing to the minor dissolution of silicates. The approach ultimately adopted was to calculate the composition of the sulfide fraction from whole-rock analytical data, or from the proportions of sulfides of a predetermined composition. Ni, Cu, Co and S analyses were carried out by X-Ray Assay Laboratories Ltd. on sulfide-bearing samples from BL, BN, BIP and Stillwater using X-ray-fluorescence techniques. Assay data provided by the Superior Mining Company were used for the KI deposit. In the case of the Maine deposits, the abundance of sulfides for each sample was determined by a "sulfide norm" calculation, where Ni, Cu, Co and S are apportioned to normative chalcopyrite, pentlandite and pyrrhotite compositions. The resultant Ni, Cu, Co, Fe and S concentrations are normalized to 100% sulfide (Table 2). This method has been used previously in the study of magmatic sulfide deposits (Hoffman *et al.* 1978). The effect of silicate Ni on this calculation is minor, owing to the very low concentrations of Ni in olivine and the low proportion of olivine in the majority of samples. A maximum error of 5% of the amount present may be introduced from the silicates in the whole-rock analysis (Thompson 1982). An additional series of Moxie samples was analyzed after physical separation of the sulfide component. The Ni, Cu and Co concentrations of the sulfide separates fell within the range determined by the above method for each occurrence, further justifying the approach.

In the case of the Stillwater samples, the abundance of sulfides in individual samples is generally less than 5%, making the calculation of a sulfide norm unreliable. However, a strong positive correlation is observed between whole-rock Ni, Cu, PGE and S (Barnes, unpubl. data) for over 40 sulfide-bearing samples from the PGE reef. Ni, Cu and Co concentrations for each sample may, therefore, be determined by normalizing to 35% S, the concentration of S assumed for the pure sulfide fraction. Iron is then found by difference for the sulfide fraction. The calculations involve a correction for silicate Ni obtained from the Ni content of olivine and the modal proportion of olivine in each sample. The uncertainty in this calculation introduces a maximum error of 30% in the Ni-in-sulfide value for each sample and is the largest contribution to the variance in the Stillwater [NiS]/[FeS] ratio. The mean and standard deviation for Ni, Cu and Co, and the [NiS]/[FeS] ratio of the sulfide fraction for the Maine and Stillwater occurrences, are given in Table 2.

The compositions of grains of magmatic sulfide in the Dumont samples were determined by combining the modal proportions and chemical compositions of the constituent minerals in the polymineralic grains. The modal proportions of pentlandite, magnetite, awaruite and native copper were determined using a Quantimet image analyzer. The mineral compositions were determined by wavelength-dispersion electron-microprobe analysis. A large number of analyses of the sulfide and alloy minerals from the mineralized part of the intrusive body have been carried out; they show that the range of compositions is very limited. Therefore, average mineral compositions have been used in calculating the bulk-sulfide compositions in Table 3. The uncertainties quoted reflect only the variance in the average compositions. An undetermined but probably much larger uncertainty arises from possible errors in the modal analyses.

Results

The sulfide compositions vary considerably among the occurrences discussed here. The scale of equilibration between olivine and sulfide is difficult to define for a particular sulfide accumulation, particularly at low concentrations of sulfide. Results from the Maine and Stillwater examples are, therefore, presented in terms of mean sample compositions of olivine relative to mean compositions of sulfide for each accumulation. This approach is reasonable in terms of the magmatic model of equilibration between an immiscible sulfide liquid and a silicate magma with olivine on the liquidus. Data are plotted from each sample for each deposit in Figures 4 through 6. For the Maine and Stillwater deposits, the composition of the sulfides is taken to be constant for each deposit, and the horizontal error-bar represents plus or minus twice the standard error of the mean for sample values of [NiS]/[FeS]. Vertical error-bars represent 95.5% confidence limits on [NiO]/[FeO] calculated using two standard deviations on NiO and FeO determinations for the mean compositions of olivine in each sample. The olivine variance in the Maine examples is clearly the major source of error in the determination of the K_D, particularly at low [NiS]/[FeS] ratios where K_D lines converge. The values of K_D calculated from the actual data-points, however, all fall between 3.7 and 14.8.

Determinations of the sulfide composition in individual samples for the Dumont body are illustrated in Figure 6. In the context of the Dumont values, we emphasize that the sulfide compositions have been somewhat modified by serpentinization. It is likely that the primary sulfide fraction contained more sulfur and less oxygen than the present compositions. Moreover, Duke (in press) has argued, on the basis of mass-balance calculations, that the relative metal content of the sulfides has increased in the order iron, nickel and cobalt. We infer that the Ni/Fe, and thus the value of $K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}$, has increased during serpentinization. This is supported in a qualitative sense by comparing the distribution coefficients in Table 3 with the specific gravities of the samples. Serpen-

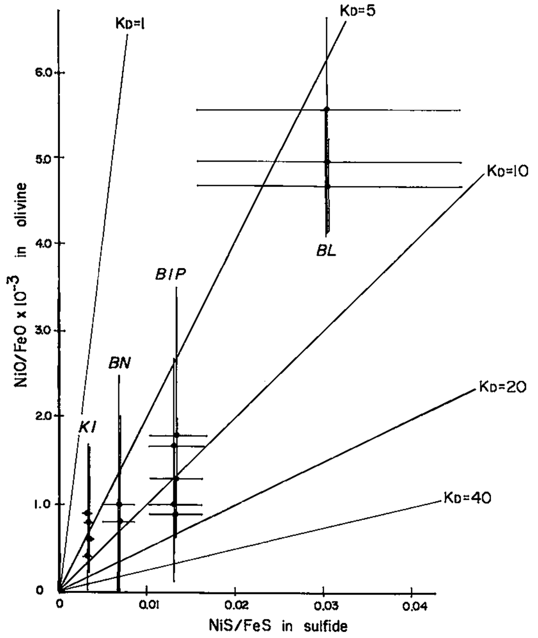

FIG. 4. NiO/FeO ratio of olivine plotted against NiS/FeS ratio of sulfide for the Moxie pluton (BL, BN, BIP) and Katahdin (KI) occurrences. Lines of constant distribution-coefficient are indicated for values of K_D of 5, 10 and 20.

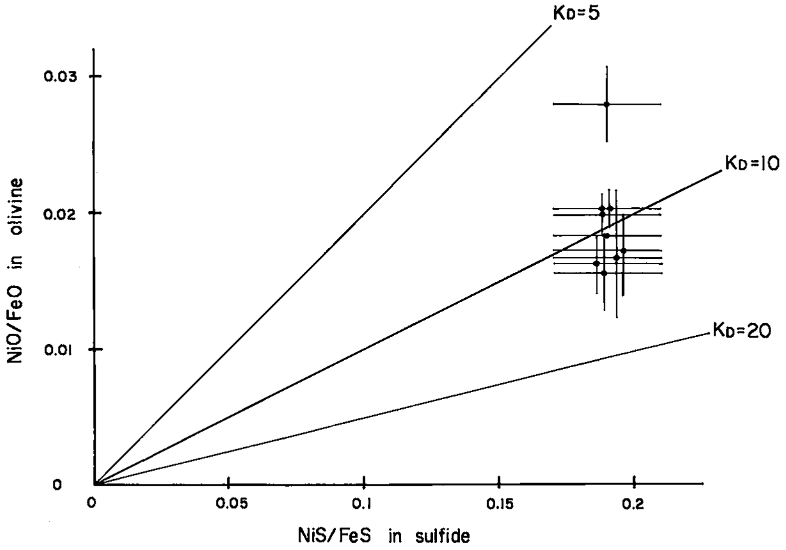

FIG. 5. NiO/FeO ratio of olivine plotted against NiS/FeS ratio of sulfide for the PGE reef of the Stillwater complex. Lines of constant distribution-coefficient are indicated for values of K_D of 1, 5, 10, 20 and 40.

tinization leads to a decrease in rock density; in the case of the Dumont samples, there is a direct linear relationship between specific gravity and the modal percentage of unaltered primary minerals. The least altered samples, with specific gravities greater than 2.7, have $K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}$ of 10 or less, whereas the samples with lower specific gravities have distribution coefficients of 11 or more. Nine of the ten distribution-coefficients fall in the range from 7 to 15, with a mean value of 10.8 ± 2.3. One sample has an anomalously high coefficient (23.5), but it is significant that this sample contains only 0.1 modal % sulfide, much less than the other samples, and thus its modal analysis is least likely to be representative.

DISCUSSION

Theoretical considerations and experimental studies

The distribution coefficient may in principle be calculated from the free-energy change of the reaction

$$\text{FeS} + \text{NiSi}_{0.5}\text{O}_2 = \text{NiS} + \text{FeSi}_{0.5}\text{O}_2 \qquad (2)$$

Thus

$$K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}} = \frac{\gamma_{\text{FeS}}^{\text{Sulf}}\,\gamma_{\text{NiSi}_{0.5}\text{O}_2}^{\text{Oliv}}}{\gamma_{\text{NiS}}^{\text{Sulf}}\,\gamma_{\text{FeSi}_{0.5}\text{O}_2}^{\text{Oliv}}}\;K_e \qquad (3)$$

where the equilibrium constant K_e is given by

$$K_e = \frac{-\Delta G_2}{RT} \qquad (4)$$

and γ_i^A is the activity coefficient of component i in phase A, ΔG_2 is the free-energy change, R is the gas constant, and T is absolute temperature. The equilibrium constant is plotted as a function of temperature in Figure 7 using the pure solids as the standard states of all four components. It would be more appropriate to use the pure liquids as the standard states for NiS and FeS, since we are interested in the distribution of elements between solid olivine and molten sulfide. However, the limited data available are imprecise and do not yield internally consistent results.

Clark & Naldrett (1972) studied the distribution of nickel and iron between fayalitic olivine and monosulfide *solid* solution at 900°C and found that

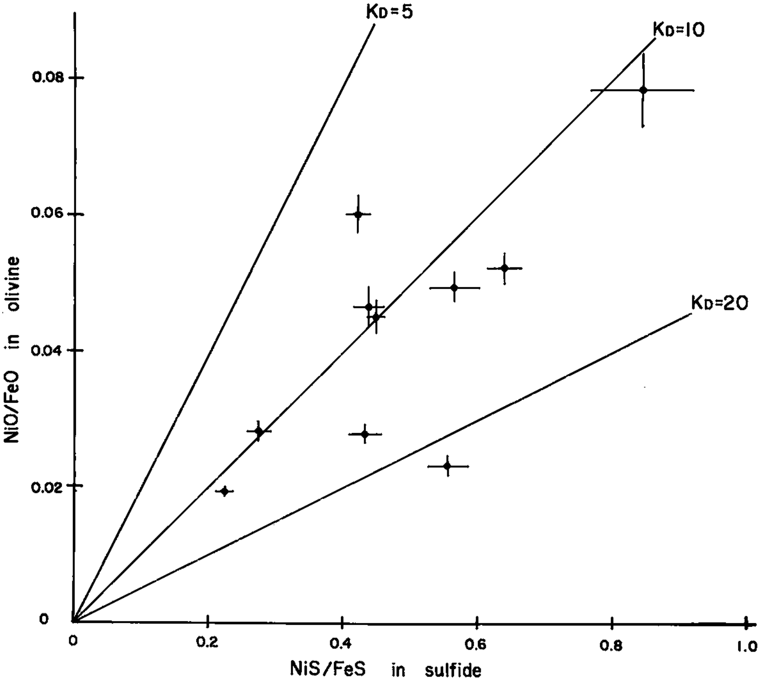

FIG. 6. NiO/FeO ratio of olivine plotted aginst NiS/FeS ratio of sulfide for the Dumont intrusive complex. Lines of constant distribution-coefficient are indicated for values of K_D of 5, 10 and 20.

TABLE 3. COMPOSITIONS OF OLIVINE AND SULFIDE IN DUMONT DEPOSIT

SAMPLE	E16-1180	E16-1380	E16-1425	E16-1480	E16-1500
Olivine Compositions					
Analyses	5	5	4	5	5
SiO_2	40.86 (0.16)	41.36 (0.31)	40.32 (0.11)	41.54 (0.24)	41.71 (0.32)
FeO	7.44 (0.11)	7.50 (0.11)	8.13 (0.06)	7.18 (0.05)	6.63 (0.05)
MnO	0.09 (0.03)	0.08 (0.03)	0.13 (0.07)	0.09 (0.02)	0.09 (0.03)
MgO	50.34 (0.23)	50.24 (0.31)	50.77 (0.06)	50.53 (0.33)	51.36 (0.28)
CaO	0.04 (0.01)	0.07 (0.04)	0.14 (0.01)	0.08 (0.02)	0.04 (0.02)
NiO	0.391 (0.008)	0.176 (0.005)	0.156 (0.009)	0.200 (0.009)	0.329 (0.006)
TOTAL	99.16	99.43	99.65	99.62	100.16
Fo	92.3	92.3	91.8	92.6	93.2
Sulfide Compositions					
% sulf.	0.24	0.10	1.80	2.00	1.70
Fe	44.18 (0.67)	43.88 (0.83)	56.59 (0.50)	45.09 (0.78)	38.96 (0.88)
Ni	28.23 (0.41)	24.49 (0.49)	12.56 (0.29)	19.42 (0.46)	21.99 (0.52)
Cu	0.09 (0.02)	0.03 (0.01)	- -	4.00 (0.00)	8.00 (0.00)
Co	0.94 (0.65)	1.13 (0.82)	0.67 (0.49)	1.04 (0.76)	1.18 (0.86)
S	19.37 (0.36)	24.39 (0.45)	14.70 (0.27)	22.71 (0.42)	25.72 (0.48)
O	7.19 -	6.08 -	15.48 -	7.74 -	4.15 -
NiS/FeS	0.639 (0.013)	0.558 (0.015)	0.222 (0.006)	0.431 (0.012)	0.564 (0.018)
K_D	12.2	23.8	11.6	15.4	11.4
Sp. Gr.	2.55	2.55	2.62	2.64	2.63

SAMPLE	E16-1550	E16-1575	E16-1600	E16-1760	E16-1910
Olivine Compositions					
Analyses	4	5	3	4	5
SiO_2	40.58 (0.13)	41.90 (0.32)	40.40 (0.37)	40.06 (0.46)	40.83 (0.10)
FeO	6.82 (0.04)	6.72 (0.14)	7.51 (0.11)	9.80 (0.19)	10.54 (0.12)
MnO	0.10 (0.04)	0.10 (0.03)	0.10 (0.04)	0.14 (0.03)	0.14 (0.03)
MgO	50.72 (0.54)	51.04 (0.35)	50.11 (0.28)	49.57 (0.56)	48.79 (0.12)
CaO	0.09 (0.02)	0.12 (0.02)	0.07 (0.03)	0.10 (0.05)	0.07 (0.02)
NiO	0.318 (0.008)	0.527 (0.015)	0.452 (0.008)	0.442 (0.008)	0.330 (0.007)
TOTAL	98.63	100.41	98.64	100.11	100.70
Fo	93.0	93.1	92.2	90.0	89.2
Sulfide Compositions					
% sulf.	1.80	2.30	0.83	0.66	1.20
Fe	48.69 (0.65)	39.99 (0.66)	49.41 (0.63)	54.16 (0.27)	53.72 (0.59)
Ni	21.38 (0.39)	35.37 (0.42)	20.81 (0.37)	24.25 (0.24)	14.85 (0.35)
Cu	0.04 (0.01)	0.15 (0.03)	0.04 (0.01)	0.16 (0.03)	- -
Co	0.90 (0.64)	0.95 (0.62)	0.87 (0.62)	0.34 (0.18)	0.80 (0.58)
S	19.04 (0.35)	18.74 (0.34)	18.37 (0.34)	5.34 (0.10)	17.37 (0.32)
O	9.95 -	4.80 -	10.51 -	15.76 -	13.27 -
NiS/FeS	0.439 (0.010)	0.884 (0.018)	0.421 (0.009)	0.448 (0.005)	0.276 (0.007)
K_D	9.4	11.3	7.0	9.9	8.8
Sp. Gr.	2.73	-	2.77	2.84	2.95

$K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}$ is 33.2 ± 3.4. The fact that their distribution coefficient is independent of the relative proportions of nickel and iron in the system, and somewhat greater than the calculated equilibrium-constant (Fig. 7), implies that the activity-coefficient product is constant but slightly greater than unity. Rajamani (1976) reported an analogous series of experiments on the distribution of Ni and Fe between orthopyroxene and monosulfide *solid* solution and found the value of the coefficient

$$K_{D(\text{Ni-Fe})}^{\text{Sulf/Opx}} = \frac{(X_{\text{NiS}}^{\text{Sulf}})\,(X_{\text{FeSiO}_3}^{\text{Opx}})}{(X_{\text{FeS}}^{\text{Sulf}})\,(X_{\text{NiSiO}_3}^{\text{Opx}})} \qquad (5)$$

to be 10.8 ± 1.5. Nickel partitions preferentially into olivine, compared to orthopyroxene in natural assemblages, with the distribution coefficient

$$K_{D(\text{Ni-Fe})}^{\text{Oliv/Opx}} = \frac{X_{\text{NiSi}_{0.5}\text{O}_2}^{\text{Oliv}}X_{\text{FeSiO}_3}^{\text{Opx}}}{X_{\text{FeSi}_{0.5}\text{O}_2}^{\text{Oliv}}\;X_{\text{NiSiO}_3}^{\text{Opx}}} \qquad (6)$$

being typically about 3. Since $K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}$ is simply the quotient of $K_{D(\text{Ni-Fe})}^{\text{Sulf/Opx}}$ divided by $K_{D(\text{Ni-Fe})}^{Oliv/Opx}$, the experimental data of Clark & Naldrett (1972) and of Rajamani (1976) cannot both be consistent with the distribution observed in natural assemblages.

In the present paper we are concerned with the distribution of nickel and iron between olivine and *molten* sulfide, of which there are three experimental studies. Fleet *et al.* (1977) equilibrated natural basaltic compositions with various proportions of synthetic NiS and FeS. The observed value of $K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}$ is 40.4 ± 6.4 in 8 experiments run at about 1160°C and 31 for the same basalt in an experiment at 1052°C. Noting the similarity of their data to those

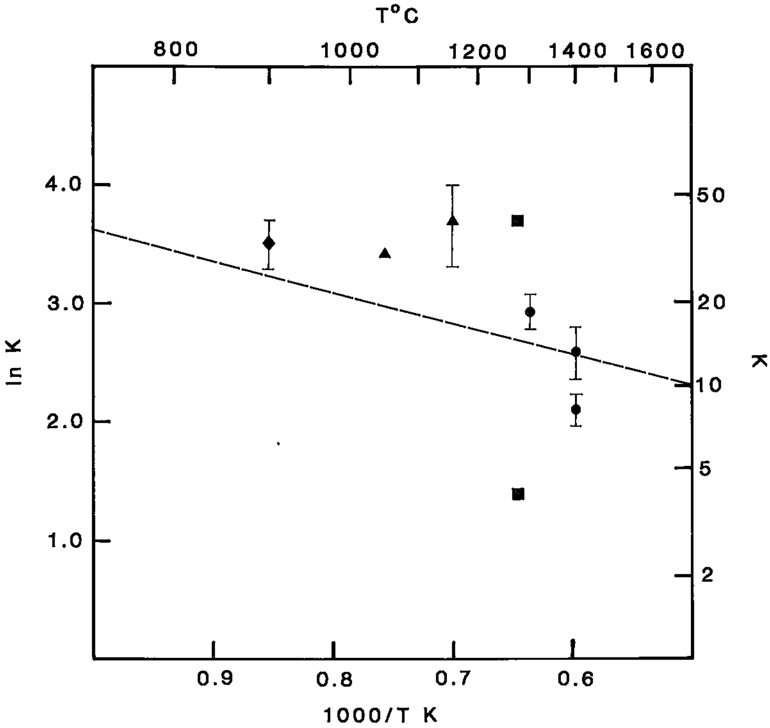

FIG. 7. Experimental determinations of the distribution of nickel and iron between olivine and sulfide; circles: Boctor (1981, 1982), triangles: Fleet *et al.* (1977), squares: Mysen & Kushiro (1976), diamond: Clark & Naldrett (1972). The sulfide phase was a solid solution in the experiments of Clark & Naldrett (1972): in all other cases it was molten. The error bars represent plus or minus two standard deviations of the mean of several determinations of the distribution coefficient at a given temperature and oxygen fugacity. The dashed line is variation with temperature of the equilibrium constant for the exchange reaction, calculated with respect to the pure solid reactants as standard states.

of Clark & Naldrett (1972), Fleet *et al.* (1977) suggested that the distribution coefficient is virtually independent of temperature and composition. Naldrett (1979, 1981) criticized these results on the basis of an apparent lack of equilibrium between the olivine and silicate liquid. Fleet *et al.* (1981) reiterated their earlier conclusions and presented additional analytical data for their charges. In doing so, however, the FeO contents of their silicate liquids were calculated assuming equilibrium compositions of olivine, an assumption shown to be inappropriate by Naldrett (1981). Mysen & Kushiro (1976) equilibrated samples of Allende meteorite at 1275°C, and values of 40 and 4 for the distribution coefficient are calculated from data for experiments run at oxygen fugacities of $10^{-10.5}$ and $10^{-12.0}$, respectively. Boctor (1981, 1982) determined distribution coefficients as a function of temperature, $f(O_2)$ and $f(S_2)$ in a series of reversed experiments. He found that $K_{D(Ni\text{-}Fe)}^{Sulf/Oliv}$ varies inversely as temperature and oxygen fugacity, and is essentially independent of sulfur fugacity. Boctor's average values range from 8.18 ± 0.56 at 1400°C and $f(O_2) = 10^{-8}$ to 18.1 ± 1.44 at 1300°C and $f(O_2) = 10^{-9}$.

The work of Mysen & Kushiro (1976) and Boctor (1982) indicates that $f(O_2)$ exerts a strong influence on the partition coefficient. However, the equilibrium constant for the exchange reaction (2) is independent of oxygen fugacity. We interpret the influence of $f(O_2)$ to be a result of the nonideality of the sulfide melt. Although the exchange reaction (2) is written in terms of FeS and NiS end-members, the sulfide melt would rarely have monosulfide stoichiometry. The metal-to-sulfur ratio is variable and is generally greater than 1. A decrease in oxygen fugacity tends to increase the metal-to-sulfur ratio in the sulfide melt as illustrated, for example, by the experiments of Mysen & Kushiro (1976) and the metal-rich natural sulfides described by Pedersen (1979). The activity coefficients of FeS and NiS decrease markedly as the metal-to-sulfur ratio in the sulfide is increased, but γ_{NiS} decreases much more rapidly than does γ_{FeS} in the respective binary systems (Nagamori *et al.* 1969, Nagamori & Ingraham 1970). If the activity coefficients behave similarly in the ternary system, the effect of decreasing oxygen fugacity is to decrease γ_{NiS} more than γ_{FeS}, leading to a net increase of the distribution coefficient by virtue of equation (3). Boctor (1982) noted that his experiments were conducted at oxygen fugacities somewhat lower than those typical of most terrestrial magmas. Therefore, his distribution coefficients at a given temperature are probably higher than would prevail in most natural assemblages.

The distribution coefficient may also be calculated indirectly from experimental data on the distribution of nickel and iron between sulfide melt and silicate liquid and between silicate liquid and olivine. Naldrett (1979) calculated a range of $K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}$ between 5 and 7 using the relationships derived by Duke & Naldrett (1978) from the experimental data of Roeder & Emslie (1970), Arndt (1977) and Rajamani & Naldrett (1978).

Distribution coefficients in natural assemblages

There are only limited data on the distribution of iron and nickel between olivine and sulfide in natural assemblages. Clark & Naldrett (1972) reported K_D values of 10.8 for the Giant Nickel deposit, B.C., and 17.0 for Duluth. Binns & Groves (1976) obtained a value of 23 by analyzing coexisting olivine and sulfide assemblages at Perseverance, Western Australia. The silicate mineral assemblage indicates maximum temperatures of 500–700°C, and the K_D is interpreted as the result of metamorphic equilibration at these temperatures. This is generally consistent with the reaction curve in Figure 7. Rajamani (1976) calculated a mean value of 5.3 from the data of Häkli (1963) for a number of Finnish deposits. Pedersen (1979) determined a distribution coefficient of 63 in a native-iron-bearing dyke from Disko Island, Greenland, with an inferred quenching temperature of 1200°C. He attributed the high K_D value to the fact that the sulfide phase was abnormally metal-rich.

TABLE 4. DISTRIBUTION COEFFICIENTS DETERMINED IN NATURAL ASSEMBLAGES

Occurrence	$K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}$	Reference
Moxie (Mean)	8.3 (3.1)	This study
Black Narrows	5.8 (0.5)	This study
Burnt Nubble	7.2 (1.0)	This study
Big Indian Pond	10.4 (3.2)	This study
Katahdin	5.0 (1.7)	This study
Stillwater	11.4 (4.8)	This study
Dumont	10.8 (2.3)	This study
Giant Nickel	10.8	Clark & Naldrett (1972)
Finland	5.3	Häkli (1963)
Duluth	17	Clark & Naldrett (1972)
Perseverance	23	Binns & Groves (1976)
Disko Island	63	Pedersen (1979)
Mean	9.8 (4.1)	

Mean excludes Perseverance and Disko data, and counts Moxie pluton as one occurrence.

The mean distribution-coefficients calculated from natural olivine–sulfide assemblages in this and previous studies are listed in Table 4. Excluding the values for Perseverance, which is believed to represent equilibration under metamorphic rather than igneous conditions, and Disko, which apparently equilibrated under unusually reducing conditions, the mean coefficients range from 5 to 17, and all but one are less than 12. Our data suggest that the distribution coefficients representing equilibration under igneous conditions are most likely to fall toward the lower end of the range defined by the previously reported values. The data for natural assemblages, with the exceptions noted above, are consistent with the experimental results of Boctor (1981, 1982) and with the distribution coefficients deduced indirectly by Duke & Naldrett (1978) and Naldrett (1979).

CONCLUSIONS

Fleet *et al.* (1977, 1981) have argued that the high value of the distribution coefficient indicated by their experiments (*i.e.*, ~40 at 1160°C) undermines the validity of the magmatic segregation hypothesis for the origin of nickel–copper sulfide deposits. An implication of their argument is that the distribution coefficients that we have calculated are too low to represent magmatic equilibration. However, we believe that the weight of the evidence from natural assemblages and experimental studies supports the view that the distribution coefficient $K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}$ will achieve values in the range of 5 to 20 during equilibration under typical magmatic conditions, and will most commonly be toward the lower end of this range.

The distribution coefficient is expected, on theoretical grounds, to increase with decreasing temperature; a small increase may be expected owing to subsolidus re-equilibration during the cooling of some intrusive bodies. The experimental studies of Boctor (1982) have demonstrated a strong inverse relationship between $K_{D(\text{Ni-Fe})}^{\text{Sulf/Oliv}}$ and oxygen fugacity; we have suggested that the nonideality of the molten sulfide phase provides an explanation of this relationship. The data of Pedersen (1979) indicate that atypical values of the distribution coefficient may result under unusually reducing conditions in nature. Additional experimental work under carefully controlled conditions, such as that of Boctor (1981, 1982), may eventually allow the distribution coefficient to be used as a quantitative indicator of the conditions that prevailed during the formation of magmatic sulfide deposits.

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