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DISTRIBUTION OF NICKEL BETWEEN THE SILICATE AND SULPHIDE PHASES IN SOME BASIC INTRUSIONS IN FINLAND

BY

AULIS HÄKLI

WITH 17 FIGURES AND 18 TABLES IN TEXT

HELSINKI 1963

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PREFACE

This study is part of a programme which has been carrid out for a few years in the Research Laboratory of the Outokumpu Co, and which seeks to contribute to the knowledge of the mode of occurrence of nickel in the upper lithosphere and to elucidate the factors controlling its behaviour under different geological conditions. The samples were collected during the years 1960—1962, and studied in the laboratory during the same period.

Numerous persons have facilitated my work. To the chief geologist of the Outokumpu Company, Dr. Paavo Haapala, who has shown a keen interest in my study from the very beginning, I wish to express my cordial thanks. His support and extensive knowledge about nickel deposits have been of the greatest assistance. At the same time I extend my grateful acknowledgement to the Outokumpu Company for permission to publish this paper.

It also gives me pleasure to express my appreciation to Dr. Vladi Marmo, Director of the Geological Survey of Finland, for arranging the publication of this paper as a Bulletin of the Geological Survey. Further, I am greatly indebted to professor K. J. Neuvonen and professor Th. G. Sahama for their invaluable aid in reading the manuscript, pointing out errors, and suggesting important improvements.

To the head of the Exploration Department of the Outokumpu Company, Dr. Veikko Vähätalo, who has generously supported my work at all its stages, I should also like to address my special thanks. Similarly, I wish to express my great indebtedness to the mining geologists of the Kotalahti Mine, Mr. J. Koskinen M.Sc. and Mr. M. Järvinen M.Sc., for having always been very helpful with information, guidance and discussions.

My cordial thanks go also to other members of the geological staff of the Outokumpu Company, particularly to Mr. O. Helovuori M.Sc., Mrs. Maija Huhma M.Sc., Mr. A. Huhma M.Sc., Mr. J. Kujanpää M.Sc., Mr. E. Pehkonen M.Sc., Dr. E. Peltola, Mr. P. Rouhunkoski Ph.Lic., Mr. E. Viluksela M.Sc. and Mr. K. Vormisto M.Sc., whom I have often consulted on choosing the samples used in this investigation.

CONTENTS

ABSTRACT

The present paper deals with the distribution of nickel between olivine, pyroxene and amphibole and the coexisting sulphide phase. Material from 25 Finnish sub-silicic intrusions has been used. The chemical equilibrium prevailing in the partition of nickel between the different phases in basic and ultrabasic rocks is established. For the value of the distribution coefficient between the atomic ratio Ni/Mg in olivines and the nickel percentage of the coexisting sulphide phase $K = 0.000344$ is obtained. For pyroxene and amphibole the distribution coefficients are calculated between the nickel percentages of the silicate and sulphide phases. The value for pyroxene is 0.00755. The values for K of amphiboles show a considerable variation depending mainly on whether the amphiboles are primary or secondary. For the former $K = 0.0134$, and for the latter $K = 0.00755$ is obtained. Finally, the genesis of the skarn type of nickel ores is discussed on the basis of the distribution law.

INTRODUCTION

From the point of view of physical chemistry, rocks can be considered as systems composed of a number of different phases. At equilibrium every element in a system is distributed between the phases in such a way that its chemical potential is constant throughout all phases. Briefly, the chemical potential μ of an element distributed between two phases I and II is in phase I

$$\mu_{,} = \mu_{,}^{\circ} + RT \ln a_I$$

and in phase II

$$\mu_{,,} = \mu_{,,}^{\circ} + RT \ln a_{II}$$

where a_I and a_{II} are the activities of the element in the two phases, and $\mu_{,,}^{\circ}$ and $\mu_{,}^{\circ}$ are quantities depending only on temperature and pressure. At chemical equilibrium the two values of the potential are equal and, since $\mu_{,}^{\circ}$ and $\mu_{,,}^{\circ}$ are constant at definite temperature and pressure, it follows that

$$a_I/a_{II} = \text{constant.}$$

If the phases behave ideally, the activities can be replaced by concentrations. This is possible whenever the concentration of an element is low. Therefore, it may be expected that the trace elements in minerals obey the distribution law in a reasonably satisfactory manner.

The potential of an element depends on the composition and structure of the phase. The more the properties of an element — like ionic radius, valence and affinity — resemble those of another one already present in the phase, the more easily it can replace the latter and the higher its concentration in the phase will be.

The sulphide-bearing basic and ultrabasic intrusions can be considered as systems composed of two mutually immiscible liquids, the sulphide and silicate melts. When such systems cool down sufficiently, a number of minerals — both silicates and sulphides — crystallize, and the number of the phases is the same as that of the mineral species formed. If we are mainly intersted in the distribution of nickel between the silicate and sul-

phide phase, we can, however, make a simplification by considering the sulphides as a single phase. This is justified because the temperature at the time of the setting of the chemical equilibrium is so high that at least the main part of the sulphides is molten and forms a homogeneous liquid (Vogt, 1923; Hawley, Colgroove and Zurbrigg, 1943; Lundquist, 1947a and b).

DeVore (1955a and b), Kretz (1959) and recently Barth (1961) have calculated some distribution coefficients for a number of major and minor constituents between different rock-making minerals, mainly silicates. Very little has, however, been published about the distribution of elements between the silicates and the sulphides. Due to its thiophile and lithophile character, nickel offers excellent subject for such a study.

The aim of this paper is to illustrate the partition of nickel between some iron magnesium silicates and the coexisting sulphide phase.

ON THE GEOCHEMISTRY OF NICKEL

Nickel, together with cobalt and iron, forms the iron family in the Periodic System. According to Ahrens (1952) the ionic radius of Ni^{+2} is 0.69 Å and those of Co^{+2} and Fe^{+2} 0.72 Å and 0.74 Å, respectively. The size of magnesium ion (0.66 Å) is nearly the same as that of nickel ion, and consequently, nickel follows magnesium readily into early iron magnesium minerals. Nickel has a strong affinity for sulphur. When a sulphide phase separates from silicates, nickel enters the sulphides, thus separating itself from magnesium. In addition to the thiophile and lithophile tendencies, nickel also has a very prominent siderophile character.

In accordance with this siderophile tendency nickel is strongly concentrated in the metal phase of meteorites. According to Goldschmidt (1954) nickel-iron meteorites contain 8.49 per cent nickel and 0.57 per cent cobalt with the cobalt to nickel ratio 0.07. The sulphide phase of meteorites is relatively poor in nickel. Rankama and Sahama (1955) give an average value 0.1 per cent for troilite. Higher values have, however, been reported (Clark and Kullerud, 1960). Still, the sulphides of meteorites contain conspiciously less nickel than sulphides of terrestrial rocks having the same amount of nickel in silicates. The low nickel content of troilite in meteorites can readily be explained by the studies on the ternary system Fe-Ni-S. Clark and Kullerud (1960) have paid special attention to the threephase field in which troilite coexists together with alpha and gamma alloy. The compositions of normal iron meteorites fall within this field. The nickel content of troilite is less than 1 per cent at 500°C. It increases with rising temperature, being about 4 per cent at 700°C, but decreases again to less than 2 per cent at 800°C. At the transformation temperature of the sulphur-saturated iron, i.e. at 913°C, the composition of troilite approaches FeS. Similarly, the nickel content of troilite becomes small at low temperatures due to the small solubility of nickel in FeS. It is inferred from the nickel content of coexisting gamma alloy that the formation of iron meteorites has generally taken place at temperatures below, rather than above, 700°C. Under those conditions most of the nickel enters the iron phase leaving troilite almost free from it.

Table 1. The average nickel content of igneous rocks. According to Vogt (1923).

Rock type	Ni per cent
Peridotites	0.14
Pyroxenites	0.08
Norites	0.035
Gabbros	0.030
Diorites etc.	0.006
Granites	0.0005

As pointed out by Vogt (1923), the nickel content of an igneous rock depends on its magnesium content. The rocks richest in magnesium, like dunites, contain up to 0.3 per cent nickel. Du Rietz (1956) gives an average value for Swedish peridotites as 0.2 per cent nickel. With increasing content of silica the amount of nickel diminishes and the nickel content of granites is only about 0.0005 per cent. This relationship between the nickel and magnesium contents is readily seen in Table I.

According to Goldschmidt (1937), peridotite contains 3160 p.p.m., gabbro 158 p.p.m., diorite 40 p.p.m., and granite 2.4 p.p.m. nickel on an average.

The decrease of the nickel content with increasing silica is further seen in Fig. 1, which is reproduced from a paper by Wilson (1953).

The nickel to magnesium ratio is not constant in igneous rocks, but varies from one intrusion to another. The plutonic rocks of the Loch Doon Complex in Scotland contain nickel from 35 p.p.m. to 200 p.p.m. (Higazy, 1954). The average nickel content in the granitic and feldspathized types is 89 p.p.m. and that of the pyroxene-bearing rocks 134 p.p.m., respectively.
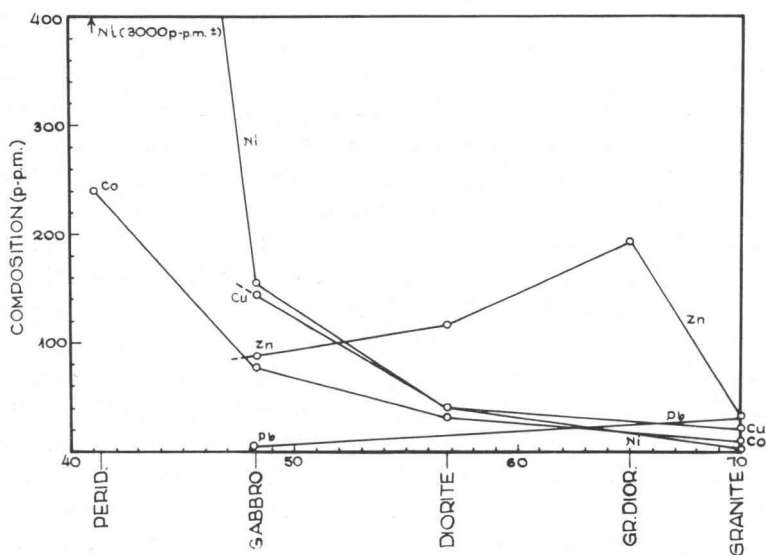

Fig. 1. Nickel, copper, cobalt, zinc and lead of igneous rocks plotted against silica. After Wilson (1953).

Table 2. Stillwater Complex trace element distribution. After Turekian and Carr (1960).

	Station	Plagioclase		Orthopyroxene		Clinopyroxene			
		Cr	Ni	Cr	Ni	Fe %	Cr	Co	Ni
		(p.p.m.)		(p.p.m.)		(p.p.m.)			
Upper Gabbro ..	EB 41	16	34	93	310	—	—	—	—
» ..	EB 134	18	26	270	650	11.3	215	108	460
» ..	EB 133	16	36	360	650	11.1	240	118	480
Anorthosite	EB 142	13	17	330	490	14.9	340	114	380
»	EB 155	16	25	—	—	—	—	—	—
Lower Gabbro ..	EB 171	—	—	560	890	10.4	570	86	590
» ..	EB 172	16	26	—	—	—	800	—	590
» ..	EB 173	14	67	670	1 400	9.6	980	86	630
» ..	EB 174	21	54	700	1 100	8.4	1 050	99	1 400
» ..	EB 176	16	44	1 000	1 350	8.4	1 350	74	660
» ..	EB 218	50	74	1 000	830	—	1 400	—	470
» ..	EB 216	45	66	1 150	1 300	8.4	1 800	74	640
» ..	EB 210	19	135	1 650	2 000	11.1	1 300	79	1 300
Norite	EB 207	14	34	970	1 150	—	415	—	610
»	EB 182	14	42	1 050	10 000	10.7	1 200	104	650

In the Stillwater Complex of Montana (Turekian and Carr, 1960) nickel shows the highest concentration in the lower gabbro zone in all mineral phases (see Table II). Throughout the Complex clinopyroxene contains less nickel than orthorhombic pyroxene, obviously because there are more Fe and Mg sites for nickel in orthopyroxene per gram than in calcium-bearing clinopyroxene. Plagioclase is relatively rich in nickel and its nickel content seems to vary sympathetically with that of pyroxene.

Tiller (1959) studied the distribution of trace elements in the Mt. Wellington dolerite sill and found that nickel occurs in early pyroxene. The nickel content of the rock is about 15 p.p.m. in the upper parts of the sill increasing downwards and reaching 120 p.p.m. in the lower parts.

Of the early magmatic silicates olivine shows the highest nickel content. For the magnesium-rich olivine of the dunites, saxonites and olivine basaltic bombs Vogt (1923) gives values for the NiO content varying from 0.19 to 0.50 per cent. Iron-rich olivine contains NiO 0.15—0.32 per cent with an average of 0.21 per cent. Hyperstene shows generally lower NiO contents, the values varying from 0.062 to 0.081 per cent. Monoclinic pyroxene contains usually slightly less nickel than the orthorhombic types (0.04—0.05 per cent NiO), while the nickel content of the amphibole can reach values twice as high as those for pyroxene (0.02—0.10 per cent).

DeVore (1955a) has shown that the nickel content of amphibole depends on the metamorphic facies to which the rock belongs. The average values for the NiO content of amphibole in epidote amphibolite facies is 878 p.p.m., in amphibolite facies 171 p.p.m. and in granulite facies 20 p.p.m..

Economically and geochemically the most important nickeliferous sulphide is pentlandite, which contains 18.4—39.9 per cent nickel (Hawley, Colgrove and Zurbrigg, 1943). In many nickel deposits it is practically the only valuable nickel-bearing mineral. In certain ore bodies associated with copper and iron sulphides, a cobalt analogue of pentlandite (Kouvo, Huhma and Vuorelainen, 1959) is met with. Its nickel content can be as low as 9 per cent, while that of cobalt reaches fifty per cent. In addition to pentlandite, violarite and millerite are found sometimes, especially in the weathering zone of nickel deposits. Pyrrhotite is almost free from nickel. Due to the error caused by the possible pentlandite impurities the analyses are not always very reliable. Generally, the nickel content of pyrrhotite is considerably lower than one per cent. In pyrite, independent of its temperature of formation, the content of cobalt is higher than that of nickel (Rankama and Sahama, 1955).

The nickel content of a sulphide phase is fairly constant and characteristic of the rock it is associated with, as pointed out by Wilson (1953). For example, the Frood ore body in Sudbury has a sulphur to nickel ratio which varies very little, lying in the range of 5: 1 to 6: 1. Even units as small as hand specimens always show the same sulphur to nickel ratio.

Table 3. Relationship of nickel content of sulphide phase with rock type. After Wilson and Anderson (1959).

Locality [1]	Rock type	Nickel—% in sulphide phase
Werner Lake, Ontario	Peridotite	10.0
Rankin Inlet, N.W.T.	Serpentine	10.0
Shebandowan, Ontario	Peridotite	9.0
Norpax, Ontario	»	8.5
Alexo, Ontario	»	8.0
Thompson, Manitoba [2]	»	7.5
Bruvand, Norway	»	7.0
Mystery Lake, Manitoba [2]	»	5.4
Choate, B.C.	Pyroxenite	5.0+
Espedelen, Norway	»	4.5
Hosander, Norway	Norite	6.5
Sudbury, Ontario	»	3.0—6.0
Rice Island Manitoba	»	5.0
Herb Bay, Manitoba	»	4.0
Bamle, Norway	»	3.75—4.0
Romsaas, Norway	»	3.5—3.75
Yakobi Island, Alaska	»	3.0
Klefva, Sweden	»	2.6
Emo, Ontario	Gabbro	3.1
Lake Athabaska, Saskatchewan	Diorite	1.0
Chibougamou, Quebec	Anorthosite	0.5

[1] The data for the Scandinavian deposits are those of Vogt (1923)
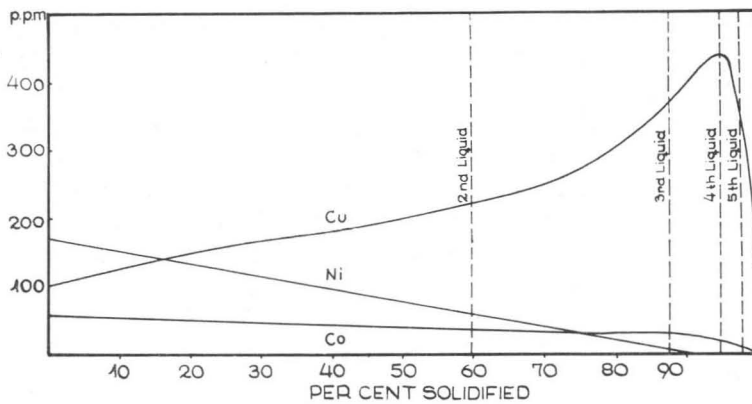[2] Thompson and Mystery Lake from a few specimens.

Fig. 2. Nickel, copper and cobalt in residual liquids of the Skaergaard intrusion. Data from Wager and Mitchell (1951).

Vogt (1923) has shown that in Norwegian nickel deposits the nickel content of the sulphide phase is related to the type of rock in which the ore occurs. The ultrabasic rocks have sulphides richest in nickel, the nickel content decreasing with increasing silica or decreasing magnesium content of the host rock. In Table III the data of Vogt are presented together with those of Wilson and Anderson (1959).

Wager and Mitchell (1951) and Wager et al. (1957) determined the distribution of nickel, copper and cobalt in the Skaergaard intrusion and calculated the metal content in the magma (Fig. 2) and in the rocks (Fig 3) at successive stages of crystallization. The original magma contained about
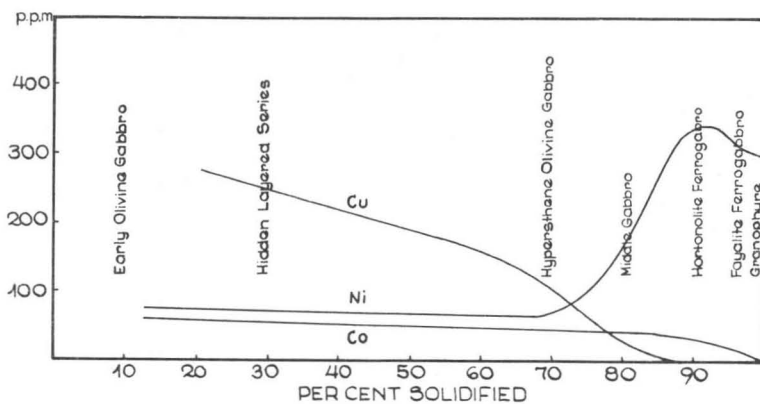

Fig. 3. Nickel, copper and cobalt in the rocks of the Skaergaard intrusion. Data from Wager and Mitchell (1951).

180 p.p.m. nickel which in residual liquids decreased continuously on pro-
gressing crystallization, the last ten per cent of the liquid being practically
free from nickel.

The behaviour of nickel and copper is especially instructive. Their
proportion in the differentiating magma changes in the same way as in
the nickel deposits. In the nickel ores associated with ultrabasic rocks
nickel invariably preponderates over copper, but in ores associated with
more silica-rich rocks the amount of copper relative to nickel increases
in such a way that the sulphide phase may finally contain more copper
than nickel.

The distribution coefficients between the sulphide and silicate melts
during the different stages of crystallization were also estimated in the
Skaergaard intrusion (Wager et al., 1957). In the bornite-rich horizon

$$K = \frac{X_{Ni}^{Sulph}}{X_{Ni}^{Silic}} < 100$$

where X_{Ni}^{Sulph} = the concentration of nickel in the sulphide phase, and
X_{Ni}^{Silic} = the concentration of nickel in the silicate melt. In the pyrrhotite
horizon the value for K is 50 and in the acidic granophyre 0.04, respectively.

METHODS

PREPARATION OF MATERIAL

The material used in this work has been gathered from different localities in Finland investigated by the Exploration Department of the Outokumpu Company. Most of the specimens have been collected from outcropping rocks, but some are from loose boulders. The latter have been included to obtain material from as many different intrusions as possible.

The sizes of the specimens, regardless of their locality, have been kept approximately constant, viz. about 2—3 kg.

For separation, the specimens were crushed with a jawcrusher to a suitable size and ground in a swingmill. The latter was used to prevent contamination caused by iron filings. The powder was then sieved and the fraction 200—250 mesh was taken for further treatment. The dust was washed away, and the sulphide phase separated out with Clerici solution. In case the specimen contained oxides in addition to sulphides the latter were separated using ordinary flotation methods. This procedure was needed very seldom. The samples usually contained only small amounts of oxides. The possible error in the composition of the sulphide phase caused by the oxide contamination was quite negligible.

After removal of the sulphide phase the separation was continued as follows: first, olivine was separated using Clerici solution with a density of about 3.3. After that pyroxene was extracted with a suitable liquid and, finally, amphibole using a solution with a density of 2.9—3.10 or even higher, depending on the composition of the amphibole. Whenever possible, all three minerals were separated from the same sample. This could be done seldom, however. Usually the specimens contained two or, in some cases, only one of the minerals mentioned.

To remove all possible traces of sulphides, the mineral fractions were treated with a hot mixture of diluted hydrochloric and nitric acid. This procedure was carried out very carefully to prevent any dissolving of silicate nickel. To check that the acid used was not too strong, some samples were submitted to acid treatment several times und their nickel content was determined with an X-ray spectrometer after every treatment. No

change in the nickel content was detected. Finally the minerals were puri-
fied by running them though a Franz type isodynamic magnetic separator
using a strong magnetizing current for removing grains that contained
oxide inclusions. The purity of the minerals obtained was checked by ex-
amining them in immersion liquids under the microscope and by running
a powder chart. Only the purest material was accepted for analyses.

ANALYTICAL METHODS

The sulphide phases were analyzed chemically in the Keretti laboratory
of Outokumpu Co under the supervision of Mr. L. Kosomaa, M.Sc., using
the following methods. The sulphides were burned in an air stream and
the gases conducted into a neutralized H_2O_2-solution. SO_3 was then titrated
with NaOH. Nickel was determined spectrophotometrically after the di-
methylglyoxime precipitation. Iron was determined iodometrically, as well as
copper if its percentage was higher than 0.5. In case the copper content was
lower, a colorimetre was used. Cobalt was also determined colorimetrically.

For characterizing the chemical composition of a natural nickel-bearing
sulphide phase the determination of iron, nickel, copper and sulphur is
mostly sufficient. In this paper, however, the fifth component, cobalt, has
been included. Arsenic and zinc have been omitted. All the rocks inves-
tigated contained these two elements only in negligible amounts.

The nickel content of the silicates and in certain cases the contents of
iron, calcium and chromium were determined with a North American
Philips X-ray spectrometre provided with a tungsten tube and a LiF crystal.
Most of the determinations were carried out with a proportional counter,
but in some cases a scintillation counter was also used. The operation volt-
age for the X-ray tube was 45 kv and the current 40 ma. A fixed-time
method was used, since it is convenient to use, the accuracy being prac-
tically the same as that of a fixed-count method (Birks and Brown, 1962).

For the determination of the nickel content, the intensity of the $NiK\alpha$
line at $2\theta = 48.65°$ was measured and, from the value obtained, the intensity
of the background measured at $2\theta = 47.00°$ was subtracted. Because the
position of the $NiK\alpha$ peak did not remain completely steady during the
measurements, an attempt was made to eliminate the error caused by this
shift. Accordingly, a series of measurements was made across the $NiK\alpha$
peak, changing the 2θ -angle 0.01 degrees at a time and adopting the high-
est value obtained. In this way the coefficient of variation [1] of the repeated

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[1]) The coefficient variation (V) is a measure of relative dispersion

$$V = \frac{s}{\bar{x}}$$

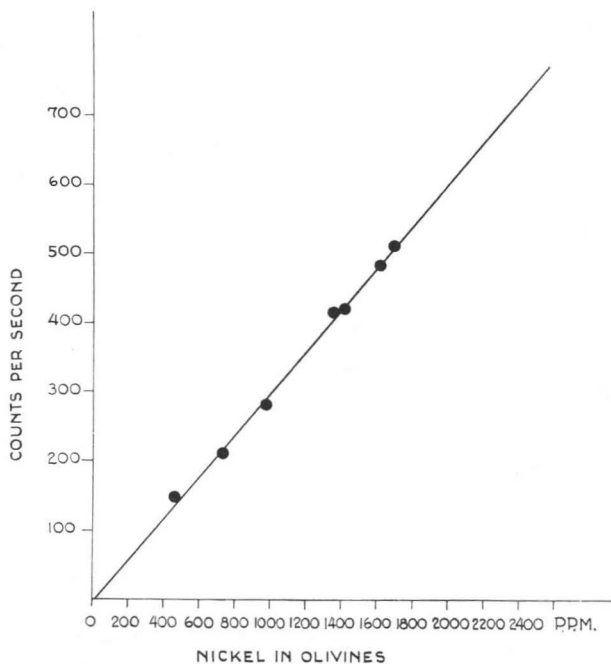where s = standard deviation and $\bar{x}$ = arithmetic mean.

Fif. 4. The calibration curve for the determination of nickel
in olivine. LiF crystal, 45 kv/40 ma.
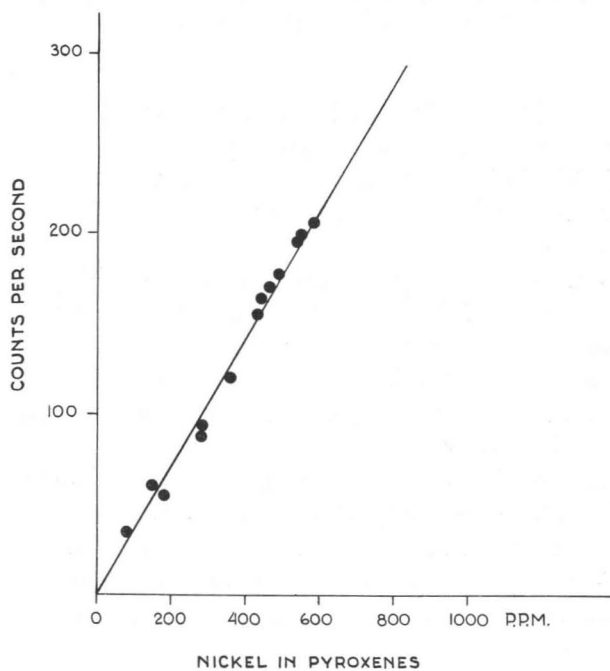
Fig. 5. The calibration curve for the determination of nickel
in pyroxene. LiF crystal, 45 kv/40 ma.
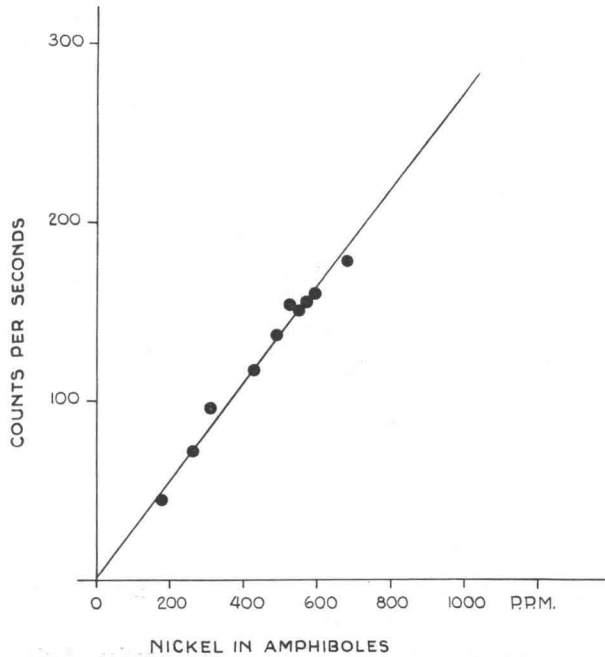
Fig. 6. The calibration curve for the determination of nickel
in amphibole. LiF crystal, 45 kv/40 ma.

measurements was kept as low as 1 %. A number of chemically analyzed silicates were used as standards. Since there is a certain difference between the matrix effects of olivine, pyroxene and amphibole, a Ni-determinative curve was made for each of the silicates mentioned. These curves are presented in Figs. 4—6.

The composition of olivine — more exactly, its Fo-percentage — was calculated on the basis of the equation given by Yoder and Sahama (1957), according to which the Fo-percentage of an olivine is a linear function of the d-value of the 130 plane. A routine goniometre procedure was applied. The possible error in the peak position was corrected by using silicon powder as an internal standard.

All the silicate analyses were done in the Central Laboratory of Outokumpu Co in Pori under the supervision of Mr. J. Kinnunen, M.Sc.

For the determination of the density a pycnometre was used. The compositions of the plagioclases were evaluated measuring the maximum extinction angles in a zone normal to 010 (Winchel and Winchel, 1951).

PETROGRAPHY OF THE SPECIMENS

Virtually all specimens used in the present investigation are from basic and ultrabasic intrusions situated in a schist belt extending from Southwest to Central and East Finland. Despite the rather extensive areal distribution of the samples, they, most probably, belong to the same orogenic phase. A detailed discussion about the very interesting geographical distribution of these rocks is, however, beyond the scope of this paper.

Petrographically the rocks can be divided into three groups: a) peridotites and related rocks, b) pyroxene gabbros, and c) amphibole gabbros, all of which contain sulphides in varying amounts. The primary sulphides are almost invariably the same in every specimen — pyrrhotite, pentlandite and chalcopyrite — and only their mutual amounts vary. Arsenic, zinc and cobalt minerals are almost completely lacking. They have been observed only in a few polished sections as accessory constituents.

In the following a brief petrographical description of the specimens is given. Because of economic importance connected with the results, the names and the geographical locations of the intrusions have been omitted. The intrusions are labeled only by numbers, with the exception of the Kotalahti intrusion. This may cause inconvenience, but since in the present paper, attention is devoted only to the partition of nickel between the different phases, the locations of the intrusions are not very important.

In this paper the terms peridotite, pyroxenite and hornblendite are used, based on the classification given by Johannsen (1949). Accordingly, peridotites are rocks with olivine, pyroxene and/or amphibole as the main constituents. Pyroxenites and hornblendites are nearly monomineralic rocks. They are usually free from olivine. The main constituent in the former is pyroxene and in the latter, hornblende, respectively.

PERIDOTITES AND RELATED ROCKS

Intrusion No 1. The Kotalahti Mine, which is situated in Central Finland in the parish of Leppävirta about 40 kilometres south of the town Kuopio, plays a very important role in this investigation. Due to
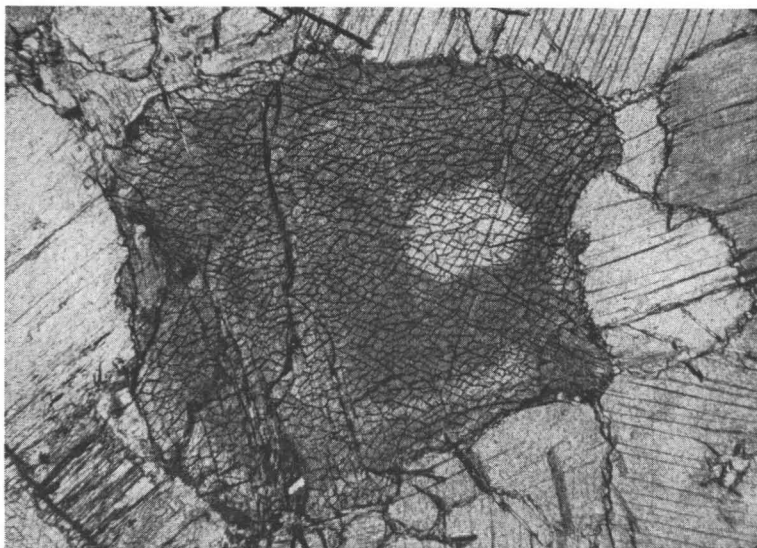
Fig. 7. Kotalahti pyroxenite with well preserved orthopyroxene. One Nicol.
30 x.

mining, the intrusion is well known, above all in its upper parts (Koskinen, 1960). More specimens have been taken from there than from the other intrusions.

The sub-silicic rock series, which contains a number of ore bodies, is composed mainly of the following rocks: a) peridotites, b) pyroxenites, c) hornblendites, d) gabbros including diorites and e) massive sulphides.

Peridotites of Kotalahti are saxonites according to the classification given by Johannsen (1949). They are coarse-grained rocks with variable amounts of disseminated sulphides. The main constituents are olivine, which is often partly serpentinized, and orthopyroxene. In addition, tremolite, carbonate, spinel and pale brown biotite occur. Only three sulphides are present: pyrrhotite, pentlandite and chalcopyrite. Ilmenite is practically the only oxide and is found merely in small amounts.

Pyroxenites are rather uncommon. They are also coarse-grained and are closely related to peridotites. The most common mineral is orthopyroxene. Some talc, amphibole and plagioclase are also present. The sulphides are the same as in the peridotites.

Hornblendite is the most common rock in Kotalahti. Megascopically it is a dark green, coarse-grained rock with some disseminated sulphides. Its main constituent is hornblende which is, in thin section, almost colourless and often contains relics of orthopyroxene. Monoclinic pyroxene and phlogopite also occur. Labradorite may be found sometimes in such amounts

Fig. 8. Typical texture in hornblendite. Orthopyroxene is altered almost completely into amphibole. Pyroxene relics at different stages of alteration characterize the rock. One Nicol. 30 x.

Fig. 9. Iron-rich hornblende crystals in massive sulphides. The Kotalahti Mine. One Nicol. 30 x.
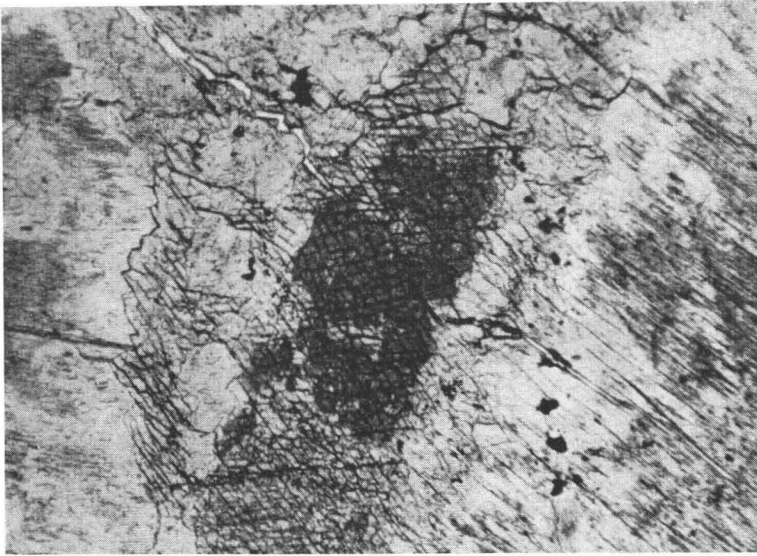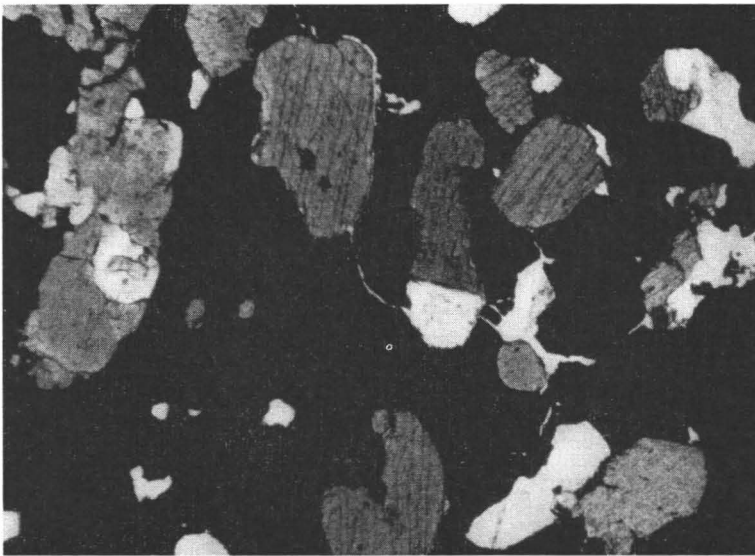
that the rock may be called a gabbro. In addition to hornblende, hornblendite invariably contains cummingtonite, both amphiboles being extremely closely related to each other. Usually one half of a crystal is hornblende and the other half cummingtonite. Pyrrhotite, pentlandite and chalcopyrite are the only sulphides present in amounts worth recording. The occurrence of orthopyroxene relics in hornblende crystals seems to indicate that the rock originally crystallized as pyroxenite, and was later hydrometamorphosed.

Gabbros are almost invariably amphibole gabbros. Both hornblende and cummingtonite occur. The composition of plagioclase varies between 45 and 60 An %. Biotite, sericite, carbonate and apatite are the usual accessories. Sulphides are the same as everywhere in Kotalahti.

Massive sulphides are found in a number of ore bodies. The sulphides are: pyrrhotite, pentlandite and chalcopyrite. Plagioclase, with a composition 40—50 An %, biotite and hornblende are the most common silicates. Hornblende is invariably richer in iron than the hornblende of any other rock in Kotalahti. Cummingtonite is present too, as well as apatite, carbonate and zircon. Oxides are almost completely lacking. Only a few ilmenite grains are sometimes found.

I n t r u s i o n   N o   2. The specimens have been taken from a small, partly hydrometamorphosed peridotite intrusion, the longest dimension of which is about 100 metres. The main minerals are, in thin section, colourless monoclinic amphibole, orthopyroxene and olivine. Serpentine is present in a considerable quantity, primarily as an alteration product of olivine. The sulphide phase is represented by pyrrhotite, violarite[1], chalcopyrite and marcasite. Pyrite and marcasite are of secondary origin, as well as magnetite which occurs as an accessory mineral closely related to pyrite.

I n t r u s i o n   N o   3. A rather coarse-grained, to a considerable degree hydrometamorphic peridotite, the minerals of which are typical of many peridotites: almost colourless hornblende, olivine and serpentine. In addition to these constituents, some chlorite and carbonate also occur. Pyroxene is completely altered into various water-bearing minerals. Disseminated sulphides, pyrrhotite, chalcopyrite and pentlandite fill the interspaces between the silicate grains.

I n t r u s i o n   N o   4. Peridotite with disseminated sulphides, the main constituents of which are tremolite, serpentine and olivine. Sometimes a few relics of pyroxene can be seen. Phlogopite and chlorite occur as accessory minerals. The most common sulphides are pyrrhotite, pentlandite, chalcopyrite and violarite, the latter being an alteration product

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[1] In addition to this specimen a number of other samples has been studied for violarite-looking minerals by the X-ray diffraction and spectrometric methods. All the minerals were found to be true violarites.

of pentlandite. Furthermore, some cubanite crystals are encountered. The amount of chalcopyrite is remarkably low.

I n t r u s i o n   N o   5. Peridotite rich in sulphides. The most common mineral is pyrrhotite. Pentlandite shows a tendency to alter into violarite. In addition, some chalcopyrite also occurs. Serpentine, olivine, augite and tremolite are the principal silicates.

I n t r u s i o n   N o   6. Amphibole-bearing peridotite (Cortlandite, Johannsen, 1949), the main constituent of which is a light green hornblende. Orthopyroxene, olivine and serpentine also occur, as well as the characteristic sulphides: pyrrhotite, pentlandite and chalcopyrite. Now and then some magnetite grains are encountered.

I n t r u s i o n   N o   7. A tremolite-chlorite rock with a remarkable sulphide dissemination. The rock is closely associated with a serpentine intrusion which encloses a small ore body. Pyrrhotite, pentlandite and chalcopyrite are the principal sulphides.

I n t r u s i o n   N o   8. A rather small peridotite lens with unevenly distributed sulphides. Colourless hornblende, olivine and augite are the most characteristic silicates. On account of hydrometamorphism, part of the olivine is altered into serpentine.

Pentlandite is very rare; it has been converted almost completely into violarite. Pyrrhotite and chalcopyrite are also present, and sometimes a few magnetite grains can be detected.

I n t r u s i o n   N o   9. An olivine-bearing dolomite rock closely connected with a serpentine intrusion. Dolomite, tremolite, olivine and phlogopite are the most common non-opaque minerals. As usual, pyrrhotite, pentlandite and chalcopyrite are the representatives of the sulphide phase.

I n t r u s i o n   N o   10. An epidote-tremolite rock with a sulphide dissemination. It is probably associated with a serpentinite lens. The conclusive proof is, however, lacking. In addition to epidote and tremolite, the rock contains sphene, quartz and chlorite. Pyrrhotite, pyrite, pentlandite and chalcopyrite are the constituents of the sulphide phase.

I n t r u s i o n   N o   11. The samples have been collected from different parts of a rather long, but relatively narrow intrusion series, the most important members of which are peridotites, pyroxenites and metagabbros.

The peridotites are megascopically dark, rather coarse-grained rocks. In addition to olivine they contain orthopyroxene, augite, serpentine as alteration product of olivine, talc, colourless hornblende and chlorite. The texture is distinctly hypidiomorphic.

The pyroxenites are in most cases well preserved, coarse-grained rocks, the main constituents of which are orthopyroxene and augite, the former predominating. Sometimes labradorite, epidote and sericite occur in varying quantities.

The metagabbro is a norite which has undergone considerable hydro-metamorphic alteration. Saussuritized labradorite and pale green hornblende characterize the rock. In the centre of some grains of the latter, pyroxene relics can still be seen. They are mainly orthopyroxene. The most common sulphide is chalcopyrite, but pentlandite and pyrrhotite occur as well.

<div align="center">PYROXENE GABBROS</div>

I n t r u s i o n   N o 12. A sulphide-bearing norite with a distinctly hypidiomorphic texture, characterized by subhedral orthopyroxene crystals surrounded by anhedral labradorite. In addition, biotite, hornblende and quartz frequently occur. Apatite is the predominant accessory. Pyrrhotite, pentlandite and chalcopyrite are practically the only sulphides encountered. Graphite is not uncommon and has obvioisly been incorporated from the adjacent mica gneisses. Some ilmenite and magnetite grains are seen.

I n t r u s i o n   N o 13. Hypidiomorphic norite with idiomorphic labradorite crystals. The most prevalent mafic minerals are orthopyroxene and augite. In addition, biotite and cummingtonite also occur. Some specimens are, however, almost free from amphiboles. Pentlandite is partly altered into violarite. Otherwise the sulphides are the same as in the previous intrusion. Ilmenite and magnetite are sometimes found as accessories.

I n t r u s i o n   N o 14. Pyroxene gabbro which contains, in addition to pyroxene, variable amounts of hornblende. The sulphide phase is composed of pyrrhotite, pentlandite and chalcopyrite.

I n t r u s i o n   N o 15. The samples are from a norite intrusion, the dimensions of which are about 2×3 kilometres. Some olivine gabbro differentiates are also found connected with the main norite body. Norite shows a distinct hypidiomorphic texture with subhedral orthopyroxene and augite crystals. Labradorite, as well as hornblende and biotite, have clearly crystallized later than pyroxenes. Pyrrhotite, pentlandite and chalcopyrite occur in variable amounts. The mineral composition of the olivine gabbros is the same as that of the norites, except that they also contain some olivine.

I n t r u s i o n   N o 16. A small norite intrusion, rich in sulphides. Orthopyroxene has crystallized before labradorite, the latter surrounding pyroxene crystals as anhedral grains. Hornblende and biotite also occur, even though in lesser amounts. The sulphide phase is characterized by pyrrhotite, chalcopyrite and pentlandite, the latter being partly altered into violarite.

I n t r u s i o n   N o 17. A hypidiomorphic norite containing sulphides in variable amounts. Labradorite and orthopyroxene are the most abundant silicates. In addition to them biotite, tremolite and talc occur. Apatite

is a predominant accessory. Violarite replaces pentlandite almost comple-
tely. Pyrrhotite, chalcopyrite and pyrite are the additional sulphides.

I n t r u s i o n N o 18. Pyroxene gabbro with a distinct hypidio-
morphic texture. The predominant mafic minerals are orthopyroxene and
augite. Labradorite has crystallized later than the pyroxenes and, conse-
quently, occurs as anhedral grains surrounding the pyroxenes. Biotite,
hornblende and chlorite are minor constituents of the rock. Pyrrhotite,
pentlandite and chalcopyrite are the components of the sulphide phase.

I n t r u s i o n N o 19. The samples are from small peridotite and
olivine gabbro differentiates, which belong to a rather extensive norite
intrusion. Peridotite contains both orthorhombic and monoclinic pyroxe-
nes. They show hardly any sign of alteration. Olivine, however, is partly
serpentinized. Chlorite, hornblende and carbonate are the most important
accessories. A part of pentlandite is altered into violarite, otherwise the
sulphides are the same as above.

The main constituents of olivine gabbro are pyroxenes, labradorite and
olivine. Variable amounts of pyrrhotite, pentlandite and chalcopyrite also
occur.

I n t r u s i o n N o 2 0. Olivine gabbro with sulphide dissemination.
In addition to orthopyroxene and augite, olivine, labradorite, pale green
hornblende, apatite and chlorite characterize the rock. The sulphide phase
is relatively abundant in chalcopyrite. Pyrrhotite and pentlandite also
occur. The latter has partly altered into violarite. Some ilmenite crystals
are found.

AMPHIBOLE GABBROS

I n t r u s i o n N o 2 1. Cummingtonite gabbro, which is brecciated
by sulphides. The essential constituents are cummingtonite and labradorite.
In addition, pale green hornblende, biotite, graphite, apatite and sericite
occur in variable amounts. Some orthopyroxene relics are surrounded by
hornblende. Pentlandite is completely altered into violarite. Pyrrhotite,
chalcopyrite and marcasite are additional sulphides. Occasionally a few
grains of sphalerite, as well as ilmenite are present.

I n t r u s i o n N o 2 2. Hornblende gabbro with variable amounts of
sulphides. Hornblende is the predominant mafic mineral. Labradorite,
epidote and chlorite are also present. In some specimens, grains of hyper-
stene and augite are met with. Quartz and biotite occur accessorily. The
sulphide phase is composed of pyrrhotite, pentlandite, partly altered into
violarite, pyrite and chalcopyrite.

I n t r u s i o n N o 2 3. Sulphide-bearing hornblende gabbro. Its
hornblende is a pale green, magnesium-rich variety. In addition, the rock
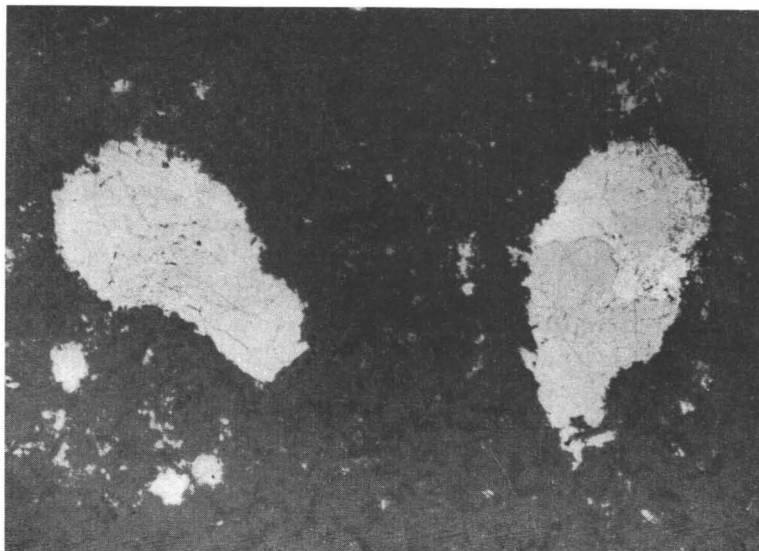
Fig. 10. Sulphide drops in gabbro. The order of the sulphides in the drops
is from bottom to top as follows: pyrrhotite, pentlandite and chalcopyrite. 4 x.

frequently contains cummingtonite. The composition of plagioclase varies
from 60—70 An %. Biotite, rutile and graphite are additional constituents.
The sulphides are the same as usual, i.e. pyrrhotite, partly violaritized
pentlandite and chalcopyrite.

   Intrusion No 24. Hornblende gabbro with disseminated sul-
phides. The principal silicates are labradorite, pale green hornblende and
biotite. Pyrrhotite, pentlandite, chalcopyrite and violarite are the charac-
teristic sulphides. Ilmenite is a frequent accessory.

   Intrusion No 25. Hornblende gabbro containing sulphide drops
the sizes of which vary from a few millimetres to a few centimetres. The
sulphides have arranged themselves invariably in the same order in the drops.
Pyrrhotite is on the bottom, in the middle there is pentlandite and on the
top chalcopyrite (Fig. 10). Hornblende and labradorite are the main sili-
cates.

MODE OF OCCURRENCE OF NICKEL IN KOTALAHTI

SULPHIDE PHASE

The sulphides occur, generally speaking, all over the formation of subsilicic rocks of Kotalahti. However, their amount varies considerably from one place to another. Naturally, the ore bodies are richest in sulphides but the rocks outside them also contain variable quantities of disseminated sulphides. Altogether, 38 specimens have been taken from different parts of the deposit. These specimens represent various rock types and, consequently, give a reliable estimate of the properties of the sulphide phase. The values in Table 4 show the average content of nickel, cobalt, iron, copper and sulphur, as well as the standard deviations and coefficients of variation of 38 sulphide samples.

The coefficient of variation for copper is distinctly greatest — 71 % — showing that copper is a very mobile element compared with the other components of the sulphide phase. The corresponding values for nickel and cobalt, only about one third of that of copper, viz. 21 %, are still considerable. On the other hand, the contents of iron and sulphur show only a small fluctuation. The coefficient of variation for sulphur is 6.1 % and that for iron even less, i.e. 4.2 %.

The distributions of nickel, cobalt and iron are nearly normal. As a consequence the plotting of the distribution functions for nickel, cobalt and iron on the probability paper yields straight lines (Fig. 11). The distributions for copper and sulphur are different (Fig. 12). The frequency distribution for copper shows a remarkably positive skewness, i.e. the distribution is not symmetric but has a long tail on the positive side. Sulphur shows a negative skewness, but it is not as conspicuous as that of copper.

Table 4. Chemical composition of the sulphide phase of the Kotalahti deposit.

	Ni %	Co %	Cu %	Fe %	S %
mean	6.04	0.26	1.74	55.90	36.06
standard deviation	1.28	0.0552	1.23	2.35	2.20
coefficient of variation	21	21	71	4.2	6.1
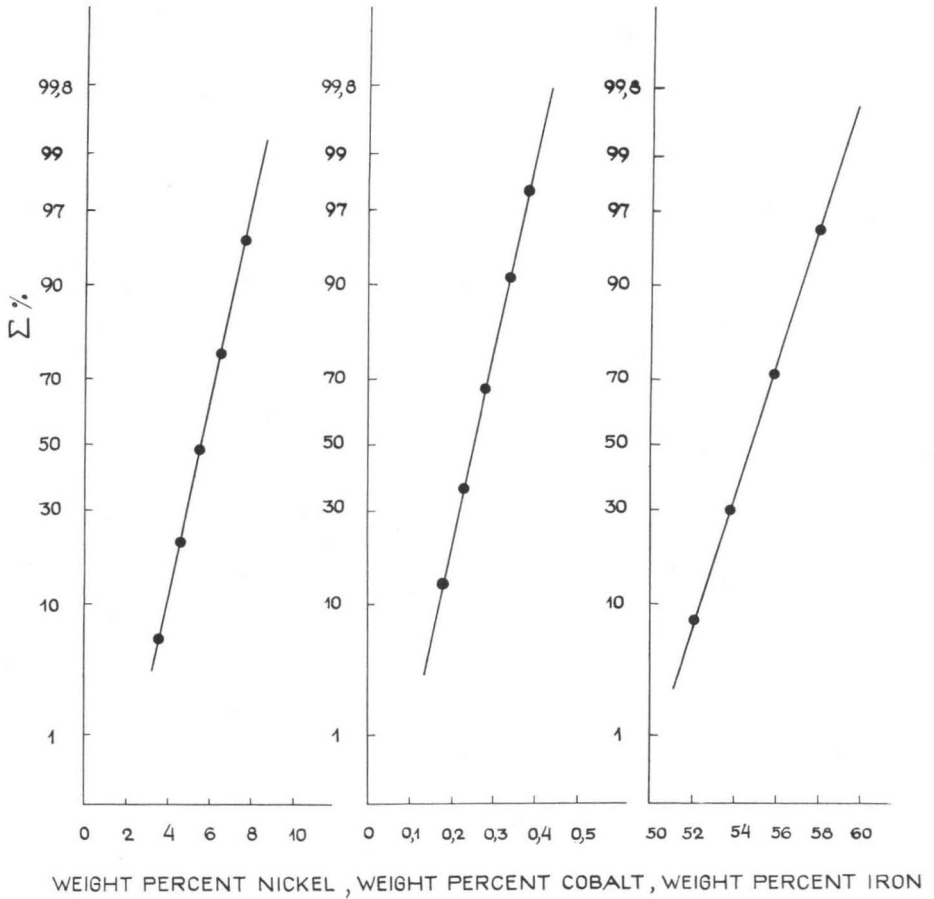
Fig. 11. The distribution of nickel, cobalt and iron of the sulphide phase in Kotalahti. The distribution functions are plotted on probability paper.

The number of the analyses for the sulphide phase is too small for detailed examination of the frequency distributions. The topic has been treated comprehensively by different authors (Ahrens, 1953, 1954a and b, 1957; Aubrey, 1954; Griffiths, 1960; Rogers, 1960; Tennant et al, 1959; and Vistelius, 1960).

Almost all the components of the sulphide phase are mutually independent. Between nickel and cobalt, however, a significant positive correlation exists, as is seen in Table 5, where the correlation coefficients [1] between the components of the sulphide phase in Kotalahti are given.

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[1] In this paper the coefficients of correlation have been calculated and their significance tested using the methods and tables given by Cramér (1958) and Fisher (1958).
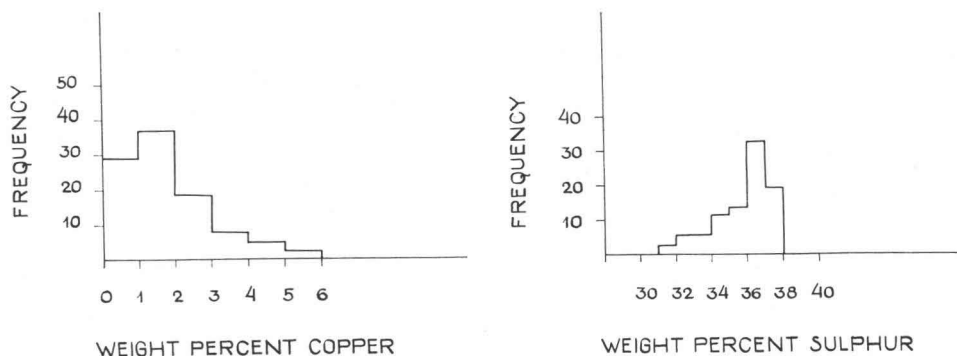
Fig. 12. The frequency distribution of sulphur and copper of the sulphide phase in Kotalahti.

In addition, an inverse dependence is seen to exist between iron and sulphur. Generally speaking, with increasing iron content that of sulphur tends to decrease and vice versa. This tendency is clearly shown by the value of correlation coefficient between sulphur and iron, which is —0.738. The correlation is significant with the 0.01 level of significance.

Table 5. The correlation coefficients between the percentages of elements of the sulphide phase in Kotalahti.

	Ni	Co	Cu	Fe	S
Ni	—	0.621	—0.182	—0.202	—0.189
Co	0.621	—	0.245	—0.198	—0.280
Cu	—0.185	0.245	—	—0.353	—0.168
Fe	—0.202	—0.198	—0.353	—	—0.738
S	—0.189	—0.280	—0.168	—0.738	—

OLIVINE

Peridotite is the only rock in Kotalahti which contains olivine sufficiently for separation. The composition of olivine is not constant, but the Fo content fluctuates between 80 and 95 mole per cent. This variation in magnesium tenor has a remarkable effect upon the nickel content, as already pointed out by Vogt (1923). The more magnesium the olivine contains, the more nickel-bearing it is on an average. A significant positive correlation exists between these two elements, as is seen in Table 6. This table gives the magnesium and nickel contents, as well as the densities of ten olivines from Kotalahti together with the nickel contents of the coexisting sulphide fractions.

Table 6. Fo, Mg, Ni contents, densities and Ni/Mg ratios of ten olivines from Kotalahti with the Ni percentages of the coexisting sulphide fractions.

Fo %	Mg %	Ni %	Ni/Mg × 10³	Ni % in sulph.	D (g/cm³)
80.2	27.8	0.129	1.92	6.15	3.449
83.6	28.9	0.141	2.02	8.05	3.376
83.9	29.0	0.132	1.88	5.79	—
83.9	29.0	0.153	2.18	7.11	—
85.1	29.5	0.138	1.93	7.63	3.438
86.9	30.1	0.159	2.19	6.88	3.441
87.6	30.3	0.150	2.06	6.64	3.391
88.8	30.7	0.148	1.97	4.74	3.412
89.0	30.8	0.162	1.94	2.70	3.421
95.1	32.9	0.172	2.16	6.39	3.417
mean 86.4	29.9	0.148	2.03	6.21	3.418

Using the values in Table 6 for the calculation of the correlation coefficient between magnesium and nickel, $r = 0.854$ is obtained. The correlation is significant with the 0.01 level of significance. The same mutual correspondence which exists between nickel and magnesium contents in olivines is also seen in Fig. 13.

Due to this correlation, the atomic ratio Ni/Mg has been given in the fourth column of Table 6. This ratio is remarkably less variable than the mere nickel percentage. Actually, in Kotalahti, the ratio is almost constant.

A feature characteristic of the Kotalahti intrusion appears in the fifth column of Table 6. If the nickel content of olivine is compared with that of the coexisting sulphide fraction, no correlation seems to be detectable.
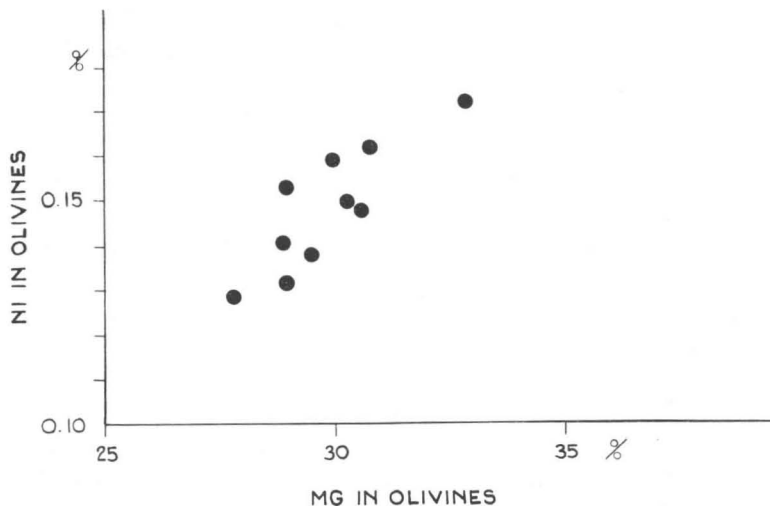

Fig. 13. The nickel contents of ten olivines from Kotalahti plotted against their magnesium contents.

No significant correlation prevails between the Ni/Mg ratio and the nickel contents of the sulphide fractions either. Using the values in Table 6 the coefficient in question is found to be 0.363. The value is too low to have any significance. It is to be emphasized, however, that this does not mean that chemical disequilibrium prevails in the distribution of nickel between the olivine and sulphide phase. The result obtained only indicates that the nickel content of olivine crystals is not directly proportional to that of the sulphide phase immediately surrounding them. However, chemical equilibrium exists between the average nickel content of the sulphide phase and that of the olivine phase. The sulphide phase of an intrusion — especially if brecciated — is so heterogeneous that the correlation in question disappears. This is caused by the great fluctuation in the nickel content of the sulphide phase of the relatively small (2—3 kg) samples.

In Kotalahti, the average nickel content of olivines is 0.148 % and the average atomic ratio Ni/Mg 2.03 $\times$ 10^{-3}, respectively. The mean nickel content in the sulphide phase is 6.21 %. Using these values the distribution coefficient (K) for the partition of nickel between the olivine and sulphide phases can now be calculated as follows

$$K = \frac{X_{Ni}^{Oliv}}{X_{Ni}^{Sulph}} = 0.0238$$

where X_{Ni}^{Oliv} is the Ni-percentage in the olivine and X_{Ni}^{Sulph} is Ni-percentage in the sulphide phase.

If the atomic ratio Ni/Mg is used instead of the nickel percentage of the olivine phase, another value for K is obtained. In this case

$$K = \frac{X_{Ni/Mg}^{Oliv}}{X_{Ni}^{Sulph}} = 0.000327$$

This value agrees well with the values for the distribution coefficients of other intrusions which contain nickel in variable amounts in the sulphide phases. Closer attention is given to the subject in the next chapter.

PYROXENE

It has already been mentioned in the last chapter that the pyroxenes in Kotalahti are mainly orthorhombic and magnesium-rich with the compositions showing only slight variation between different parts of the basic rock series. In Table 7 the chemical compositions of ten orthopyroxenes from Kotalahti and the coefficients of correlation, r_{Ni}, between nickel and

Table 7. The weight percentages of Fe, Al, Ca, Mg, Si and Ni for ten orthopyroxenes from Kotalahti with densities.

D (g/cm³)	Fe +²	Fe +³	Fe total	Al	Ca	Mg	Si	Ni
3.273	5.90	1.70	7.60	0.90	0.25	18.76	25.6	0.035
3.308	8.30	1.10	9.40	1.43	0.44	16.89	25.6	0.036
3.330	5.90	1.30	7.20	0.79	0.40	18.82	25.3	0.043
3.292	5.57	0.93	6.68	2.12	0.82	18.62	24.1	0.044
3.255	6.00	1.40	7.40	0.42	0.32	19.30	25.1	0.046
3.333	7.10	1.10	8.20	1.06	0.37	16.29	25.7	0.047
3.253	6.60	0.28	6.88	1.66	0.82	18.23	24.6	0.049
3.222	6.10	1.10	7.20	1.64	2.21	16.71	24.2	0.054
3.259	6.70	1.30	8.00	0.79	0.70	18.16	24.9	0.055
3.321	6.68	1.32	8.00	2.38	1.74	16.89	24.0	0.058
r_{Ni}	—0.109	—0.204	—0.213	—0.341	0.707	—0.324	—0.685	—

other elements are given. The analyses are not complete, only the main constituents having been determined in addition to nickel. However, it is seen that the compositions of the orthopyroxenes correspond to that of bronzite (Hess, 1949).

Vistelius and Sarmanov (1961) have proposed a method for calculating the correlation coefficient between the percentage values. According to their method, the distortion in the correlation coefficients caused by a constant sum is eliminated by dividing the percentage values by the percentage of the component with a constant content. In many minerals the amount of oxygen is nearly constant. On the other hand, Chayes (1960) has shown that if the quantity

$$(s_j^2 + s_k^2) << \overset{M}{\Sigma} s_i^2 ,$$

the effect of the closed form of statement can be ignored. In the above equation s_k^2 and s_j^2 are the variances of the components between which the correlation is to be calculated and $\overset{M}{\Sigma} s_i^2$ is the total sum of variances. The variance of the nickel percentage is small compared with those of the major components including calcium. Hence the correlation coefficients between the nickel and other components have been calculated using ordinary methods (Cramér, 1958; Fisher, 1958).

A significant correlation exists between the percentage of nickel and calcium. This holds true, however, only for the pyroxenes of Kotalahti, and vanishes completely when pyroxenes from different intrusions are compared with each other. The correlation between nickel and calcium is not easily understandable, since nickel ion can replace calcium ion only difficultly, due to the considerable difference between their ionic radii. Accord-

ing to DeVore (1955a), adsorption is the principal factor controlling the distribution and fractionation of minor constituents in minerals. Most trace elements do not occupy regular lattice sites but occur on growth surfaces, imperfections, dislocations and various interfaces within the crystal. This explanation does not offer a solution in Kotalahti since calcium surely occupies a regular lattice position in orthopyroxene. Nickel may be on interfaces even though it is highly improbable. Anyway, nickel and calcium occupy such positions in the pyroxene of Kotalahti that a significant positive correlation exists between them. Whether the same correlation is also present in other intrusions remains to be seen.

In addition to the positive correlation mentioned, a negative one, though less prominent, exists between the nickel and silicium contents, according to which the amount of nickel tends to increase on decreasing silicium content.

The average nickel percentage of 15 Kotalahti orthopyroxenes is 0.047 % with a standard deviation 0.00786 %. Using the value 6.2 % for the average nickel percentage of the sulphide phase, the value

$$K = \frac{X_{Ni}^{Pyr}}{X_{Ni}^{Sulph}} = 0.00758$$

is obtained as the distribution coefficient. Practically the same value for K is obtained, using pyroxenes from different intrusions with variable nickel contents.

AMPHIBOLE

The amphiboles of Kotalahti can readily be divided into two distinctly different groups. The first group is composed of the amphiboles of peridotites, hornblendites and gabbros. Their properties and modes of occurrence are very similar. The most common amphibole is a pale green, magnesium-rich variety of hornblende, which is usually accompanied by a variable amount of cummingtonite. Frequently, relics of orthopyroxene are seen surrounded by amphibole grains, indicating the secondary origin of the latter. The amphiboles of the second group are strikingly different from those of the first. Petrographically they are completely limited to massive sulphides where, together with labradorite and biotite, they form the main silicate constituent of the rock. The hornblendes of this group are considerably richer in iron than those of the first and, moreover, their iron content varies extensively. No pyroxene relics are connected with these hornblendes and, accordingly, they must be considered as primary amphiboles.

Table 8. The weight percentages of Fe, Al, Ca, Mg, Si and Ni for ten amphiboles from Kotalahti with densities.

D (g/cm³)	Fe + ²	Fe + ³	Fe total	Al	Ca	Mg	Si	Ni
—	0.60	7.98	8.58	4.67	3.37	12.78	24.4	0.035
3.040	3.10	1.30	4.40	1.59	8.38	12.61	24.1	0.038
—	3.70	3.10	6.70	2.01	5.12	14.00	23.5	0.043
3.129	1.82	6.23	8.15	4.24	8.57	9.01	23.2	0.053
3.111	6.10	1.10	7.20	2.38	8.08	10.31	24.4	0.055
3.132	7.40	1.40	8.40	3.65	8.97	9.05	23.0	0.057
3.05	4.90	1.10	6.00	1.53	5.19	13.81	24.4	0.057
3.188	1.97	7.97	9.94	7.12	8.17	7.34	21.0	0.061
3.182	8.60	1.30	9.90	5.82	9.27	8.02	21.1	0.067
3.306	4.04	12.65	16.69	7.15	7.45	4.15	19.5	0.078
r_{Ni}	0.431	0.297	0.702	0.541	0.516	—0.722	—0.717	—

In Table 8 the main percentages of ten amphiboles from Kotalahti are given. Only the main constituents and nickel have been determined. All the amphiboles belong to the first group except the three last which are from massive ore. The coefficients of correlation between nickel and the other constituents are given on the bottom line.

The most important result obtained from the values of Table 8 is, perhaps, the significant positive correlation which exists between the nickel content and that of the total iron. In other words, the more iron the amphibole contains the higher is its nickel percentage. Surprisingly enough, a conspicuous negative correlation seems to prevail between nickel and magnesium. This is rather astonishing, since, according to common belief, (Vogt, 1923; Goldschmidt, 1954), nickel should replace magnesium in iron magnesium silicates and a positive correlation between them would be expected.

It is obvious, that nickel is able to follow different ions depending on the structure of the mineral in question. In olivine a prominent correlation prevails between magnesium and nickel. In amphibole nickel seems to have abandoned magnesium and substitutes now for iron. This diversity in the behaviour of nickel is evidently due to the difference in the lattice energy which favours the Ni-Mg correlation in olivine but the Ni-Fe correlation in amphibole.

In addition to the amphiboles in Table 8, thirty other hornblendes have been analysed for nickel (Table 10). The average nickel content of amphibole in peridotites is 0.052 % with a standard deviation 0.0058 %. For that of hornblendites the corresponding values are 0.055 % and 0.0087 %, and that of gabbros 0.055 % and 0.0033 %, respectively. The nickel content of all these amphiboles varies within strikingly narrow limits. The hornblende of the massive sulphides, however, shows a considerably higher

Table 9. The iron contents and densities of 14 amphiboles from Kotalahti.

Fe %	D (g/cm³)
4.7	3.085
7.2	3.111
7.8	3.077
8.1	3.110
8.2	3.129
8.3	3.132
9.5	3.137
9.8	3.143
9.9	3.182
9.9	3.188
10.3	3.120
10.3	3.147
10.8	3.212
16.7	3.306

Table 10. The densities and nickel percentages of 30 amphiboles from Kotalahti.

Ni %	D (g/cm³)
0.041	2.928
0.042	3.085
0.046	3.05
0.048	3.04
0.049	3.05
0.049	3.063
0.052	3.120
0.054	3.143
0.054	3.111
0.055	3.129
0.055	3.132
0.055	3.072
0.056	3.098
0.057	3.05
0.058	3.064
0.059	3.075
0.059	3.05
0.059	3.147
0.059	3.110
0.059	3.124
0.061	3.212
0.062	3.140
0.063	3.182
0.063	3.153
0.063	3.188
0.065	3.306
0.069	3.123
0.071	3.126
0.077	3.137
0.080	3.201

nickel tenor. The average nickel percentage is 0.066 with a rather large standard deviation 0.0073 %. Hornblende of the massive sulphides invariably contains more iron than the amphiboles of other rocks and, accordingly, also has a higher density. The density of amphibole is a prominent indicator of the iron percentage, as is shown in Table 9.

The correlation coefficient between the density and the total iron percentage of the amphiboles is 0.900. This means a significant correlation with a significance level lower than 0.01. Due to this correlation, another one is to be expected, i.e. the correlation between the density and the nickel percentage, because, as already noted, the nickel content of amphibole depends on its iron content. The values in Table 10 show that this assumption is correct to a certain degree.

The correlation coefficient between the densities and the nickel percentages of Kotalahti amphiboles is 0.637, being significant with the 0.01 level of significance.

Table 11. The average nickel contents of amphiboles and the coexisting sulphide phases with the values for the distribution coefficients in some rocks in Kotalahti.

ore body	rock type	Ni % in amph.	Ni % in sulph.	$\dfrac{X_{Ni}^{Amph}}{X_{Ni}^{Sulph}} \times 10^3$
Mertakoski	peridotite	0.053	6.14	8.63
Mertakoski	hornblendite	0.059	6.37	9.26
Mertakoski	mass. sulph.	0.067	6.60	10.15
Vehka	hornblendite	0.055	5.91	9.32
Vehka	gabbro	0.056	6.16	9.09
Vehka	mass. sulph.	0.062	5.54	11.19

A certain variation exists in the nickel contents of the amphiboles in different rocks at Kotalahti, as well as in the nickel contents of the sulphide phases. Due to this fact, the coefficients of distribution are not constant, but vary somewhat. The values for K are noticeably higher in massive sulphides than in other rocks. In addition to the possible difference in temperature, this is a consequence of the higher iron content of the amphiboles of the former and of the correlation which prevails between the iron and nickel percentages.

The values of K for the amphiboles of peridotites, hornblendites and gabbros in Table 11 show only slight variation, indicating that all the amphiboles in Kotalahti, excluding those of the massive ores, were formed under similar conditions.

DISTRIBUTION OF NICKEL BETWEEN THE SILICATE AND SULPHIDE PHASES IN SOME BASIC INTRUSIONS IN FINLAND

In the previous chapter attention was devoted to the distribution of nickel between the silicate and sulphide phases in Kotalahti. In the following, attention is focused upon the dependence of the nickel content of the silicates on that of the coexisting sulphide phase using material collected from 24 other basic and ultra basic intrusions.

Due to the common occurrence of amphiboles in nickel-bearing rocks, more distribution coefficients for hornblendes have been obtained than for any other silicates. In this respect, olivine-bearing rocks are most scarce. However, the material at hand is comprehensive enough to give a reliable idea of the distribution of nickel between different phases, and permits the drawing of some general conclusions.

Before discussing the properties of the silicates, attention is devoted to the sulphide phases of the intrusions used in this investigation.

SULPHIDE PHASES

In Kotalahti a significant correlation exists between the nickel and cobalt percentages of the sulphide phase. On comparing the sulphide phases of the different intrusions with each other the same correlation between these two elements is encountered. The nickel contents vary from nearly zero to eight per cent. This is seen in Table 12, where the compositions of the sulphide phases of 25 Finnish Pre-Cambrian basic and ultrabasic intrusions are given. The percentages for cobalt are low depending, to some degree, on those of nickel.

Wilson and Anderson (1959) have compared the Ni/Co and Ni/Cu ratios of some well-known nickel deposits with the associated rocks (Tables 13 and 14). The values of both ratios for the Finnish rocks are about the same order of magnitude as those given by Wilson and Anderson, excluding the abnormally high values of the Thompson-Mystery Lake zone.

Table 12. The compositions of the sulphide phases of 25 Finnish intrusions. The numbers in the second column refer to the intrusions described earlier in this paper.

Rock type	intrusion	Ni %	Co %	Cu %	Fe %	S %	Ni/Co	Ni/Cu
Peridotite ...	1	6.04	0.26	1.74	55.90	36.06	23.2	3.5
» ...	2	7.08	0.22	5.42	47.48	39.80	32.2	1.3
» ...	3	2.22	—	1.22	58.26	38.30	—	1.8
» ...	4	6.87	0.27	1.57	54.81	36.48	25.4	4.4
» ...	5	4.98	0.22	2.77	57.43	34.60	22.6	1.8
» ...	6	4.70	0.21	2.90	53.75	38.44	22.4	1.6
» ...	7	4.14	0.30	0.77	56.94	37.85	13.8	5.4
» ...	8	5.36	0.29	8.24	49.73	36.38	18.5	0.7
» ...	9	3.80	0.16	0.08	59.29	36.67	23.8	47.5
» ...	10	5.51	0.47	2.73	44.85	46.44	11.7	2.0
» ...	11	6.20	0.25	9.01	48.89	35.65	24.8	0.7
Norite	12	2.98	0.20	1.47	55.46	39.89	14.8	2.0
»	13	0.68	0.20	0.89	61.02	37.21	3.4	0.8
»	14	0.72	0.10	1.86	58.81	38.51	7.2	0.4
»	15	3.93	0.23	1.33	58.28	36.33	17.1	3.0
»	16	4.01	0.23	0.79	56.87	38.10	17.5	5.1
»	17	1.48	0.11	0.54	59.66	37.81	13.5	2.7
»	18	2.38	0.20	0.86	56.58	39.98	11.9	2.8
»	19	2.85	0.30	2.01	57.76	37.08	9.5	1.4
»	20	8.02	0.25	10.06	47.37	34.30	32.1	0.8
Gabbro	21	2.74	0.21	2.20	56.16	38.69	13.0	1.2
»	22	1.02	0.16	0.12	57.17	41.54	6.4	8.5
»	23	0.82	0.07	0.29	60.93	37.89	11.7	2.8
»	24	5.9	0.3	4.6	52.2	37.0	19.7	1.3
»	25	3.97	0.17	8.17	52.99	34.70	23.4	0.5

The striking tendency of the values for the Ni/Co and Ni/Cu ratios to decrease with the increasing silica content of the associated rock, so clearly seen in Tables 13 and 14, is less prominent in Table 12. However, the trend is the same. The average value of Ni/Co ratio for the Finnish peridotites

Table 13. Ni/Cu ratios in ores comparered to rock type according to Wilson and Anderson (1959).

Deposit	Ni/Co	Associated rock
Thompson, Man.	66	Peridotite
Rankin Inlet, N.W.T.	52	»
Werner Lake, Ont.	47	»
Moak Lake, Man.	40	»
Norpax, Ont.	39	»
Mystery Lake, Man.	36	»
Hudson Yukon, Y.T.	28	»
Falconbridge, Ont.	24	Norite
Emo, Ont.	19	Gabbro
St. Stephen, N.B.	15	»
Contact Bay, Ont.	11	»
Reddit, Ont.	11	Diabase
New Manitoba, Man.	6	Gabbro

Table 14. Ni/Cu ratios in ores compared to rock type,
according to Wilson and Anderson (1959).

Deposit	Ni/Cu	Associated rock
Thompson, Man.	330	Peridotite
Mystery Lake, Man.	142	»
Moak Lake, Man.	49	»
Kenogaming twp., Ont.	12.1	»
Alexo, Ont.	11.7	»
Rankin Inlet, N.W.T.	4.0	»
Norpax, Ont.	2.4	»
Werner Lake, Ont.	1.5	»
Shebandowan, Ont.	1.4	»
Hudson Yukon, Y.T.	1.4	»
Choate, B.C.	2.8	Pyroxenite
Rice Island, Man.	3.3	Norite
Kenbridge, Ont.	1.9	»
Yakobi Island, Alaska	1.6	»
Sudbury, Ontario	1.0	»
St. Stephen, N.B.	1.7	Gabbro
Pardee twp., Ont.	1.4	Diabase
Regcourt, Que.	0.9	Gabbro
Shakespeare twp., Ont.	0.9	»
Mayville, Man.	0.7	»
Emo, Ont.	0.7	»
Reddit, Ont.	0.6	Diabase
Contact Bay, (Wabigoon), Ont. ..	0.5	Gabbro
New Manitoba, (Cat Lake), Man.	0.4	»

is 23.3, for the pyroxene gabbros 14.1 and for the amphibole gabbros 14.8, respectively. Similarly, the average Ni/Cu ratio for the peridotites is higher (6.4) than those for the pyroxene gabbros and amphibole gabbros (2.1 and 2.9, respectively).

In Table 15. the coefficients of correlation between the components of the sulphide phases of the Finnish sub-silicic rocks are given. Contrary to the Kotalahti sulphide phase, a significant positive correlation exists between the nickel and copper percentages, when the sulphide phases of the different intrusions are compared with each other. This correlation is slightly higher than that prevailing between nickel and cobalt. The corre-

Table 15. The correlation coefficients between the components of the sulphide phases of Table 12.

	Ni	Co	Cu	Fe	S
Ni	—	0.556	0.654	—0.774	—0.247
Co	0.556	—	0.251	—0.632	0.341
Cu	0.654	0.251	—	—0.762	0.236
Fe	—0.774	—0.632	—0.762	—	—0.198
S	—0.247	—0.341	0.236	—0.198	—

lation Ni-Cu may be nearly zero in some intrusions, especially if a brecciation occurred and sulphides form massive bodies, as in Kotalahti. This is partly due to the relatively high mobility of the copper ion which causes a great variation in the copper content. On the other hand, on comparing the sulphide phases of the different intrusions with each other, the correlation between nickel and copper becomes evident.

Together with the correlation mentioned, an inverse one exists between the nickel and iron percentages. Similarly, a negative correlation is seen to prevail between the percentages of copper and iron. On the other hand, no correlation whatsoever can be shown to exist between sulphur and the cations. All the correlations are too low to have any significance.

DISTRIBUTION BETWEEN OLIVINE AND SULPHIDE PHASE

Olivine has been separated from ten intrusions, and its nickel content, as well as that of the sulphide phase, has been determined. The values obtained are given in Table 16. In the third column the atomic ratio Ni/ Mg is given. As in the Kotalahti area, the nickel content of olivine from the intrusions labeled in Table 16, is, to a certain degree, correlated to the magnesium content of the mineral. Due to this correlation the distribution coefficients in Table 16 have been calculated between the Ni/Mg ratio of olivine and the nickel percentage of the sulphide phase. Thus, the source of error, caused by comparing olivines of different Fo content with each other, has been avoided.

The effect of the magnesium content upon the nickel content in olivine and upon the values of K is clearly seen in Figs. 14 and 15. In Fig. 14 the nickel percentages of the olivines given in Table 16 are plotted against the

Table 16. The nickel contents of olivine and the sulphide phase from ten intrusions with the Ni/Mg ratios in olivine and the distribution coefficients. The numbers in the first column refer to the rocks described earlier in this paper.

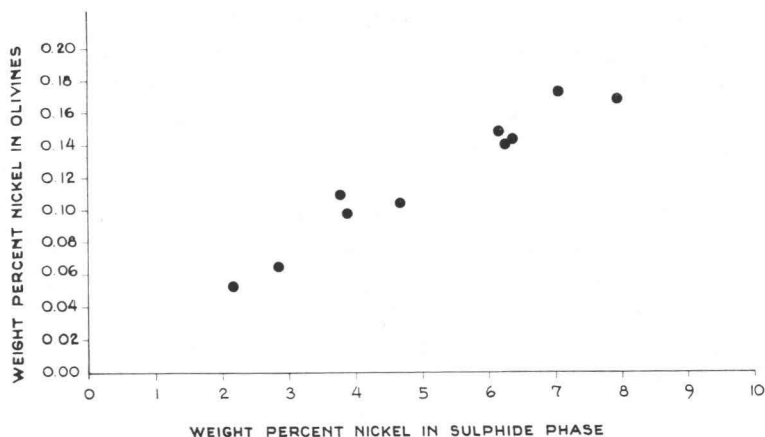| Intrusion	Ni %	Ni/Mg × 10³	Ni % in Sulph.	K × 10⁴
1	0.148	2.03	6.2	3.27
2	0.162	2.39	7.1	3.36
3	0.053	0.80	2.2	3.63
4	0.144	2.10	6.4	3.27
6	0.105	1.62	4.7	3.45
9	0.110	1.42	3.8	3.75
11	0.140	2.01	6.3	3.18
15	0.098	1.40	3.9	3.58
19	0.064	0.98	2.9	3.38
20	0.168	2.82	8.0	3.52

Fig. 14. The nickel percentages of ten olivines plotted against those of the
coexisting sulphide phases.

nickel contents of the coexisting sulphide phases. The nickel content of
olivine increases with the increasing nickel content of the sulphide phase,
but the points obtained do not lie exactly on a line. The deviation from the
straight line disappears, however, almost entirely, when the variation in
the magnesium percentages of olivine is taken into consideration, i.e. when
the atomic ratio Ni/Mg is plotted against the nickel percentage of the sul-
phide phase. This is done in Fig. 15 and the points now lie, within the
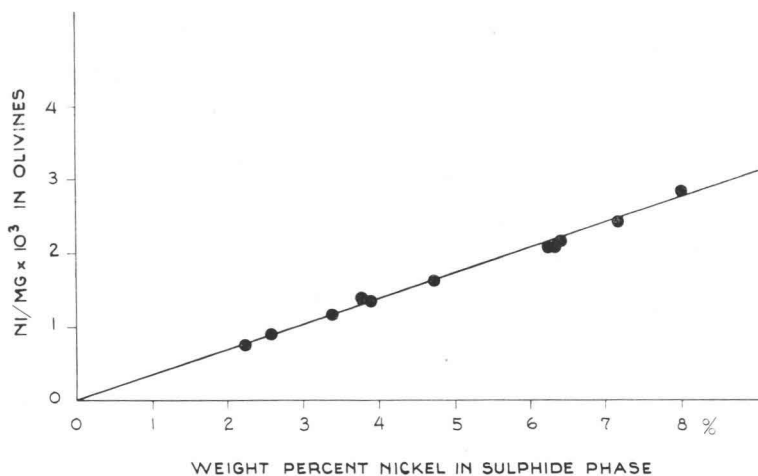limits of analytical errors, on a line.

Fig. 15. The atomic ratio Ni/Mg of the ten olivines plotted against the
nickel percentages of the coexisting sulphide phases.

The results show indisputably that the nickel content of olivine, more exactly the Ni/Mg ratio, varies linearly with that of the coexisting sulphide phase. Using the values in Table 16, the distribution coefficient K = 0.000344 is obtained between the Ni/Mg ratio of olivine and nickel percentage of the coexisting sulphide phase. This value for K corresponds to certain temperature and pressure conditions which are, however, unknown. These conditions and the rate of cooling of the basic rocks investigated must have been nearly constant, since the variation in numerical values for the distribution coefficient K is so small. Actually, the variation is so slight, that it could be entirely due to analytical errors.

The value for K can now be used for the evaluation of the nickel content of the sulphide phase by determining the nickel and magnesium contents of olivine and multiplying the Ni/Mg ratio by the factor 2 910. This method gives, in the case of deposits like Kotalahti, a more accurate estimate for the nickel percentage of the sulphide phase than its direct determination from the sulphide fractions. Using the diagram of Fig. 15 for that purpose, the standard deviation of the nickel percentage for the sulphide phase is about 0.1 % whereas that of the Kotalahti sulphide phase, determined directly from sulphide fractions, is 1.3 %. According to the statistics, to obtain the results with equal accuracy a hundred times as many specimens should be taken for the direct determination of the nickel percentage for the sulphide phase, as if it had been determined from olivine using the above curve.

DISTRIBUTION BETWEEN PYROXENE AND SULPHIDE PHASE

Among the 25 intrusions investigated, 13 contained pyroxene in amounts sufficient for separation. The nickel content of the sulphide phases of the rocks studied varies from 0.5 % to 8 %, thus giving a reliable idea about the influence of the nickel content of the sulphide phase upon that of pyroxene. The pyroxenes were mainly orthorhombic, but some few augites were also encountered. The latter are characterized by higher calcium contents. This is seen in Table 17, where the Ni, Fe and Ca percentage of a number of pyroxene specimens are given, together with the nickel contents of the coexisting sulphide phases. The numbers in the first column refer again to the petrographical description of the specimens. From the same intrusion a number of specimens was studied and, consequently, most of the values given in Table 17 represent average values.

Fig. 16 shows the nickel content of pyroxene plotted against that of the coexisting sulphide phase. The values are the same as in Table 17.

Table 17. The Ni, Fe and Ca contents of pyroxene from 13 sub-silicic intrusions with the Ni contents of the coexisting sulphide phases and the values for the distribution coefficients.

Intrusion	Ni %	Fe %	Ca %	Ni % in Sulph.	$\dfrac{X_{Ni}^{Pyr}}{X_{Ni}^{Sulph}} \times 10^3$
1	0.047	7.7	0.8	6.2	7.5
2	0.056	11.1	1.1	7.1	7.9
6	0.031	10.2	1.2	4.7	6.6
11	0.043	7.1	5.7	6.3	6.8
12	0.025	16.3	0.5	3.0	8.4
13	0.005	11.7	11.3	0.7	7.2
14	0.008	15.3	3.0	0.7	11.4
15	0.028	10.4	2.2	3.9	7.2
16	0.025	11.5	0.8	4.0	6.3
17	0.012	11.5	0.8	1.5	8.0
18	0.023	5.2	14.8	3.0	7.7
19	0.024	12.1	0.8	3.3	7.3
20	0.063	9.9	4.2	8.0	6.9

The variation of the nickel content in pyroxene with that of the coexisting sulphide phase is satisfactorily linear, the correlation coefficient being 0.981. Using the values mentioned

$$K = \frac{X_{Ni}^{Pyr}}{X_{Ni}^{Sulph}} = 0.00755$$

is obtained for the value of the distribution coefficient. This is very nearly the same as that for the Kotalahti pyroxene, i.e. $K = 0.00758$.
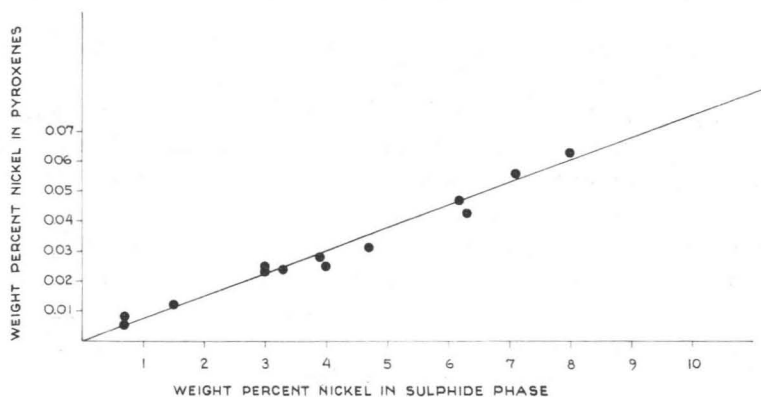

Fig. 16. The nickel content of pyroxene plotted against that of the coexisting sulphide phase.

A significant positive correlation prevails in Kotalahti between the nickel and calcium percentages in pyroxene. If the pyroxenes from the different intrusions are compared with each other, no correlation is found any more. Using the values in Table 17, r = —0.051 is obtained as the value for the correlation coefficient between the calcium percentages of pyroxenes and the distribution coefficients, indicating that the quantities in question are quite independent. How is this difference in the behaviour of the Ni—Ca correlation in Kotalahti and in other intrusions to be explained? The material at hand is inadequate to give a definite answer to the question. However, under certain conditions the nickel and calcium ions seem to occupy such positions in pyroxene that a significant correlation exists between them.

The distribution coefficient K is, to a certain degree, dependent on the iron content of pyroxene, the correlation being 0.510. The correlation is, however, too low to be useful for making the deviation existing in the values for the distribution coefficients smaller in the same manner as was done in the olivines, taking into consideration the correlation prevailing between the nickel and magnesium percentages. Still, the nickel content of pyroxene can be used for the evaluation of the nickel content of the coexisting sulphide phase, provided that a chemical equilibrium is reached at the same temperature which prevailed in the intrusions investigated. The nickel content of pyroxene is only to be multiplied by the factor 130 to yield that of the coexisting sulphide phase. The average error thus obtained is about 0.3 %, which is three times as much as that calculated from the Ni/Mg ratio of olivine. This seems to indicate that the temperature of formation for pyroxene generally varies more than that for olivine.

DISTRIBUTION BETWEEN AMPHIBOLE AND SULPHIDE PHASE

The nickel content of olivine varies linearly with the nickel content of the coexisting sulphide phase. In pyroxene this dependence is still sufficiently linear, but in the amphibole it is already considerably more diffuse. Generally speaking, the nickel content of amphibole increases with the increasing nickel content of the coexisting sulphide phase, but the linearity is no longer good, as is seen in Fig. 17.

In Table 18 the nickel contents of amphibole and the sulphide phase of a number of intrusions are given. In the last column the distribution coefficients are listed. In many cases, more than one determination has been made from the same intrusions and the values given in Table 18 represent the averages of these determinations.

As has already been said, there is a conspicuous fluctuation in the nickel contents of the amphiboles. This fluctuation is, however, not random.
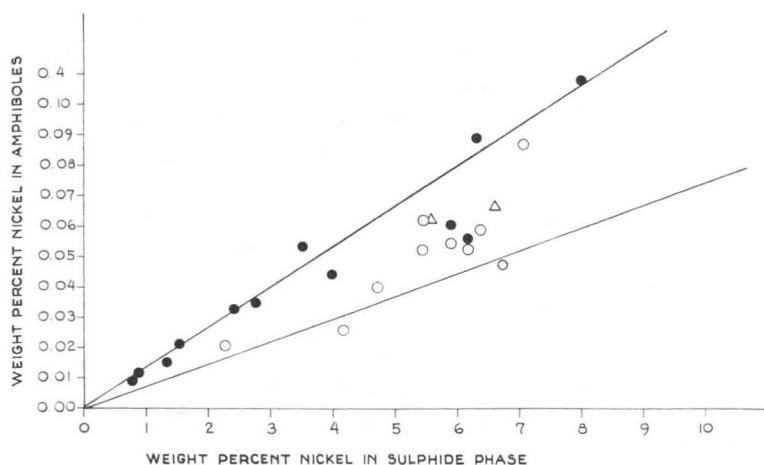
Fig. 17. The nickel contents of amphiboles plotted against those of the co-
existing sulphide phases. Solid circles: amphiboles of gabbros. Open circles:
amphiboles of ultrabasic rocks. Triangles: amphiboles of massive sulphides
from Kotalahti.

Table 18. The nickel content of amphibole and the coexisting sulphide phase from
18 sub-silicic intrusions, with the distribution coefficients.

Intrusion	Rock type	Ni %	Ni % in Sulph.	$\dfrac{X_{Ni}^{Amph}}{X_{Ni}^{Sulph}} \times 10^3$
1	Peridotite	0.053	6.1	8.6
1	Hornblendite	0.059	6.4	9.3
1	Ore	0.067	6.6	10.2
1	Hornblendite	0.055	5.9	9.3
1	Gabbro	0.056	6.2	9.1
2	Peridotite	0.087	7.1	12.3
3	»	0.021	2.2	9.5
4	»	0.047	6.7	6.8
6	»	0.040	4.7	8.5
7	»	0.026	4.1	6.3
8	»	0.053	5.4	9.9
10	»	0.062	5.5	11.3
11	Gabbro	0.089	6.2	14.4
12	»	0.053	3.0	17.7
17	Norite	0.021	1.5	14.0
18	»	0.033	2.4	13.8
20	Gabbro	0.108	8.0	13.5
21	»	0.035	2.7	12.8
22	»	0.009	0.8	11.8
23	»	0.012	0.8	14.5
24	»	0.060	5.9	10.2
25	»	0.044	4.0	11.0

If Fig. 17 is considered it is realized immediately that the amphiboles of the ultrabasic rocks contain almost invariably less nickel than those of the gabbros having the same nickel content in the sulphide phase. The lower nickel content of the amphibole of the ultrabasic rock is, in all likelihood, due to the fact that the amphibole is usually secondary, formed from pyroxene by hydrometamorphism. This assumption can often be verified in thin section where pyroxene relics are surrounded by amphibole grains. It may be that during the metamorphism the sulphide phase and the amphibole have not been able to attain chemical equilibrium and hence the nickel content of amphibole is virtually the same as that of the original pyroxene. This explanation is further supported by the fact that the lower limit for the nickel content of the amphibole of the ultrabasic rocks coincides well with the nickel content of pyroxenes, the latter being represented by the lower line in Fig. 17.

On the other hand, the observed difference in the values of the distribution coefficients for the amphiboles might also be due to the variation in the temperature. Barth (1961) has shown that the value of the distribution coefficients for Na, Ca, Sr and Ba between plagioclase and alkali feldspar depends indisputably on temperature.

The distribution coefficient for primary amphibole is considerably higher than that for secondary. Using the values for K of the primary amphibole in Table 18, $K = 0.0134$ is obtained as an average for the distribution coefficient. The upper line in Fig. 17 is drawn using this value. Most of the Ks for natural amphibole seem to vary between this value and that of the distribution coefficient for pyroxene, viz. 0.00755, depending on the origin and the temperature of formation.

SUMMARY AND CONCLUSIONS

The aim of this investigation was to study the nickel content of some iron magnesium silicates and of the coexisting sulphide phase and, in addition, to find the possible correlations existing between them. For that purpose special attention was paid to the Kotalahti deposit which, due to the mining operations, acted as an excellent source for specimens. An attempt has been made to elucidate the properties of the different components of a typical nickel-bearing intrusion using the material from there. Together with the correlations prevailing between some characteristic elements of a single intrusion, the relationships existing between those of the different intrusions have also been studied. The results obtained can be summarized as follows.

The components of the sulphide phase of an intrusion (Kotalahti) are relatively independent. Between the nickel and cobalt contents, however, a significant positive correlation exists. Another correlation, negative in sign, prevails between the sulphur and iron percentages. On the other hand, no correlation seems to exist between nickel and copper. It is to be emphasized, however, that the value of the correlation coefficient between Ni and Cu varies considerably from one formation to another, and from one part of a formation to another, and that its value should be thus considered only as a feature characteristic of the population in question.

If the components of the sulphide phases of the different intrusions are compared with each other, a correlation between nickel and cobalt as well as between nickel and copper will be found. Two negative correlations also exist. One between nickel and iron, and another between copper and iron.

Magnesium ion is replaced by nickel ion in the lattice of olivine. Consequently, the nickel content of olivine does not only depend on the nickel content of the coexisting sulphide phase, but also on its magnesium content. Accordingly, the distribution coefficients have been determined between the Ni/Mg ratio of olivine and the nickel percentage of the coexisting sulphide phase. The correlation thus obtained is nearly linear. The fact that K for the different intrusions is nearly constant, viz. 0.000344, shows that

the intrusions were formed under similar conditions. The intrusions studied belong to the same orogenic phase, which could partly, but not completely, explain the small value, viz. v = 4.9 %, for the coefficient of variation observed in the values for the distribution coefficients. Since the temperature and pressure conditions could hardly have been exactly the same in all intrusions, the cooling rates must have played an important role as a controlling factor. If the cooling is slow enough, the chemical equilibrium is always maintained in regard to the distribution of nickel between the different phases. Finally a temperature is reached at which the reaction rate, mainly controlled by diffusion of the nickel ion, has become so slow that a state of equilibrium cannot be maintained any more. The system »freezes». The values for K obtained probably correspond to this temperature. The temperatures might have been different at the beginning of the cooling, but if the cooling has been slow enough, the same »freezing» temperature is always reached finally, and, consequently, the values for the distribution coefficients are also constant.

On the other hand, many facts seem to indicate that the values of K change very little with temperature. This may also be one of the main reasons for the stability of the distribution coefficients observed in rocks.

In pyroxene, no correlation corresponding to that of Ni/Mg in olivine, can be shown to exist between nickel and any other element. Partly for that reason, the values obtained for K are less constant. The nickel content of pyroxene depends, however, to some degree on its composition, above all on the iron content, but since this dependence is not sufficiently linear, the values for K vary somewhat. As a matter of fact, the K = 0.00755 obtained is an average value, the value which seems to occur most often in Nature. The deviation observed in the values for K can be caused by errors in determination but may also indicate the differences in the crystallization conditions. The significant positive correlation between the nickel and calcium percentages in Kotalahti pyroxenes is puzzling. Whether it is a special feature characterizing Kotalahti only, or whether it prevails in other intrusions as well, remains to be seen.

No definite difference has been established in the values for K between orthopyroxene and augite. The material used in this study is, however, insufficient for excluding the possible existence of such a difference. According to Vogt (1923), orthopyroxene as a whole contains slightly more nickel than augite if crystallized under identical conditions.

A considerable variation exists in the K values for the amphiboles collected from the different deposits. This variation is clearly greater than that observed in orthopyroxene and olivine. However, it shows a certain regularity. The values for K of amphibole of the ultrabasic rocks are almost invariably smaller than those of the more silica-rich rocks. For the latter

an average value $K = 0.0134$ is found, whereas the corresponding values for the amphiboles of the ultrabasic rocks are smaller, approaching the values typical of orthopyroxene, viz. $K = 0.00755$. This difference in the values for K can be explained by taking the fact into consideration that the amphiboles of the ultrabasic rocks are usually secondary, having been formed from pyroxene, whereas those of the gabbros are mainly primary, representing a different temperature of formation.

The difference between the primary and secondary amphiboles also becomes evident in another way. If the distribution coefficients for nickel between pyroxene and amphibole are calculated, a diversity is observed in the values of the primary and secondary amphiboles. For the former

$$K = \frac{X_{Ni}^{Pyr}}{X_{Ni}^{Amph}} = 0.53$$

is obtained as an average value, and for the latter $K = 0.79$, respectively. This same tendency becomes perhaps still more apparent in the partition of chromium between pyroxene and amphibole. Utilizing the most obviously primary and secondary amphiboles used in this investigation

$$K = \frac{X_{Cr}^{Pyr}}{X_{Cr}^{Amph}} = 0.42$$

is obtained as an average value for the distribution coefficient of chromium between pyroxene and primary amphibole. For secondary amphibole the value is considerably higher, viz. $K = 2.9$. Accordingly, by determining the value for the distribution coefficient, it is possible to estimate whether an amphibole is primary or secondary.

Very few reliable data are obtainable in the literature dealing with the distribution of nickel between silicates and the coexisting sulphide phase. Aho (1956) gives some nickel contents for amphibole and the coexisting sulphide phase. When the distribution coefficients are calculated, based on his figures, the values vary from 0.012 to 0.015. The agreement between the data obtained in this paper and those provided by Aho is excellent.

For comparison a few determinations of the distribution coefficients have been made using material outside Finland. The author had an opportunity to collect some samples from the Sudbury district (Davidson, 1948; Halferdahl, 1929; Lochhead, 1955; Mitchell and Mutch, 1956; Wandke and Hoffman, 1924; Yates, 1948). For a hornblende of a disseminated ore type from the Frood Mine at 1000-level $K = 0.011$ was obtained, corresponding closely to the values typical of the massive ores in the Kotalahti Mine.

Another determination was made using a specimen from the Sherritt Gordon Mine in Lynn Lake (Allen, 1950; Muter, 1955; Ruttan, 1955). The sample was taken from the A ore body at the 1000-level. The rock was an amphibole gabbro with a nearly colourless hornblende. $K = 0.0145$ was obtained, again agreeing excellently with the above values.

The values of the distribution coefficients for the nickel between the silicate and sulphide phases decrease in the sequence: olivine-amphibole-pyroxene. According to Ramberg (1952), the distribution of the metal ions among the silicates is governed to a great extent by the electronegativity values of the metal and oxygen atoms in the silicates. The value for the oxygen is lowest in orthosilicates and increases stepwise through metasilicates to tectosilicates. The most electronegative metals tend to combine with the least electronegative oxygen. Hence the concentration of nickel in olivines is higher than in amphiboles and pyroxenes because the nickel ion has a higher affinity for the oxygen in olivines than in metasilicates.

Using the values for K calculated in this paper, the distribution coefficients for nickel between olivine, pyroxene and amphibole can now be estimated. For K between olivine and pyroxene

$$K = \frac{X_{Ni}^{Oliv}}{X_{Ni}^{Pyr}} = 3.15$$

is thus established. Similarly

$$K = \frac{X_{Ni}^{Oliv}}{X_{Ni}^{Amph}} = 1.83—3.2$$

is obtained for K between olivine and amphibole. Further,

$$K = \frac{X_{Ni}^{Pyr}}{X_{Ni}^{Amph}} = 0.56—1.0$$

between pyroxene and amphibole. It is now interesting to compare the above values with the values determined directly from the coexisting minerals. DeVore (1955b) calculated the distribution coefficients for nickel between olivine and pyroxene, and between pyroxene and amphibole. His average value for

$$K = \frac{X_{Ni}^{Oliv}}{X_{Ni}^{Pyr}} = 3.2$$

and that for

$$K = \frac{X_{Ni}^{Pyr}}{X_{Ni}^{Amph}} = 0.76$$

The agreement between the values derived by the two different methods is excellent. It shows that the partition of nickel between certain phases in rocks obeys Nernst's law reasonably well, with the consequence, that the values for the distribution coefficients are nearly independent of the other coexisting phases.

Perhaps the most important result obtained from this study is the fact that, as a rule, a chemical equilibrium prevails in the distribution of nickel between the silicate and sulphide phases.If the values for K under the different temperature and pressure conditions were known experimentally, it might be possible to use the K-values for the determination of the temperature of formation. These seem to be approximately constant, or the values for K change very little with temperature. The variation in K-values for amphibole seems, however, to indicate that temperature has an effect upon the values for the distribution coefficients.

The fact that the state of equilibrium in the distribution of nickel is so easily attained has some interesting consequences upon the formation of some particular nickel ore types. Consider a silicate, nickel-rich magma containing very little or no sulphides, which comes into contact with a nickel-poor sulphide material. For example, an ultrabasic magma penetrates an iron sulphide formation assimilating sulphidic material. If the temperature remains high long enough for the attaining of the chemical equilibrium, the main part of the nickel is transported from the silicates into the sulphide phase, giving rise to nickel-bearing sulphides. Due to that passing of nickel from one phase to another, a sulphide nickel ore is formed, the nickel of which was originally incorporated in silicates. Similarly, a reaction occurs when a sulphidic material without nickel forms dikes cutting sub-silicic rocks, rich in nickel-bearing silicates. As a consequence of the distribution law, a nickel-bearing sulphide phase is formed again.

Processes like these are certainly not very uncommon in Nature. Skarn rock type nickel deposits are formed, the sulphide phases of which are frequently rich in nickel and poor in copper. These rocks are distributed, e.g. in the province of North Karelia together with serpentinites and black schists but a detailed discussion on their mode of occurrence is beyond the scope of this paper.

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