

REPORT
of
Committee on Thesis

The undersigned, acting as a Committee of
the Graduate School, have read the accompanying
thesis submitted by Henry Ray Aldrich
for the degree of Master of Science.

They approve it as a thesis meeting the require-
ments of the Graduate School of the University of
Minnesota, and recommend that it be accepted in
partial fulfillment of the requirements for the
degree of Master of Science.

W. H. E. Munnous,
Chairman

Frank F. Shout

I. H. Derby

May 21 1917

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REPORT
of
COMMITTEE ON EXAMINATION

This is to certify that we the undersigned, as a Committee of the Graduate School, have given Henry Ray Aldrich final oral examination for the degree of Master of Science. We recommend that the degree of Master of Science be conferred upon the candidate.

Minneapolis, Minnesota

May 21 1917

W. H. Emmons
Chairman

Frank E. Shront

I. H. D. [unclear]
C. N. Stauffer

THE ENRICHMENT OF NICKEL ORES

A Thesis Submitted to the Faculty of the Graduate School

of the

University of Minnesota

by

HENRY RAY ALDRICH

In partial fulfillment of the requirements for the degree

of

Master of Science.

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I. Introduction.

This paper is a discussion of experiments on the solution and precipitation of nickel.

Many ore deposits are workable only in those zones that have been enriched by weathering and related processes. In some of them enrichment takes place by solution and removal of valueless constituents of the ore or protore; in others by solution of valuable metals and precipitation in depth generally about a groundwater level. There are many field and laboratory data bearing on the chemistry of secondary enrichment of metalliferous deposits, especially of deposits of iron, copper, silver, and gold. But little has been done on the problem of the chemistry of enrichment of nickel deposits. The secondary enrichment of a deposit involves solution, transportation, and precipitation.

II. Dissolution of nickel from its minerals.

General chemistry of nickel.

Chemically, nickel is a close relative to iron and cobalt, occupying a position with these metals in group VIII of the first long period in the Periodic Table. Most nickel salts are soluble in water. The carbonate and phosphate are insoluble. The sulphide is said to be soluble in boiling water with evolution of hydrogen sulphide.¹ It is also soluble in solutions containing much mineral acid or acetic acid. The solubilities in water at 18°-25°C. are shown in the following table from Tower - Qualitative Chemical Analysis.

1. Bull. 616 U. S. Geol. Survey, p. 630.

Chloride - readily soluble
Bromide - very soluble
Cyanide - slightly soluble
Hydroxide- exceedingly slightly soluble
Carbonate- " " " - hydrolizes
Sulphide - 0.00036 grams anhydrous solute in 100 gm. H₂O
Sulphate - readily soluble
Phosphate- exceedingly slightly soluble
Arsenate - " " "

Nickel occupies a mid-position in the electromotive series.

This series with the common metals of commerce is as follows:

Mn, Zn, Cr, Cd, Fe(ous), Fe(io), Co, Ni, Pb, Cu, Bi, Hg(ous), Hg(io), Ag, Au. The position of iron with respect to the more valuable metals is fortunate. Most common of the sulphides are those of iron. As shown by Schuerman's¹ series, all the more precious metals may be precipitated as sulphide from a solution of those metals in contact with iron or manganese sulphide.

Qualitative tests for nickel are very delicate. Throughout the experiments which have been made, nickel has been detected with an alcoholic solution of di-methyl glyoxime. A brilliant crimson precipitate is thrown down which varies in intensity of color with the amount of nickel. This test is sensitive to one part of nickel in 400,000 parts of water.

1. Bull. 625 U. S. Geol. Survey, p. 119.

The occurrence of nickel. its minerals.

Nickel oxide, NiO, is said to constitute 0.026 per cent of the earth's crust.^{1/} A great number of analyses of igneous rocks have been compiled,^{2/} many of which show small quantities of nickel. These analyses are from rocks of intermediate and basic composition. Probably a greater number of similar rocks would show a nickel content had the metal been tested for. Other occurrences are in meteorites^{3/} and in certain oceanic clays.^{4/}

Most common among the many nickel minerals are the following. The stars indicate those used in the experiments discussed here.

Native nickel	Ni
Morenosite	NiSO ₄ .7H ₂ O
Bunsenite	NiO
Zaratite	NiCO ₃ .2Ni(OH) ₂ + 4H ₂ O
*Garnierite	H ₂ (NiMg)SiO ₄ + aq
*Genthite	2NiO.2MgO.3SiO ₂ .6H ₂ O
Annabergite	Ni ₃ As ₂ O ₈ + 8H ₂ O
*Millerite	NiS
*Niocolite	NiAs
*Chloanthite	NiAs ₂
*Gersdorffite	NiAsS
*Pentlandite	(Ni,Fe)S
Polydymite	Ni ₃ FeS ₅

1. Bull. 616 U. S. Geol. Survey.
2. Prof. Paper U. S. Geol. Survey No.14.
Bull. 419 U. S. Geol. Survey.
3. Bull. 91, U. S. Geol. Survey.
4. Challenger Reports.

Nickel is found also in olivine, biotite, amphiboles, and pyroxenes. In these the nickel is probably present as a silicate or oxide, and constitutes only a small per cent of the mineral.

Of these minerals, only those of the list are present in the greater number of the ore deposits, although there is abundant evidence that the nickeliferous silicates of the gabbro rocks are the very important protores of the hydrous silicates genthite and garnierite which form the essential ores of the New Caledonia deposits. The latter were examined during the course of the experiments.

Character of the solutions of the vadose zone. Vadose waters in the zone of fracture originate in meteoric precipitation. To these waters there are added various substances from the atmosphere. Carbon dioxide is most worthy of mention in this connection. The interaction between atmosphere and lithosphere may produce sulphuric acid, sulphurous acid, and carbonic acid. Basic sulphates by decomposition furnish a certain amount of sulphuric anhydride. Minerals such as chlor-apatite and sodalite contain chlorine which may dissolve during weathering. Through feldspathic decomposition, carbonates of the alkalis are formed, which are potent solvents of silicate minerals. The origin and composition of such vadose waters have been discussed in detail^{1/} and it is here necessary only to stress the point that where sulphides and especially pyrite are present, the solutions will invariably carry free sulphuric acid. When these minerals are absent carbonates of the alkalis and alkaline earths predominate in the solutions.

1. W. H. Emmons and G. L. Harrington, Econ. Geol., vol. 8, p. 653.
E. T. Hodge, Econ. Geol., vol. 10, p. 123.

This contrast is important because secondary sulphide enrichment is effected by the former type of solution, silicate and carbonate enrichment by the latter type.

Experiments on the dissolving effects of solutions.

The minerals used in making these experiments were obtained through the courtesy of Dr. Merrill of the United States National Museum at Washington, and from the mineral collection of the University of Minnesota. Following is a list of the minerals, their nickel content, and their source.

<u>Mineral</u>	<u>% Nickel as analyzed</u>	<u>Source</u>
Nicolite	40.49	?
Chloanthite	29.93	Franklin Furnace, N.J.
Pentlandite	14.14	Sudbury, Ontario.
Millerite	55.92	?
Gersdorffite	46.42	Gem Mine, Hardscrabble District, Fremont County, Colorado.
Serpentine	0.367	Fosters Farm, Juno, N.C.
Olivine	0.12	Schreibers Nickel Mine Webster, N. C.
Genthite	12.28	

The complete separation of a given mineral from the included grains of carbonate and silicate is not always possible. For instance, a pure pentlandite could not be separated from the associated chalcopyrite and pyrrhotite. The method of using heavy solutions is not applicable to most sulphides, arsenides, and antimonides because of the corrosive action of the solutions. Separation with the electromagnet was unsatisfactory. A small spitzlutte was of some use in ridding the sample of certain associated minerals. However, the purpose of the experiments is in no way impaired by the presence of the other minerals. To be sure there is considerable evidence to show that the presence of two or more sulphides in contact may possibly accelerate the so-

lution of the one of least potential, due to galvanic effects.^{1/} Calcite would consume acid if present, and conclusions as to reactivity of the solution based upon changes in acidity would be decidedly in error. However, there were no analyses made on acidity, and there was no carbonate present as far as known, and after considering all factors, it was concluded that the most satisfactory way for preparing these mineral samples was to crush coarsely in an agate mortar, hand pick the purer fragments, and then reduce to the proper size of grain in the mortar. A binocular microscope was used in this work. All selected material was ground to pass an eighty mesh screen (Tyler standard), and sampled for analysis.

Some mention should be made concerning the accuracy of the determinations. As stated elsewhere, the glyoxime test is probably the most delicate. Quantitatively, this method is extremely accurate,^{2/} but owing to the nature of the precipitate, the tedious filtration, and the usual objections to gravimetric analysis, this method was not used for quantitative work. The potassium cyanide titration was considered sufficiently accurate. The general course of this method consists in making the solution slightly ammoniacal, adding 5 c.c. of a solution of potassium iodide, and titrating with potassium cyanide in the presence of silver nitrate. Rather than precipitate the iron before the determination, a solution of tartaric acid was used to hold it in solution. In case ferrous sulphate is present, the solution is oxidized with nitric acid before addition of the tartaric acid.

1. Gottschalk and Buehler, Econ. Geol., vol. 7, p. 15.

2. Covitz, Met. and Chem. Eng., Jan. 1917.

In conducting a test on the effect of solutions on the several minerals, small samples of the crushed material were weighed out into small, wide-mouthed, glass-stoppered bottles. Twenty c.c. of the several solutions were added from a pipette, the stoppers were placed, and the bottles set aside for a time. These bottles were shaken each day.

The effect of sulphuric acid.

No mine water analysis shows so simple a composition as the tenth normal sulphuric acid solution which was used in these tests. However, the analyses indicate that many waters are fully as strong as the present solution, but that there are many salts dissolved. The activity of the mine water is due to the free sulphuric acid. The salts in solution are, for the most part, those of alkalies and alkaline earths, salts which give no acid reaction, and have no oxidizing or reducing powers. Salts of iron in both stages of oxidation, on the other hand, have acid reaction, and are capable of producing changes in oxidation under proper conditions. The effects of these salts are considered under subsequent headings.

Before making the quantitative tests, a preliminary experiment was made to obtain some idea as to the probable solubility of the several minerals. The experiment was conducted in the same way, but at intervals of a few hours a small portion of each solution was removed for a qualitative test. The glyoxime test is properly made in a solution slightly alkaline. In testing, glyoxime was added to the solution without first making them ammoniacal. If a precipitate formed without the addition of ammonia, it was considered an indication that the solution had become some-

Table I. The Qualitative Effect of N/10 Sulphuric Acid.

		I	II	III	IV	V	VI	VII	VIII	IX	X
	Minerals	Serpentine	Niccolite	Olivine Oregon	Genthite	Fresh olivine, N.C.	Gersdorffite	Millerite	Chloanthite	Wea.**Pent-Oliv.	landite
A	Glyoxime Not alk.	White ppt.	-	-	-	Slight Ni reaction White ppt.	Slight	Slight <VI White ppt.	-	-
B	Glyoxime Made alk.	Slight	Slight	Slight	Slight	Slight	Strong	Strong <VI	strong >VII	Slight	Strong
C	(NH ₄) ₂ S	Color	Ppt.	-	-	-	Ppt.	-	Ppt.	-	Ppt.
D	Glyoxime Not alk.	-	White ppt.	-	-	-	Strong	Slight	Stronger than in A	-	Trace
E	Glyoxime Made alk	Slight	Stronger than in B	Color	Strong color (6)*	Color	Strongest (1)	Strong (2)	Strong <VII (4)	Strong color (5)	Strong (3)

* These figures give estimated order of solubility

** Weathered olivine from N. C.

what less acid during the test. If no reaction for nickel occurred, the test must be carried out by addition of ammonia in order to be sure whether nickel has been dissolved. Ammonium sulphide was employed also in making these tests. Following are the roughly quantitative results as estimated from the intensity of these tests.

In every case nickel was dissolved by the acid solution. Comparison of the two horizontal series, B and E, shows that the amount dissolved increases rapidly. From those minerals which contain nickel in oxidized form the metal enters solution very slowly. This is illustrated by I, III, V, and IX. It is also shown that pentlandite and millerite, two very common ore minerals, are readily dissolved. The compounds of nickel and arsenic appear to be somewhat irregular in regard to their solubility. Solution of niccolite is slow, chloanthite is more rapid, and gersdorffite, the arseno-sulphide, is most soluble of all minerals tested. V and IX are fresh and weathered specimens of olivine from North Carolina. Apparently some change has taken place during weathering which affects the nickel content, for olivine after weathering is more soluble.

Actual analyses of mine waters confirm the observations made here, for at Broken Hill, New South Wales, 6.71 per cent of nickel was found in an acid mine water with cobalt and zinc.

Tests were made to ascertain quantitatively the effect of solutions on minerals which were readily dissolved in the experiments recorded above. One gram samples were used in every case except for genthite of which there was but a small supply, necessitating the use of one-half gram sample. Ten c.c. of tenth normal

sulphuric acid were used. The bottles were left four days, and were then opened, their contents filtered, and the filtrate analyzed for nickel. During the four days, progress of solution could be noted from the gradually deepening green color of the solution. The samples were shaken each day.

Results of the analyses and calculations are tabulated. Pentlandite gave a greater percentage of its nickel content to solution than any of the other minerals. Genthite is also readily dissolved. The supply of gersdorffite was small, and it is not very important as an ore mineral. The qualitative tests are sufficient to indicate that it is highly soluble in the sulphuric acid solution used here. The olivines and serpentine were omitted for the reason that their slight amount of nickel and the relative unimportance of the minerals did not justify treatment and analysis by the present methods. It is sufficient to know they give their nickel readily to solution. There are no large bodies of sulphides in the vicinity of the larger nickel deposits of silicate origin. Consequently the vadose waters around these localities are not likely to be acid sulphate solutions.

Table II. The Quantitative Effect of N/10 Sulphuric Acid.

	Pentlandite	Nicolite	Chloanthite	Millerite	Genthite
Gms. Ni in sample taken	0.1414	0.4049	0.2993	0.5592	0.1225
Gms. Ni in solution	0.0064	0.0081	0.0054	0.0078	0.0051
Nickel dissolved	4.5%	1.99%	1.82%	1.40%	4.16%

The effect of sulphuric acid and ferric sulphate.

The interaction of sulphuric acid and iron or iron-nickel, or iron-copper sulphides produces ferrous sulphate. In the oxidizing zone this salt is unstable, and is readily oxidized to ferric sulphate. Since ferric sulphate gives an acid reaction, and is active as an oxidizing agent, experiments were arranged to test the effect of ferric sulphate on the various sulphides and sulphosalts of nickel. Many mine waters which have been analyzed are shown to contain ferric iron as the sulphate.

The first test to be made consisted in the ordinary leaching test common to most of these experiments, namely, the addition of a certain amount of solution to a weighed sample of mineral. One-gram samples were used except for the genthite of which a one-half-gram sample was used. The solution was N/10 H₂SO₄ to which had been added 6.6 grams of ferric sulphate per liter. In the test, 20 c.c. of solution were used, and allowed to act for four days. The results are stated below.

Table III. The effect of N/10 H₂SO₄ and N/10 Fe₂(SO₄)₃

	Pentlandite	Niccolite	Chloanthite	Millerite	Genthite
Gms. Ni in sample	0.1414	0.4049	0.2993	0.5592	0.1223
Gms. Ni in solution	0.0126	0.0140	0.0002	0.0145	0.0034
Nickel dissolved	8.92%	3.46%	0.668%	2.59%	5.55%

From comparison of tables II and III, it is apparent that the presence of ferric sulphate of this strength does not increase the solvent action on these minerals. It should be approximately true that twice the quantity of solvent should dissolve twice the amount of nickel. Were the ferric sulphate to have no effect upon

the reaction, the quantity of nickel in solution in table III should be twice that in table II. The discrepancy may be ascribed to experimental error, to differences in sample. It is concluded that the addition of ferric sulphate has no effect on this solution.

The question arose as to whether a stronger concentration of ferric sulphate might be more effective. In arranging a test to determine this point, it was intended to use constantly increasing amounts of ferric sulphate, and to plot a curve from the results.

Owing to the difficulty and probable error in weighing out insignificant amounts of ferric sulphate, a strong solution containing fifteen grams of the salt in 100 c.c. of tenth normal sulphuric acid was made, and this solution measured out from a burette. The mineral samples each consisted of one-half-gram of millerite in a one hundred c.c. flask. Twenty c.c. of the sulphuric acid were added, and the ferric sulphate run from a burette. The flasks were stoppered with rubber corks.

Table IV. The effect of N/10 H_2SO_4 + 15% $Fe_2(SO_4)_4$ on millerite.

C.c. H_2SO_4	20	20	20	20	20	20	20	20
C.c. $Fe_2(SO_4)_3$	0	1	2	3	4	5	6	9
Per cent nickel dissolved	3.76	3.53	3.05	3.66	3.45	3.08	3.66	3.34

The test continued for approximately eleven days. The solutions were filtered and titrated with KCN. Another portion of the millerite was completely dissolved in acid for analysis. The percentages were calculated on the basis of the total content of nickel per sample as determined from this analysis.

Although there are irregularities in the results shown, these are to be explained as experimental errors. The rubber in some of the corks showed corrosion. Samples containing 7, 8, and 10 c.c. of ferric sulphate which had been included in the series were thrown out because of accidents. In titrating with KCN, the solution must be ammoniacal, and to keep iron from precipitating, a solution of tartaric acid was used. With increasing amounts of ferric iron, the solution becomes very dark, obscuring the end point. After considering all factors, the conclusions are that addition of ferric sulphate has a negligible effect on the attack of nickel sulphide by acid. Although this is true for millerite, it need not necessarily be true for other nickel minerals.

Stokes^{1/} working on the problem of distinguishing pyrite from marcasite, tested various samples with ferric sulphate solution, and determined the reducing power of the minerals. Speaking of the effect of nickel and cobalt as impurities in the sulphides, he says they show a very strong elevating influence on the oxidation coefficient. No data as to the amounts of nickel are reported from his specimens from which these conclusions are drawn, and furthermore he has no statement that nickel is taken into solution.

The effect of sulphuric acid and ferrous sulphate.

Ferrous sulphate is nearly always present in deposits of sulphide ore.

Its effect on millerite and genthite was tested in the same way as with ferric sulphate. The solution was tenth normal with re-

1. Stokes, Bull. 186, U. S. Geol. Survey, p. 32.

See also W. H. Emmons, Bull. 625 U. S. Geol. Survey, p. 460.

spect to ferrous iron and to sulphuric acid. The test of these two minerals with twenty c.c. of solution for four days gave percent solutions of 2.33 and 9.47. These are of the order of magnitude expected from table II, assuming that the ferrous sulphate has no effect. The conclusion is that ferrous sulphate has no appreciable effect upon the solubility of the two minerals.

Effect of sodium bicarbonate.

Carbonate waters are known in certain localities making it of interest to test solubility of the nickel minerals in such solutions. In the first test, made for qualitative purposes only, a tenth normal solution of sodium acid carbonate was used. The tests were conducted as already described for acid solutions. Two grams of the minerals were treated with twenty c.c. of solution. No indication of the progress of the test was to be obtained from the color of the solution, as was possible with sulphuric acid. After four hours, one cubic centimeter of solution was removed by pipette. The estimated strengths of reactions with glyoxime were in the order, pentlandite, millerite, gersdorffite. No nickel could be detected in the remaining solutions. After twenty-four hours of leaching, tests were made again, and chloanthite then gave a reaction. After ten days, the filtrate was tested and the strength was in the following order; gersdorffite, chloanthite, niccolite, millerite, genthite, pentlandite. From these tests it was evident that alkali carbonate solutions slowly dissolve certain nickel minerals, but the reaction with the nickel-bearing silicates is very slow.

The work of Grout^{1/} in which he experimented upon the order of activity of 1 per cent acid carbonate solutions, showed that millerite was attacked and that the reaction was increased about two-fold by a increase in the temperature from 25° to 50°C. Niccolite, on the other hand, he found was less affected. This apparent discrepancy with the results given here can be ascribed to the difference in the tests made. Grout tested his solution for sulphide by means of a solution of silver sulphate and sulphuric acid. Although the solubility product for silver sulphide is extremely small, and the precipitate readily detected, it does not show that nickel has dissolved as the glyoxime test.

Quantitative tests were made with the same solution of carbonate. For the reason that carbonate waters are especially abundant in silicate rocks, olivine was included in the experiments. The results of this test are shown below.

Table V. The effect of sodium bicarbonate.

	Pentland- ite	Niccol- ite	Chloan- thite	Miller- ite	Genthite	Olivine
Gms. Ni in sample	0.1414	0.4049	0.2993	0.5592	0.1228	0.0012
Gms. Ni in solution	0.0002	0.0005	0.0004	0.0002	0.0004	0.0005
Nickel dissolved	0.141%	0.123%	0.133%	0.358%	0.326%	0.416%

1. Grout, F. F., On the behavior of cold acid sulphate solutions of copper, silver, and gold with alkaline extracts of metallic sulphides: Econ. Geol., vol. 8, p. 427

Effect of sodium carbonate with CO₂ under pressure

Another test was made with the carbonate solution applying also a considerable pressure of carbon dioxide. A tube six feet long with half-inch bore was filled to within a foot of the top with nickeliferous olivine from North Carolina crushed to pass a ten mesh screen and remaining upon a twenty mesh. Through this mineral column five hundred cubic centimeters of the sodium bicarbonate solution were allowed to percolate. After the mineral was thoroughly saturated, a carbon dioxide generator was attached to the base. The carbon dioxide was allowed to bubble through the solution for a few minutes after which the top was corked. The pressure was rather strong, but decreased as the acid in the generator was gradually neutralized by the limestone. The contents of the tube were allowed to drain into a separate bottle. This process was repeated several times and finally the solution caused to percolate slowly for a day. The generator was again attached, and at each draining of the tube a test for nickel was made. After the reaction for nickel was obtained, the experiment was stopped. The solution which had passed through the mineral column several times became clouded with a white precipitate on standing. This was tested with sodium phosphate and proved to contain magnesia.

This experiment shows that nickel is dissolved under the action of carbonic acid, and at the same time magnesia goes into solution. The reaction is slow, but with time enough all the nickel could be dissolved from the olivine.

The effect of magnesium carbonate. The alteration of olivine to serpentine gives as a product of the reaction magnesium carbonate. 1/

The study of reports concerning the deposits of Riddles, Oregon, indicates that nickel is dissolved during weathering and is again precipitated. This fact suggested that one or the other of the products of the reaction acted as a solvent and transporting agent. Magnesium carbonate, although very insoluble, is probably the only one of these products to be considered. Further than this, garnierite and genthite both contain magnesium. From these two suggestions it was thought advisable to test the effect of various nickel minerals in magnesium carbonate.

Approximately one-twentieth of a mol of the pure salt was added to a liter of water, making a solution supersaturated at ordinary temperatures. One gram of the fresh olivine and one-half gram of the genthite were each treated with ten c.c. of the solution. In ten days only a slight trace of nickel was detected in solution.

The reaction, then, is very slow. In the natural condition, the serpentine, which forms still retains part of the nickel which would indicate that the leaching action, by whatever the solvent, is very slow. It is therefore possible that magnesium carbonate may in a longer period account for the removal of nickel during the process of weathering.

1. Van Hise, Treatise on metamorphism, Mon. 47 U. S. Geol. Survey, p. 309/

The effect of sodium sulphide.

Mercury, gold, zinc, and iron are soluble in solutions of sodium sulphide, forming double salts with those of sodium.^{1/} Copper is soluble to a slight extent in such a solution, and an experiment was made to ascertain what effect such a solution might have upon nickel sulphide.

A small sample of pentlandite was treated with a solution of Na_2S . After twenty-four hours the glyoxime test showed no trace of nickel. The experiment was continued after adding a small quantity of NaOH , and again tested after twenty-four hours. There was no trace of nickel in the solution. It was concluded, therefore, that at room temperatures, alkaline sulphides probably are not strong solvents of nickel sulphides.

General conclusions concerning the effects of various solvents.

The following conclusions are drawn from the experiments referred to above. Nickel sulphides and arsenides, together with the iron-nickel minerals, and the hydrous silicates are readily dissolved by acid sulphate waters. Pentlandite and millerite, the two which furnish the bulk of the sulphide ores, are among the most soluble. From the fact that these two minerals occur associated with pyrite, chalcocopyrite, and pyrrhotite, which through oxidation invariably furnish earth waters with free sulphuric acid, it seems probable that nickel is dissolved readily from sulphide ores.

Carbonates of alkalies and alkaline earths, and especially the corresponding bicarbonates will dissolve small amounts of nickel from nickel silicates and from sulphides. This is especially significant in the case of the nickel-bearing silicates of primary or secondary origin.

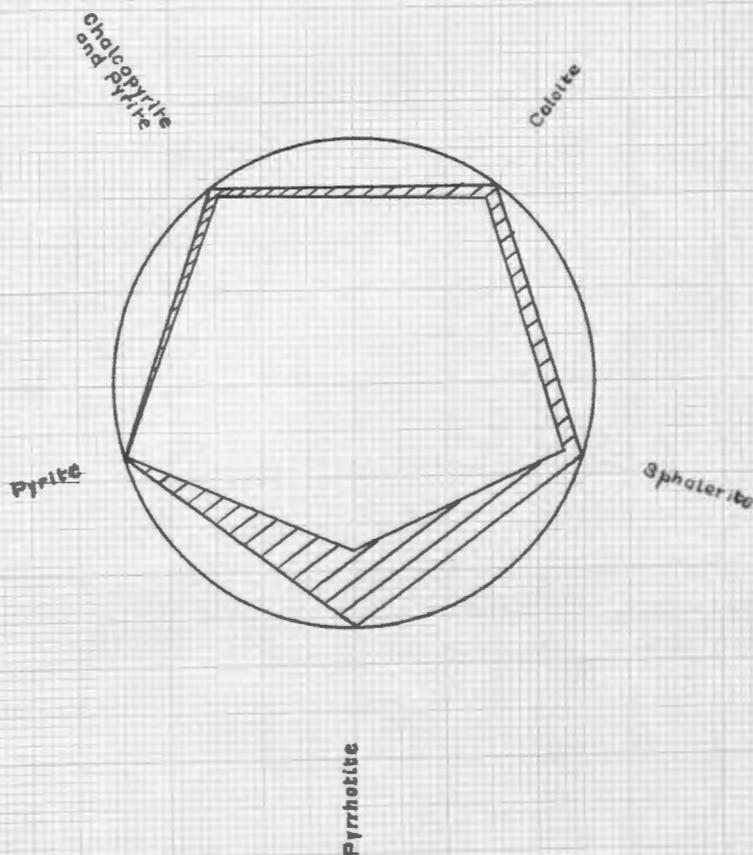
1. Dr. W. H. Mellville, in Mon. XIII, U.S. Geol. Survey, Chap. 15.

III. The Precipitation of Nickel from Solution.

The second part of the problem of secondary enrichment concerns the probability that the given metal will be redeposited from solution by minerals present in the deposit. The Schuerman series referred to above, indicates that both ferrous and ferric iron are of higher potential than nickel, and that it is very probable that iron sulphides will throw nickel out of solution. Copper, however, occurs below nickel in the series. The most abundant of the associated sulphides in nickel deposits are pyrrhotite, pyrite, and chalcopyrite.

Tests were made by placing twenty-five grams of pyrite, pyrrhotite, sphalerite, calcite, and an equi-volume mixture of pyrite and chalcopyrite each in a flask with fifty c.c. of an acid solution of nickel sulphate made to tenth normal strength with respect to both the acid and to nickel. All minerals were crushed and sized to pass a ten-mesh screen, and were caught on twenty mesh. The flasks were set aside, shaken occasionally, and examined periodically for evidences of reaction. No odor of hydrogen sulphide was detected. The calcite showed reaction with the acid.

The tests were continued for four weeks. After filtering the solutions and washing the mineral thoroughly, the solutions were made up to 500 c.c. and 100 c.c. taken for analysis in duplicate. The results are shown in the appended table.



The radius of the circle represents the nickel content of the synthetic solution. The five points on the circle at the apices of the regular pentagon mark the five precipitants used. The apices of the inner pentagon are plotted along the radii of the outer, distances from the center showing to scale the nickel content after the test. The cross-hatched area indicates the amount of precipitation in the five tests.

Mineral	Ni in 50 c.c. originally	Ni in 50 c.c. finally	Difference	Precipitation in per cent
Pyrrhotite	0.1310	0.0870	0.043	32.8
Sphalerite	0.1310	0.116	0.015	11.5
Calcite	0.1310	0.118	0.013	9.93
Pyrite and Chalcopyrite	0.1310	0.124	0.007	5.34
Pyrite	0.1310	0.130	0.001	0.7

The results are also shown on an accompanying diagram.

During the test, change in the color of solution denoted that reactions had been taking place. In the flask with calcite there was accumulation of bubbles of gas on the grains of mineral, probably indicating the formation of carbon dioxide, but there was no appreciable diminution in the intense green color of the nickel solution. In the pyrrhotite flask, the green of the original nickel sulphate became gradually cloudy with a brown precipitate which might have been iron oxide. In filtering off the solution this precipitate was retained on the filter. None of the other flasks showed any visible change.

Examination of the mineral residues in some instances gave some ideas concerning the reactions which had taken place. Most striking of all was the pyrrhotite. Instead of the bronze color characteristic of fresh pyrrhotite, the residue as a whole shows a dull brownish red color. Among them may be seen some which show a brassy yellow tarnish resembling chalcopyrite very closely. This may possibly be millerite, or possibly one of the iron-nickel sulphides. The brown grains are no longer of metallic luster, but are filmed with a brown amorphous substance. Very likely some of this is ferric oxide, for the reaction of sulphuric acid with pyrr-

hotite is as follows:



By oxidation with air in the flask, ferric sulphate would form, which in turn must hydrolyze with a precipitation of ferric oxide. The extent to which this can take place will depend upon the supply of air. It is believed that much of the brown powder is sulphide of nickel, or of combined iron and nickel. In the experiment in the large tube in which precipitation from percolating solutions was tested, the precipitate was of a very similar appearance. Test of the precipitate on the filter noted above showed the presence of considerable nickel.

The pyrite, chalcopyrite, and sphalerite do not show visible alteration or precipitation. Calcite is not very markedly altered in appearance. There is very little etching noticeable, although here and there a cleavage piece is to be seen with a dull surface. The entire residue, although it has been thoroughly washed, shows a faint green tint which suggests some interaction with the nickel sulphate.

Discussion of precipitation tests.

Pyrite is attacked by acid nickel sulphate solutions very little if at all. Examination shows the surfaces of the grains to be as fresh and free from films of precipitated minerals as originally. The pyrite-chalcopyrite mixture evinces a rather marked increase over the pyrite. It is probably true that the precipitating power is due to the chalcopyrite. Almost invariably chalcopyrite has a tarnish of secondary sulphides which have been shown to be more rapid precipitants than chalcopyrite. ^{1/} Sphalerite showed considerable activity in precipitation. Palmer and Bastin, Econ. Geology, vol. VIII.

tating nickel from the solution. The most marked reaction of the series was shown by pyrrhotite. In this connection it is to be noted that sphalerite and pyrrhotite, in reacting with acid, evolve hydrogen sulphide, which could readily account for the precipitation of nickel as sulphide. This point has been shown to be the case when copper is the metal concerned.^{1/} Calcite is also to be considered as a reasonably strong precipitant.

Pyrrhotite is about three times as active a precipitant as sphalerite, which in turn is twice as active as chalcopyrite. This is in the order of activity determined by Wells.^{2/} From it the conclusion is drawn that an ore in which nickel sulphides are associated with pyrrhotite as the chief ore mineral would, given proper enriching conditions, serve to concentrate the secondary minerals of nickel in a thin zone. Few nickel deposits with sphalerite as an important associate are on record. However, in such an occurrence the secondary zone should be shallow.

Silicate pre-
cipitation.

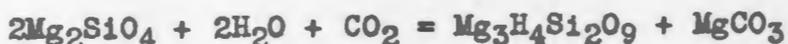
The leaching of nickel from peridotite minerals by means of carbonate solutions suggests a process which may possibly be of importance in a locality where sulphate waters are not present because sulphides are not found there. Two such localities are Riddles, Oregon, and New Caledonia. In addition, the iron-ore districts of Cuba are areas of peridotite rocks from which the ores have been produced by processes of weathering. Primary nickel occurs in these rocks as in many peridotites. A survey of the literature dealing with this locality

1. Allen, Zies, Merwin, Econ. Geology, Vol. II.

2. Wells, R. C., In Bull. 529 U. S. Geol. Survey, p. 76.

shows a certain leaching action to have taken place with transportation and concentration of the nickel. Were analyses of surface waters from these localities available, the character of the alteration by which these processes have taken place would be more easily explained. It is possible to infer the character of the solutions by comparing the composition of the ore and the protore.

The general belief is that the following reaction takes place when olivine alters to serpentine.



Carbonate waters cause the alteration. In the event that impurities such as cobalt and nickel are present in the olivine, these are dissolved if soluble in carbonate solutions. The experiments show that nickel may be leached by just such solutions. Table No. V giving the comparative results of NaHCO_3 leaching tests shows that this solution is by no means a vigorous solvent. Data from the field show that in the alterations of peridotites, the serpentine retains considerable nickel, only a portion entering the ore bodies. The proposed explanation is then quite within the limits of field observations.

Convinced that during the alteration by carbonate waters nickel is taken into solution, it became pertinent to account for its rather limited mobility. Van Hise^{1/} discusses the alterations of olivine and says that ordinarily accompanying the serpentine, magnetite, opal, and other minerals may be found. One of the most frequent combinations of minerals with serpentine is magnesite, quartz, or opal, and magnetite. If during the alteration of an

1. Van Hise, C. R., Mon. 47 U. S. Geol. Survey, pp. 308-310.

olivine to serpentine opal, or any other hydrous silica, is produced, the following reactions appear perfectly logical, especially in the light of the several reactions written by Van Hise.



During the progress of this reaction, when the CO_2 is not abundant it is conceivable that opalescent silica and soluble magnesium-nickel salts, such as the carbonates or bicarbonates, combine as shown.

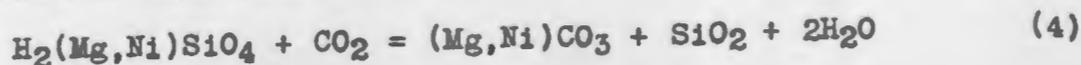


The carbon dioxide is supposed to escape. To ascertain if such a precipitation is at all possible, a solution of nickel sulphate was added to one of soluble sodium silicate and allowed to evaporate. After washing, the resulting material was of a sandy constituency, apple green in color, and in many ways resembled the silicate of magnesium and nickel found in tiny cracks in the olivine.



In writing this reaction the intention is to show what probably takes place, not to give an accurate formulation of the metathesis.

In discussing the deposits of genthite at Riddles, Oregon, G. F. Kay states that the silicates of nickel lie flat upon the serpentine. Quartz, iron-oxide, and serpentine are associated. When the silicate is thrown upon the dump and is exposed for some time, the nickel silicates are entirely redissolved. Such a reaction could be expressed in the following way which is essentially the reverse of equation number 2.



In this way could be explained the rather conflicting observations that nickel silicate forms and is dissolved under approximately analogous conditions. When the nickeliferous olivine is exposed at the surface, alteration by carbonic acid throws magnesia and nickel into solution which transports them. The amorphous silica precipitates them when CO₂ is less abundant, or where the flow of solution is at all retarded. The solution in contact with opalescent silica will combine with the latter setting free CO₂, an available agent for further alteration. This fits in well with actual occurrences at Riddles, the genthite lying as flat patches on the serpentine. Other places of deposition at Riddles have been in small veins in the joints and cracks below.

Tube test. The most instructive and striking experiment carried out to illustrate deposition from a nickel sulphate solution, was made on a larger scale than those preceding. From other experiments it was learned that nickel was precipitated by pyrrhotite. Chalcopyrite will also cause deposition. Work which had been done in connection with another problem on the influence of basic rocks in effecting rapid neutralization of ore solutions showed that, where the country rock was basic, secondary zones were shallow. A chunk of rock from Sudbury nickel district containing sulphides and basic gangue was crushed and sized to pass ten mesh screen, and the fraction caught on the twenty mesh screen was selected for this test. The sample contains pyrrhotite, chalcopyrite, pyrite, and reacts strongly for nickel. The gangue fragments are dark, basic minerals and probably in the ratio of 1:1 with the sulphides. This mixture may be regarded as an actual

Tube Test.



Surface

Zone of oxidation

Water level

Zone of saturation

brecciated ore from a typical nickel sulphide deposit.

The apparatus used consisted of a glass tube six feet long with a half-inch bore. To the lower end is fused a glass stop-cock, terminating in a small glass tube. This is filled nearly to the top with the crushed ore, by sluicing it in water. In this way no air bubbles are left in the mineral column. The tube is now placed in a rack previously provided. Attached by a rubber coupling to the discharge from the stop-cock is a smaller tube so bent as to return parallel to the larger one, to a point about two feet from the top. Here another angle is made in a direction away from the larger tube, and the end is bent down to discharge into a vessel provided. Perched above the open end of the larger tube is a separatory funnel filled with the solution to be used. This apparatus is one of a battery of such tubes which are used in studying the processes of deposition from descending ore solutions. A photograph on another page shows this battery of tubes of which the one to the extreme right contains the nickel experiment.

In preparing the apparatus for the test, water was dropped from the funnel overhead, the stop-cock at the base of the larger tube was opened, and the water rose in the small tube to the goose-neck bend at the top through which it discharged into a flask. The water in the large tube dropped to a level approximately even with the top of the goose-neck bend. The tube now may be divided, as in the photograph, into a zone above water-level corresponding to the zone of oxidation in nature, and a zone of saturation below water-level.

The experiment was conducted by allowing a tenth normal solution of nickel sulphate, which was also tenth normal with re-

spect to sulphuric acid, to drop from above and percolate through the tube. This continued for twenty-three days, after which 100 c.c. of water were passed through to wash out the solution. The discharge was collected and analyzed.

The tube was examined after the experiment was finished. The appearance of the two zones, one of oxidation extending from the surface to the water-level, and one of saturation extending from water-level to the bottom of the tube, showed clearly that the conditions in the former had been different from those in the latter, and that as a consequence, the chemical reactions which had taken place were different.

The mineral column for two or three inches immediately below the surface was fresh and unaltered. Below this a reddish precipitate of ferric hydroxide is seen which becomes gradually more abundant with depth. The zone of saturation is also fresh and unaltered with the exception of the first two or three inches below the water-level. In this narrow belt, there is a small amount of ferric hydroxide, but the sulphide minerals have a bright metallic luster.

Three chemical processes which have taken place contribute to the same effect which can be seen in that zone in which ferric hydroxide is precipitated. These processes are solution, oxidation, and hydrolysis. Solution takes place when the acid nickel sulphate comes in contact with the minerals at the surface of the column. There is no proof of this other than the common knowledge that pyrrhotite is soluble in acid of low concentration. The products of the reactions are ferrous sulphate and hydrogen sulphide. Oxidation takes place by which the ferrous sulphate is converted

to ferric sulphate by oxygen of the air. That this reaction of oxidation has taken place is shown only by the presence of ferric hydroxide. From the presence of this precipitate, it is inferred that hydrolysis of ferric sulphate has occurred producing the ferric hydroxide and sulphuric acid.

Further evidence that ferrous sulphate is formed, that it is then oxidized by oxygen from the air, and later hydrolyzed with precipitation of Fe_2O_3 , is seen in the discharge from the small tube. Near the open end of this tube the inner surface is coated with ferric hydroxide, and a precipitate of the same compound forms inside the collecting flask. The localization of the hydroxide in the open end of the tube and in the flask is explained when it is considered that the acid solution saturates the mineral column from water level to the bottom, allowing no admission of air. Nor in the small return tube is there any air except at the open end. The flask is open and permits oxidation of the solution. Since the solutions were acid even at discharge, there must have been continuation of the reaction between pyrrhotite and acid in the zone of saturation, but the ferrous sulphate is not oxidized, and there is no visible change in this part of the mineral column.

The processes of reduction of nickel sulphate and precipitation of nickel sulphide have taken place to only a slight extent. The only evidence of such secondary sulphide enrichment is seen in the shallow zone of two or three inches below water level as noted in the description. In describing the ore it was stated that some chalcopyrite was present. The fresh metallic luster, and bright brassy color which is seen on the surface of sulphide

grains in this zone may possibly be secondary chalcopyrite. The sulphuric acid may have dissolved copper in the oxidizing zone, and the pyrrhotite may have reprecipitated it as chalcopyrite. There is no way to determine whether secondary sulphides of nickel have been precipitated or not, but it is very evident that if they have been found, they are present only in this shallow zone.

It has been stated that there are two narrow zones of about the same depth, one just below the surface, and a second just below water level. The explanation which is to be made for the one may be also applied to the second. The first mentioned zone shows the dark gray color of the original ore. In explanation of this, it is thought that the acid reacted with the ore in those two or three inches, but the ferrous sulphate descended that distance before oxidation and hydrolysis had precipitated the ferric hydroxide. The maximum intensity of oxidation and precipitation ought to occur at the mid-point of the oxidized zone, or below that level, because air can penetrate to that depth very readily, while below such a point, the amount of oxygen becomes progressively less. And at the same time the addition of acid down to that point by hydrolysis of ferric sulphate is more nearly equal to the loss by neutralization by basic minerals. The amount of ferric hydroxide should be progressively less as the water level is reached. The two or three inch zone below water level which shows a small quantity of ferric hydroxide, may be due to the fact that a small amount of ferric sulphate formed above remained in the descending solution and was hydrolyzed below water level. Considering both of these narrow belts at once, the one just below the surface and the one just below water level, it appears as if the zone in which solution

oxidation, and hydrolysis were taking place, had been simply let down through those two or three inches, that distance, with the rate of percolation being a measure of the time required for the three reactions to take place.

That the amount of secondary sulphide deposition occurring in the tube is at best very slight, is suggested by the above description of the tube. The best evidence is obtained from the analyses of the original solution and of the discharge. At the start one liter of the solution of nickel sulphate was placed in the funnel above. At the end of the experiment a few hundred c.c. remained in the funnel. The nickel contents of each of these solutions and of the discharge were determined and the amount of nickel unaccounted for, that is which was deposited, was calculated as follows.

Grams of nickel in 1000 c.c. of original solution		2.80
" " " " solution remaining in funnel	= 0.758	
" " " " discharged solution	= <u>1.97</u>	
Total nickel accounted for	= 2.758	<u>2.758</u>
Total nickel unaccounted for (deposited)	=	0.042
	= 1.43 per cent	

In this experiment there has been only a very small amount of nickel deposited from sulphate solution. As shown 1.43 per cent of the nickel remained in the tube. This loss from solution may be assigned to secondary sulphides, to small amounts saturating porous grains, or to amounts imperfectly washed. The solution used is strongly acid and it is difficult to precipitate nickel sulphide from an acid solution. The discharge was still acid and therefore it is not likely that nickel sulphide would be easily

precipitated in the tube. In view of the fact that pyrrhotite is easily attacked by acid with generation of H_2S , and that basic minerals are comparatively active in neutralizing acid solutions, it would appear at first thought that conditions of slight acidity or neutrality and a presence of hydrogen sulphide ought to be reached. The oxidation of pyrrhotite and the hydrolysis of ferric sulphate both increase the acid content of the solution.

IV. General Conclusions from Experiments.

A. The experiments described above treating the effect of solutions on nickel minerals, and the precipitation of nickel from solution of acid sulphate, indicate that there is probably secondary enrichment of its sulphide deposits.

1. Primary nickel sulphides, arsenides, and sulphosalts of iron and nickel, among them the two most abundant of the recognized nickel ore minerals, are readily dissolved in waters of composition known to exist in the oxidized zones of sulphide deposits.
2. Certain minerals known to be abundant as associates of the primary nickel minerals have been found to be active in precipitating nickel from solutions such as would result from weathering of nickel deposits.

B. The experiments show that not only are the sulphide deposits secondarily enriched under ordinary conditions of weathering peculiar to those deposits, but the silicate ores owe their richness to processes of weathering peculiar to such silicate occurrences. The silicate ores are generally richer than the sulphide ores.

C. From the above data and results of other experimental work carried on in this laboratory the third conclusion is made. The neutralization of acid waters is more rapid in basic rocks such as gabbros and norites, than in acidic rocks, such as granites. Nickel deposits are characteristically related to basic igneous rocks. Rapid neutralization of acidity would result in shallow secondary sulphide zones. Thus it appears probable that secondary enrichment of nickel deposits is confined to shallow depths.

V. Field Data.

In the experimental work described, the conditions of pressure and temperature were essentially those of nature. In nature, temperatures range around 18°C. except when local conditions such as sulphide oxidation may increase the figure to around 40°C. The latter figure^{1/} is accepted as the upper limit of temperature prevailing in zones of chalcocitization. There are evidences that higher temperatures may be reached during intense oxidation,^{2/} under which conditions chemical reactions proceed with much greater velocity, solution being very rapid. Pressures are approximately atmospheric in ore deposits near the surface. Furthermore, conditions of the experiments were in no way complicated except for the shaking, which has the function of exposing fresh surfaces to contact with solutions and promoting diffusion of dissolved material. Strengths of reagents are within the range of observed compositions of mine waters. Since conditions are approximately those of nature, there should be no difficulty in finding con-

1. W. H. Emmons, Econ. Geol., vol. 10, March 1915, pp.151-160.

2. Bull. 640 U. S. Geol. Survey, p. 80.

firmatory data in the field notes of geologists who have worked in the more important of the world's nickel deposits.

The workable deposits of nickel are of two types, sulphide ores segregated in an igneous condition from basic rocks, and hydrous silicate ores formed in the belt of weathering of serpentine from olivine rocks. Of the two, in recent years the former type is productive of the bulk of the world's supply of nickel. For a number of years the silicate ores of New Caledonia furnished most of the nickel used.

The Sudbury district of Canada is probably the foremost producer of nickel at the present time. Little or no information is obtainable which bears directly upon the problem. In turning through a voluminous literature, there is found a general disagreement of authorities upon those points bearing directly upon secondary enrichment.

Upon a few points there is solid agreement. The Sudbury District of Southern Ontario occupies a position within the areas glaciated by the Pleistocene ice-sheets. Its bed rock is nowhere mantled by any considerable thickness of residual soil. Gossans are of necessity very scantily developed. The character of the associated igneous rock is also agreed upon. It is a basic rock, classified as a norite. Geologists have not yet reached agreement as to the primary origin of the sulphides, but from the literature and an examination of specimens, it is learned that they are intimately intergrown with the basic silicates. This intergrowth means a very compact texture more or less impervious to solutions. Another point established beyond doubt is that the leading sulphide is pyrrhotite with which are associated chalcopyrite, pyrite, and

the nickel mineral pentlandite.

Concerning those points which are factors in the secondary enrichment of an ore deposit, there is no such agreement. Points which should be determined in examining a sulphide ore body are the permeability of the ore to meteoric waters, either by way of faults, joints, or natural porosity; the presence or absence of water in the deeper levels; and any change in the mineralogy with a relation to the water level or the surface.

There is little information on such points. Browne^{1/} states that ore deposits are water tight; that the mines are dry, as a rule; and that there is little or no effect upon raw ore by water, indeed when it occurs on the lower levels it may be drunk by the miners. He states definitely that there is little or no evidence of secondary enrichment. But, on the other hand, S. F. Emmons^{2/} states that the location of the ores, the faulting and dislocation, seem to indicate the concentration, through percolating waters which dissolved nickel originally disseminated through the rock, in water channels formed by fault planes or zones of displacement.

Further conflict in the opinions of different authorities is seen in their statements concerning gossans. Browne states that there is little or no gossan. Coleman^{3/} describes gossan occurring on the range, and says it is sometimes very thick and may stand up as mounds and hills. After describing these brownish

1. D. H. Browne, Econ. Geol., vol. 6, no. 5, pp. 467-475.

2. A. P. Coleman, Ont. Dep. Mines, 1913.

3. S. F. Emmons, Amer. Inst. Min. Eng. Trans., vol. 22, p. 70.

red gossans as a characteristic sign of nickel, he states that probably millions of tons of nickel and copper have been dissolved and carried away, and this long wastage seems nowhere to have resulted in the concentration of the metals in workable secondary deposits. He says: "A permanent secondary compound of nickel has not been reported from the region." This is a most remarkable fact because in the experiments made and reported above, pyrrhotite is an active precipitant of nickel from an acid sulphate solution. Chalcanthite and morenosite are reported from Sudbury, indicating that the nickel has been dissolved as sulphate, and it is hardly believable that so much copper and nickel could have passed into solution, remained in contact with pyrrhotite, and not have been redeposited. It probably was removed as soon as formed, and lost in the surface waters. However, some few indications of enrichment are recorded.

Millerite occurs at Copper Cliff as blade-like crystals, and is considered to be secondary after pentlandite. Nowhere has it been found in economic quantities. Copper has been secondarily enriched at some places as at the Vermillion mine, where bornite and chalcocite were mined. They did not, however, occur very deep. Native copper, found at depths of 15 feet, is stated by Coleman to be probably reduced from sulphate solutions by organic matter carried by descending waters. This native copper might have been reduced from one of the sulphides as chalcocite by cupric sulphate which oxidizes the sulphur to sulphate. Thus it appears that secondary processes are in order at Sudbury, but that there has been practically no extensive formation of a zone of enrichment.

The absence of an important zone of secondary sulphide enrichment, in the light of the experiments presented, may be explained in part by the fact that there has not been time enough since the glacial scouring of that region to permit much accumulation of gossan. The texture of the ores is very compact and tough. Although pyrrhotite is rapidly oxidized, there is apparently little opportunity for the resulting solutions to enter the deeper ores. Careful examination of the ores close to the water level may perhaps discover the presence of a secondary zone. That this would be very shallow seems to be certain.

Fifty miles west of Philadelphia, the Gap mine at Lancaster Gap has been exploited for a number of years. The ore body is, without doubt, a magmatic segregation from a basic rock having a lenticular or stock-like shape. This deposit is described by Kemp.¹ Here again, as in Sudbury, the minerals are pyrrhotite and chalcopryrite with some pyrite. There are abundant crusts of millerite which are considered clearly secondary. These crusts occur along cracks and fractures, and are not described with regard to the water level. This deposit is outside the glaciated area, and offers greater opportunity for formation of a gossan. The ore body is described as dense and massive.

A third sulphide deposit in the United States deserving mention occurs in California about sixty miles northeast of San Diego.² The igneous rock is an amphibole-bearing olivine gabbro or peridotite. The ore minerals which segregated from the magma are mainly pyrrhotite, with some pyrite, chalcopryrite, and a nickel

1. J. F. Kemp, Am. Inst. Min. Eng. Trans., vol. 24, p. 620.

2. Bull. 640 U. S. Geol. Survey, p. 77, 1917.

mineral believed to be polydymite. The outcrop is a spongy mass of limonite with abundant malachite. The pyrrhotite is cut by closely spaced partings permitting thorough oxidation. There has been fissuring and faulting. Given this gossan, the fracturing, and the character of ore and gangue, it would seem that this might be a very excellent opportunity to make careful examination of the zone between gossan and unoxidized sulphide. No thorough examination has been made, and it is to be hoped that more careful study will be undertaken.

A review of other sulphide deposits of nickel has given some indication of deposition from cold, circulating waters. Bloome and films of annabergite, norronite, gersdorffite, and millerite have been found in relations indicating a secondary origin. However, none of these form economic deposits. The nickel, once in solution, is apparently not readily redeposited, but is widely scattered.

Bilicate deposits are best exemplified by the New Caledonia and Biddle camps. Others occur at Webster, North Carolina, and in Cuba. The nickel has been traced to a primary source in the olivines of peridotites, dunites, harzburgites, and lherzolites. Normal processes of alteration have broken these down to form serpentines, and during the alteration nickel has apparently formed garnierite and genthite. At each of the cited occurrences, the alteration products included chalcocopy. On a previous page, in discussing these ores which occur in patches above the serpentine, a process has been suggested in outline by which such nickel minerals may have formed. In every case, garnierite and genthite are secondary minerals, the ores are richer than the sulphide ores, and owe that richness to secondary processes.

Summary of field data.

In searching the literature of nickel deposits for the special purpose of collecting information bearing upon the secondary enrichment of those deposits, a number of characteristics have been observed which should bear emphasis. The world's productive nickel deposits are, almost without exception, segregations from magmas of basic composition. Stressing particularly the sulphide deposits, the study shows that, in a great majority, pyrrhotite is the leading sulphide. It has been stated above that basic rocks and pyrrhotite are readily acted upon by passing solutions, and therefore each tends to precipitate nickel very rapidly. A solution resulting from the weathering of such deposits would not descend far below the oxidizing zone before the nickel would be precipitated, and any enriched zone would be shallow. The rocks associated with nickel ores are highly basic, and therefore the effect of a country rock would be at a maximum. The pyrrhotite is most active of all common sulphides, is most conspicuous in nickel sulphide deposits, and will therefore exert a maximum effect in precipitating nickel. Both factors, being at a maximum in most nickel deposits, would have an especially important effect in confining the enriched zone.

Another characteristic is the high ratio of iron sulphides to nickel sulphides. This ratio is probably higher than a similar ratio in sulphide deposits of copper. It is also apparent, both from its solubility and from the literature, that nickel sulphides are not so readily precipitated from sulphate waters as are copper and some other sulphides. During oxidation of the primary sulphides and consequent solution of the nickel, there is invariably a loss,

either by run-off, by direct erosion, by premature deposition, or by dissipation through fissures.^{1/} On account of the high proportion of pyrrhotite, the oxidation of the ore would produce a large amount of acid, and this, tending to keep the nickel in solution, would result in a greater loss. For this reason the secondary zone would be only slightly enriched, as well as shallow.

A third characteristic follows directly from the origin of the sulphide deposits. The texture of magmatic segregations is a tough, compact, intergrowth of sulphides, oxides, and silicates, a texture probably impervious to percolating solutions. By this third point, the probability of a shallow zone of secondary sulphides is again emphasized.

Summary.

In summarizing experimental and field evidences, it is to be stated that enriched nickel deposits are to be expected, both in the case of sulphide segregations, and in those deposits formed during the processes of serpentinization of olivine rocks. In these experiments, natural solvents and precipitants have been found which will accomplish the enrichment. It is probable, however, that secondary sulphide deposits will be shallow and of little importance. The basic rocks, the large quantity of pyrrhotite, and the impervious texture all contribute to this result.

1. L. C. Graton and D. H. McLaughlin, Econ. Geol., vol. 12, p. 31.