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RELATIVE ABUNDANCE OF NICKEL IN THE EARTH'S CRUST

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RELATIVE ABUNDANCE OF NICKEL IN THE EARTH'S CRUST

BY

ROGER CLARK WELLS

Shorter contributions to general geology, 1943
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By Roger Clark Wells

ABSTRACT

Nickel has heretofore been considered to be about the twenty-second element in order of abundance in the earth's crust, but the results of improved analytical methods have raised some doubts about the accuracy of earlier estimates. The excellent method of Sandell and Perlich, using dimethylglyoxime as a reagent and solution of the nickel salt in chloroform as an essential step, makes it possible to determine nickel to ten-thousandths of a percent with a gram or less of material in a relatively short time. This method compares very well with the spectrographic method.

More than 150 new determinations of nickel were made on samples of rocks previously analyzed in the chemical laboratory of the Geological Survey, and they accordingly supplement the previous analyses in respect to nickel, an element that is of interest as one of the so-called strategic metals.

Nickel was determined in all the common types of rock, including the more silicic as well as the highly ferromagnesian, but it is decidedly more abundant in the ferromagnesian rocks, the content being markedly high in dunite, peridotite, and other rocks containing olivine. It is present in most shales and in many silts and clays, including abyssal oceanic red clay. It is also found in sea water, in some peat and petroleum, and in minor quantities in several minerals not generally classified as nickel minerals.

The new analyses usually showed the nickel content to be less than that indicated in the older determinations for the lighter rocks but of the same order for the heavier rocks. In general the percentage of nickel increases with the density of the rock. These new data afford a basis for recalculating the amount of nickel in the crust. The average of all new determinations of nickel in igneous rocks is about 0.008 percent, disregarding the probable increase in density of rocks with depth. This figure is believed to be a decided minimum. Instead of merely averaging the results, however, the nickel content has been correlated with density of the rock, and the distribution of ocean, sedimentary material, and igneous rock in the 10-mile crust has been given consideration. If the density of rocks in the 10-mile crust increases rapidly with depth, as indicated by Washington, the nickel content may possibly be as high as 0.033, although this figure is believed to be a maximum. It is difficult to make an accurate estimate under present limitations of knowledge, but 0.016 percent of nickel is considered a reasonable figure for the relative abundance of this element in the whole 10-mile crust.

INTRODUCTION

GENERAL PROPERTIES OF NICKEL

Although nickel has been found to be about the twenty-second element in order of abundance in the earth's crust,[1] recent advances in the analytical chemistry of nickel have cast some doubt on the older figures for the percentage of nickel in many of the rocks used in computing its relative abundance, so that a revaluation seems appropriate.

The element nickel is of interest for several reasons. Based on analogy to meteorites, the core of the earth is supposedly rich in nickel, yet this element does not seem to have worked outward as far as the crust to any marked extent. Even stony meteorites, which are believed to have contributed to the earth's surface to some extent, contain far more nickel than the earth's crust. It is therefore evident that the processes that have produced the rocks of the crust have tended to leave nickel behind, presumably at depths in the earth.

So far as known nickel consists of a mixture of five isotopes whose mass numbers are 58, 60, 61, 62, and 64, giving a mean atomic weight of 58.69. This atomic weight is slightly less than that of cobalt, 58.94, although in its properties nickel falls in the periodic arrangement beyond cobalt. It is the third element in the triad, iron, cobalt, and nickel. The atomic number of nickel is 28, and accordingly the element is neither very common nor very rare. The atomic radius of the nickel ion is 0.78 Angstrom units, which is identical with that of magnesium and comparable with 0.83 A. for iron and 1.06 A. for calcium.

In analytical operations nickel falls in the "ammonium sulfide group" with cobalt, manganese, and zinc, which for the most part remain in solution after the hydroxides of aluminum, iron, and several other elements are precipitated by ammonium hydroxide. The failure to obtain a good separation in such analyses is one reason for the present contribution and will be discussed more fully later.

A second doubt as to the correctness of the figures for the relative abundance of nickel now in current use arises from the fact that estimates have been obtained chiefly by averaging available analyses without giving any con-

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[1] Clarke, F. W., and Washington, H. S., The composition of the earth's crust: U. S. Geol. Survey Prof. Paper 127, p. 34, 1924. Fersman, A. E., Geokhimiia, tome 1, p. 145, Leningrad, 1933.

sideration to the volumes of the earth's crust occupied by the rocks analyzed—that is, to the actual relative abundance of nickel. Nor has any special consideration been given to the effect of altitude or to the tendency toward gravity differentiation in different flows of traps, lavas, and dikes. A third objection relates to the method of averaging the nickel content, as some analyses in which nickel was not determined have been included with those in which it was determined.

ASSOCIATIONS AND DISTRIBUTION OF NICKEL

Nickel is a fairly common minor constituent of igneous rocks. It has been classed among the "petrogenic" elements but seems to be concentrated chiefly with the "metallogenic" elements, and thus in fact is a kind of transition element.

Native nickel is rare and is found mainly as a minor constituent of native iron, the best known occurrences of which are in western Greenland, though small quantities have been noted elsewhere in basalts. Awarite, $FeNi_2$, occurs in the drift of the Gorge River, southern New Zealand. Josephinite, $FeNi_3$, is found in stream gravel in Oregon. The nickel antimonide, breithauptite, NiSb, has been found in Sardinia, at Cobalt, Ontario, and elsewhere.

Practically all meteorites contain nickel. In iron meteorites the nickel content ranges from 5 to 15 percent; in stone meteorites the metallic nickel content is much smaller or altogether lacking, but small percentages of a nickel silicate are always present.

Nickel is found in commercial quantities chiefly as the sulfide pentlandite (Fe,Ni)S, or as nickeliferous pyrrhotite. Pentlandite is found at Sudbury, Ontario; Espedalen, Norway; Funter Bay, Alaska; Floyd County, Va.; and numerous other localities. Millerite, NiS, though found in many localities, is far less common than pentlandite and usually occurs as hairlike crystals in cavities among other minerals.

The arsenides, niccolite, NiAs, and chloanthite, $NiAs_2$, occur in the Cobalt district, Ontario; and their alteration products, including the nickel arsenate annabergite, $Ni_3(AsO_4)_2.8H_2O$, result from weathering and oxidation. The sulfate morenosite, $NiSO_4.7H_2O$, is probably formed by the oxidation of sulfides, but in most places is soon carried away because it is markedly soluble in water. It has been noted by the writer in association with annabergite and gersdorffite, NiAsS, from the Table Mountain district, Nevada.

The principal silicates of nickel are garnierite, $H_2(Ni,Mg)SiO_4.aq$, and other minerals allied to serpentine, such as genthite, $Ni_2Mg_2Si_3O_{10}.6H_2O$, which is usually found in serpentine or associated with talc and other magnesium silicates. At Webster, N. C., veinlets of nickel silicate ores occur in dunite. Similar deposits of nickel silicates have been found near Riddle, Oreg.; Frankenstein, Silicia; and Los Jarales, Malaga, Spain. In New Caledonia a serpentine is capped with red "clay" containing from 1.64 to 3.14 percent of nickel oxide, and stringers of richer silicate ore occur through the serpentine.

Nickel has been found in pumice (0.01 percent), and nickeliferous magnetite has been reported from Hosanger, Norway. Trevorite, whose formula is believed to be $NiFe_2O_4$, occurs in the Transvaal and has been described by Crosse.[2]

The associations of nickel minerals have been described briefly by W. H. Emmons.[3] It is not necessary to list here the rare or doubtful minerals containing nickel, descriptions of which may be found in most mineralogies.

Commercial deposits of nickel ores obviously owe their origin to some type of concentrating process, which possibly depends on a series of favorable conditions. The exact mechanism of concentration in different deposits has been the subject of considerable speculation and discussion, but it is not the purpose of this paper to summarize the voluminous literature on this subject. Magmatic segregation was for a long time considered the chief mechanism, but more recently the effects of segregation are believed to have been conjoined with the action of fluids and solutions. Factors initiating deposition may be cooling, changing pH, shifting reversible reactions, or mingling of different solutions. Other concentrations of nickel may have been accomplished by adsorptive processes or, in some instances possibly, by organisms.

Nickel has been determined in sea water and reported in the ashes of marine plants. As previously indicated it is distributed in minute quantities in all kinds of rocks. Measurable quantities are found in clay, shale, and slate, but very little is found in limestone and sandstone. In silicate rocks nickel predominates in the ferromagnesian varieties, being definitely allied to rocks whose magnesium content is high and whose density is greater than 2.85. These facts require consideration in the calculation of the average relative abundance of nickel in igneous rocks and in the earth's crust.

METHODS FOR THE SEPARATION AND DETERMINATION OF NICKEL

GENERAL CONSIDERATIONS

A general criticism that may be made of most of the older analyses for nickel in rocks is that the determinations of nickel were incidental. Attention was focussed on the major constituents, which had to be determined anyway; and consequently the methods were seldom or never modified to yield correct results for the minor constituents, though figures were obtained that passed

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[2] Crosse, A. F., A rich nickel ore: Chem. Met. Min. Soc. South Africa Jour., vol. 21, p. 126, 1921.

[3] Emmons, W. H., The enrichment of ore deposits: U. S. Geol. Survey Bull. 625, 1917.

for determinations. The usual procedure was to precipitate the zinc group—including nickel, cobalt, and manganese—with ammonium sulfide after the removal of iron and aluminum. It was not then known that small quantites of nickel tend to be strongly occluded by the ammonium hydroxide precipitate. This source of error, however, has been noted by several analysts.[4] Recently the author, not fully realizing the source of error, found that as many as ten precipitations of a large excess of iron were necessary to extract completely a small quantity of nickel from the precipitate when an excess of ammonia was used as in the usual older method of rock analysis. The material was a sulfide ore containing 0.29 percent of nickel. The conclusion from this series of tests was that many of the older determinations of nickel may be low.

Another source of error has recently been pointed out by Rankama,[5] whose studies show that small percentages of nickel are frequently retained by silica. If the residue left after evaporating silica with hydrofluoric acid is not brought into solution and added to the main filtrate, this nickel will be lost. Somewhat similar behavior in these respects is shown by cobalt, manganese, and zinc, but nickel only will be considered here.

There are several ways of avoiding the difficulties referred to above, although it should be said that in aiming at the nickel some of these methods are not very well adapted to simultaneous determination of the usual major constituents. Some methods are applicable when both aluminum and iron are in large excess over nickel; others are applicable for separating iron only, which is likely to be the main problem in analyzing sulfide ore minerals. In the following discussion of methods it is assumed that silica has been removed and that the bases are present as chlorides, although some of the methods are applicable to sulfate solutions.

BASIC ACETATE METHOD

One method aims at the separation of the trivalent metals as basic acetates. Some time is required to bring the cold solutions exactly to a point where no precipitate persists before the heating and adding of the sodium acetate. Aluminum is not precipitated as completely as iron, but this will not interfere if nickel alone is being sought. The folowing directions are taken for the most part from Hillebrand and Lundell.[6]

Ordinary procedure.—For solutions containing about a gram of metals in 200 ml., add dilute ammonia (1:3) slowly in the cold, stirring constantly until the solution begins to turn red but has not formed a permanent precipitate. Next add in the same way a standard solution of ammonium carbonate until a slight turbidity seems to persist indefinitely, then add 1 or 2 drops of 1:1 hydrochloric acid. Now add boiling water until the volume is about 700 ml., heat to boiling, and add a solution of about 5 grams of sodium acetate in 10 ml. of water and continue boiling for 3 minutes. Filter, as soon as the precipitate has settled, on a paper supported by a cone. Wash moderately with a hot 1:100 solution of sodium acetate. Finally drain the precipitate by suction. One or more reprecipitations should be made until it is certain that no more nickel can be extracted.

Most of the nickel in the filtrates can be separated from the other salts as the sulfide, if desired. Add ammonium sulfide to the solution in a flask, stopper, and allow to stand over night. Filter off the sulfides on a small filter, wash slightly with a 1:50 solution of ammonium chloride containing a little ammonium sulfide, ash in a fairly large porcelain crucible, cool, dissolve in aqua regia, evaporate slowly to avoid loss by spattering, take up in hydrochloric acid, and determine the nickel with dimethylglyoxime as described on page 5.

Brunck-Funk modification.—The procedure of Brunck[7] slightly modified and extended by Funk[8] is claimed to effect a complete separation of iron, at least, from nickel in one precipitation. Considerable aluminum, if it is present, and even some iron may remain with the nickel, but this is of no consequence.

To the metallic chlorides add about three or four times their weight of potassium chloride and evaporate on the steam bath nearly to dryness, stir, and leave the dish on the bath for 5 to 10 minutes longer. Take up the residue with 20 ml. of cold water, add 1.5 parts of sodium acetate crystals for each part of iron, dilute to make a volume of 500 ml. to 1 liter, heat gradually, while stirring, to at least 70° C., let settle, decant, wash and drain the precipitate, and determine the nickel as in the ordinary procedure.

Mittasch procedure.[9]—The procedure used by Mittasch is a slight modification of the ordinary procedure. It differs in that 10 ml. of 2 N acetic acid, instead of 1 or 2 drops of hydrochloric acid, are added before introducing ammonium acetate and heating. After heating add a mixture of 5 ml. of 2 N acetic acid and 10 ml. of N ammonium acetate solution and boil a minute or so. Treat further as described under ordinary procedure.

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[4] Noyes, A. A., and Bray, W. C., A system of qualitative analysis for the rare elements, p. 389, New York, Macmillan Co., 1927. Harwood, H. F., and Theobald, L. T., The determination of small quantities of nickel in rock analysis: Analyst, vol. 58, pp. 673–682, 1933.

[5] Rankama, Kalervo, On the composition of the residue from silica in rock-analysis: Comm. géol. Finlande Bull. 126, pp. 1–35, 1939.

[6] Hillebrand, W. F., and Lundell, G. E. F., Applied inorganic analysis, p. 71, New York, John Wiley & Sons, 1929.

[7] Brunck, O., Jahresberichte der angewandten Chemie und verwandter Gebiete. Fortschritte auf dem Gebiete der Metallanalyse: Chem.-Zeitung, Band 28, p. 514, 1904.

[8] Funk, W., Die Trenung des Eisens von Mangan, Nickel, Kobalt und Zinc durch das Azetatverfahren: Zeitschr. anal. Chemie, Band 45, p. 181, 1906.

[9] Mittasch, Alwin, Ueber die Genauigkeit der Acetatemethode bei der Trennung von Eisen und Mangan: Zeitschr. anal. Chemie, Band 42, p. 492, 1903.

BARIUM CARBONATE METHOD

An old method consists in shaking the solution with a suspension of barium carbonate. The separation of the trivalent metals from manganese is said to be better than their separation from nickel and cobalt.[10] Freshly precipitated barium carbonate is more active than old or dry material. It may be prepared by adding 26 grams of sodium carbonate and 90 grams of barium chloride crystals to about 1 liter of water, shaking, and washing a few times by decantation. Barium carbonate solutions yield a pH of about 7.25, which seems a little high for the separation of nickel. The method has not been studied by the Geological Survey in connection with determining small quantities of nickel.

BLUM'S METHOD

Blum's method [11] was devised for the purpose of satisfactorily separating aluminum, but as no excess of ammonium hydroxide is involved and the precipitation of aluminum hydroxide depends in part on hydrolysis, the method effects a satisfactory separation of both aluminum and iron from nickel.

Add ammonium hydroxide to the boiling acid solution until the methyl red color changes to yellow. Iron precipitates first. At the proper stage the precipitate settles, and the color of a final drop of indicator is easily seen on the surface of the solution. Two precipitations are sufficient to extract all nickel, according to Blum's tests. The precipitated hydroxides are rather bulky and require large funnels if more than 1 gram of material is being analyzed.

ARDAGH-BROUGHALL METHOD

After testing most of the known methods for separating a little nickel from a relatively large proportion of iron, Ardagh and Broughall [12] pointed out the errors likely to arise in other methods and devised a radically different procedure based on precipitation from a concentrated solution and washing of the filtrate with relatively concentrated ammonia and ammonium chloride. Their procedure is as follows:

Evaporate the nickel solution containing hydrochloric acid to a volume of 2 or 3 ml. Add 5 grams of NH_4Cl and stir. Add 10 ml. of concentrated ammonia, break up lumps, add 25 ml. of cold water and filter. Wash back the bulk of the precipitate, using a wash solution containing 10 percent NH_4Cl and 10 percent NH_4OH. Wash six or eight times or until the volume of the filtrate is about 100 ml. in all. Concentrate the nickel in the filtrate by precipitating as sulfide, and allow to stand overnight. Filter, ignite the paper in a porcelain crucible, dissolve the ash in aqua regia, and finally determine the nickel by means of dimethylglyoxime.

Results obtained by the authors of this method are shown in the table below:

Separation of nickel from iron by the method of Ardagh and Broughall

Test	Materials used in mixture tested				Nickel in filtrate (grams)	Error (grams)
	NH_4Cl added (grams)	Concentrated NH_4OH added (milliliters)	Iron taken (grams)	Nickel taken (grams)		
1	10	20	0.1	0.0259	0.0259	0.0000
2	10	20	.1	.0259	.0259	.0000
3	10	20	.5	.0259	.0259	.0000
4	5	10	.5	.0518	.0518	.0000
5	5	10	.5	.0518	.0518	.0000

FAIRCHILD'S METHOD

The method described by Fairchild [13] is applicable to the separation of iron from nickel. It will work fairly well for separating aluminum and also probably will remove titanium and phosphates. Add potassium sulfate to the mixture of sulfates; then ammonia until a precipitate begins to persist in a volume of about 300 ml.; and, finally heat the mixture overnight in a flask immersed in a steam bath. The basic sulfates of iron, aluminum, and potassium are precipitated in a relatively dense form; and they do not carry down nickel to the same extent that the usual ammonium hydroxide precipitate does, if at all. The iron is not entirely precipitated, but this does not interfere with the subsequent determination of nickel. It may be advantageous to perform the hydrolysis in two stages, making the pH about 2.8 (just yellow to thymol blue) for the second stage. The method is especially recommended for the removal of a great excess of iron from a little nickel.

Some results obtained by Fairchild are shown in the table below:

Separation of nickel from iron and aluminum, by J. G. Fairchild

Test	Metallic oxides used in mixture tested (grams)			NiO recovered (grams)	Error (grams)
	Fe_2O_3	Al_2O_3	NiO		
1	0.5000	--------	0.0020	0.0026	+0.0006
2	.7500	--------	.0100	.0096	−.0004
3	.5000	--------	.0200	.0204	+.0004
4	.3000	0.3000	.0020	.0015	−.0005
5	.3000	.3000	.0200	.0202	+.0002

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[10] Hillebrand, W. F., and Lundell, G. E. F., Applied inorganic analysis, p. 74, John Wiley & Sons, New York, 1929.

[11] Blum, William, The determination of aluminum as oxide: Am. Chem. Soc. Jour., vol. 38, pp. 1282–1297, 1916.

[12] Ardagh, E. G. R., and Broughall, G. M., A simple, rapid, and economical method of separating nickel and copper from iron: Canadian Chemistry and Metallurgy, vol. 7, pp. 198–200, 1923.

[13] Fairchild, J. G., Basic sulfates of iron and aluminum in analytical separations: Ind. and Eng. Chemistry, Anal. ed., vol. 13, p. 83, 1941.

ETHER METHOD

Ether free from alcohol dissolves ferric chloride from hydrochloric acid solutions of specific gravity 1.1 to 1.115. No nickel is dissolved by ether unless the nickel concentration is high, which is not the case under consideration in this investigation. This method of separating iron, however, is rather tedious; it requires special apparatus; and it still leaves aluminum, if present, with the nickel. It may be useful in some circumstances. Details in regard to metals that do or do not accompany iron in the extraction are given by Hillebrand and Lundell,[14] and they need not be repeated here.

DIMETHYLGLYOXIME METHOD

The solution should not contain more than 0.03 gram of nickel. Palladium is the principal metal that may interfere in this method, but it is seldom present. Metals of the hydrogen sulfide group, if present in considerable quantity, should be removed before precipitating the nickel. Oxidize iron to the trivalent state. Add three or four times as much ammonium tartrate as the weight of trivalent salts present and enough ammonium chloride to hold bivalent metals in solution when it is made ammoniacal. Heat to 60° or 80° C. For every 0.01 gram of nickel present add 5 ml. of a filtered 1 percent solution of dimethyglyoxime in alcohol. An even larger amount of the dimethylglyoxime solution may be needed for a small quantity of nickel. Then add ammonia until a faintly alkaline reaction is obtained. Digest on the steam bath for several hours. If the quantity of nickel is very small, it may be necessary to wait several days for the nickel to precipitate. In a volume of 100 ml. or less, 0.1 mg. of nickel should show up definitely, an amount equal to 0.002 percent in a 5-gram sample of rock. If the nickel is concentrated by some means into a small volume so that the final test can be made in 1 or 2 ml., 0.01 mg. of nickel is easily recognizable qualitatively by the dimethylglyoxime test. Filter on a Gooch or glass filter, dry at 110°–120° C. for 45 minutes, cool, and weigh. The precipitate contains 20.31 percent of nickel. This appears to be the best method for determining moderate percentages of nickel, and it is also applicable for as little as a few hundreds of 1 percent if from 2- to 10-gram portions of sample are used. For very small quantities of nickel, the colorimetric method of Rollet described in the next section is preferable.

ROLLET'S METHOD

The colorimetric method devised by Rollet[15] is a very sensitive test for small quantities of nickel and is based on the fact that after oxidation an alkaline solution containing nickel dimethylglyoxime turns pink or red in proportion to the quantity of nickel. The simplest procedure is to add about 5 drops of bromine water to a hydrochloric acid solution containing the nickel, then 3 or 4 drops excess of ammonia after the color of the bromine disappears, then about 10 drops of a 1 percent solution of dimethylglyoxime in alcohol. A series of standard colors should be made up at the same time for comparison. A distinct color is produced by 0.001 mg. of nickel in 1 ml.

SANDELL-PERLICH METHOD

The method described by Sandell and Perlich[16] involves the extraction of nickel dimethylglyoxime by means of chloroform from an ammoniacal citrate solution of the rock sample. By shaking the chloroform extract with dilute hydrochloric acid, the dimethylglyoxime compound is decomposed and the nickel is brought into the aqueous phase in which it is then determined by Rollet's method. Their procedure, results, and comments are as follows:

> Weigh 0.25 gram of finely powdered basic rock (0.01 to 0.05 percent nickel), or 0.5 gram or more of acidic rock, into a platinum dish, add a few milliliters of water, 0.5 ml. of 70 percent perchloric acid, and 2.5 ml. of hydrofluoric acid (for a sample greater than 0.25 gram these amounts should be correspondingly increased). Evaporate the mixture to dryness, take up the residue in 0.5 ml. of perchloric acid and 2 or 3 ml. of water, and again evaporate to dryness. To the residue add 0.5 to 1 ml. of concentrated hydrochloric acid and 5 ml. of water. Heat to bring all soluble material into solution, add 5 ml. of 10 percent sodium citrate solution, neutralize the cold solution with concentrated ammonium hydroxide using litmus paper, and add a few drops in excess. If there is an appreciable amount of precipitate or residue in the solution at this point, filter through a small paper, wash with small portions of water, and ignite the paper and its contents. Fuse the residue with approximately 0.1 gram of sodium carbonate, add an excess of dilute hydrochloric acid to the cooled melt, and heat to effect as complete solution as possible. Add 2 or 3 ml. of 10 percent sodium citrate solution, make slightly ammoniacal, and reserve the solution.
>
> To the main solution (filtrate from any insoluble material) add 2 ml. of 1 percent alcoholic dimethylglyoxime solution, and shake vigorously for one-half minute with two or three portions of reagent-quality chloroform, each having a volume of 2 or 3 ml. In a similar manner extract the ammoniacal solution of the sodium carbonate melt. Combine all the chloroform extracts and shake vigorously with 10 ml. of 1 to 50 ammonium hydroxide solution. Draw off the chloroform, taking care that no drops of the aqueous phase accompany it, and shake the water layer with a milliliter or two of chloroform to recover any suspended drops of chloroform solution.
>
> Shake the chloroform solution of nickel dimethylglyoxime vigorously for 1 minute, with two portions of 0.5 N hydrochloric acid, each having a volume of 5 ml. (or slightly less if the solution is finally to be made up to 10 ml.). Transfer the hydrochloric acid solutions to a volumetric flask of suitable size or a flat-bot-

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[14] Hillebrand, W. F., and Lundell, G. E. F., Applied inorganic analysis, p. 106, New York, John Wiley & Sons, 1929.

[15] Rollet, A. P., Sur un nouveau dosage colorimétrique du nickel: Acad. Sci. Paris Comptes rendus, tome 183, pp. 212–213, 1926.

[16] Sandell, E. B.; and Perlich, R. W., Determination of nickel and cobalt in silicate rocks: Ind. and Eng. Chemistry, Anal. ed., vol. 11, pp. 309–311, 1939.

tomed color comparison tube (1.8×15 cm.), taking care that no appreciable amount of chloroform is carried over. For color comparison in a colorimeter the nickel concentration of the final solution should be at least 1 microgram per ml. For most acidic rocks the standard series method of color comparison will usually have to be applied because of low nickel content. A suitable series of standards for a silicic rock is 0, 1, 2 . . . 10 micrograms of nickel for a 0.5-gram sample. Whether a colorimeter or tubes are used, the final nickel concentration should not exceed 5 micrograms per ml. or else a precipitate of nickel dimethylglyoxime may be produced.

The unknown nickel solution and the standard solution diluted to about 10 ml. with 0.5 N hydrochloric acid are treated simultaneously as follows: Add 5 drops of freshly prepared saturated bromine water, mix, and then add concentrated ammonium hydroxide dropwise with shaking until the color of bromine disappears; finally add an excess of 3 or 4 drops. Next add 0.5 ml. of 1 percent alcoholic dimethylglyoxime solution, mix, and dilute to volume with water if a volumetric flask is used. The color intensity of the solutions increases slowly on standing; the unknown and standard solution should therefore be treated with the reagents at the same time.

If necessary apply a correction for nickel in the reagents.

Determination of nickel

No.	Sample	Addition (percent)	Ni taken [a] (percent)	Ni found (percent)	Error (percent)
1	Extracted [b] solution of granite.		0.0003	0.0003	0.0000
2	Synthetic basic rock		.0020	.0018	−.0002
3	Extracted solution of synthetic basic rock.		.0020	.0019	−.0001
4	Synthetic basic rock		.0060	.0060	.0000
5	do		.011	.011	.000
6	do		.021	.020	−.001
7	do		.042	.041	−.001
8	do	0.04 Co	.0030	.0028	−.0002
9	do	0.03 Cu	.010	.010	.000
10	do	0.1 Cu, .05 Co	.009	.010	+.001
11	do	1.0 Mn	.011	.011	.000
12	do	0.2 Cr ^{VI}, .05 V ^{V}	.020	.020	.000

[a] Includes nickel originally present in synthetic basic rock (0.0010 percent).

[b] Solution of sample extracted with chloroform after addition of dimethylglyoxime to remove nickel originally present, and nickel then added to extracted solution.

The results obtained by applying the foregoing directions are given in the table. One-fourth gram samples were used and the color comparison was made in a Duboscq colorimeter when the nickel content was 0.005 percent or greater. The sensitivity of the method is great enough to allow the detection of less than 0.0001 percent of nickel when a 0.5-gram sample is taken.

Copper, cobalt, manganese, chromium, and vanadium in the amounts that are likely to be encountered in most igneous rocks do not interfere. It may be expected that much copper and cobalt will lead to high results. One hundred micrograms of cobalt carried through the procedure gave a color corresponding to about 1.5 micrograms of nickel, and 100 micrograms of copper gave no color. Manganese in large quantities may cause trouble by oxidizing nickel to the nickelic condition in the ammoniacal solution during shaking, and the results for nickel will then be low, because nickelic dimethylglyoxime is not extracted by chloroform.

Under the conditions specified above for the final determination of nickel, Beer's law is closely followed up to a concentration of about 6 micrograms of nickel per milliliter. Above this concentration a precipitate may separate.

The solubility of nickel dimethylglyoxime in chloroform at room temperature corresponds to approximately 50 micrograms of nickel per milliliter.

The only minerals not easily brought into solution, in the writer's experience with this method, were sillimanite and manganese oxides.

ELECTROLYTIC METHOD

Although nickel in a pure salt—for example, nickel sulfate—is easily precipitated completely by electrolysis in solutions containing ammonium sulfate, ammonium hydroxide, or ammonium acetate, its electrolytic separation from other metals is not generally feasible; and preliminary separations by other methods are necessary. In solutions containing considerable nickel but no other metals, very accurate electrolytic determinations of nickel are possible. The methods described previously are generally necessary or suitable for rocks and minerals in which nickel is generally a minor constituent; and, except in very rare instances, they are sufficiently accurate for such materials.

NICKEL CONTENT OF DIFFERENT ROCKS AND MINERALS

The chemical laboratory of the Geological Survey is fortunate in having on file small samples of many rocks that have been studied petrographically and analyzed chemically by its staff. A wide range of rock types and an extensive geographical distribution are represented in these samples, thereby affording an excellent opportunity to make new or original determinations of nickel in a great variety of rocks. Only small portions were needed for the determination of nickel. Practically all the new determinations were made by the Sandell-Perlich method. The densities of the rocks were also determined from these samples, without loss of material. The descriptions of the rocks give citations to the complete analyses in Geological Survey Bulletins 591 [17] and 878.[18]

The densities given in this paper were determined by the Jolly balance if lumps were available, unless the specimen had a visible porosity. For such porous specimens and also for about half the samples for which only crushed material was available, the density was determined in a pycnometer on the powder. There was generally very little difference between the densities determined in the two ways.

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[17] Clarke, F. W., Analyses of rocks and minerals from the laboratory of the United States Geological Survey, 1880 to 1914: U. S. Geol. Survey Bull. 591, 1915.

[18] Wells, R. C., Analyses of rocks and minerals from the laboratory of the United States Geological Survey, 1914–36: U. S. Geol. Survey Bull. 878, 1937.

IGNEOUS ROCKS

RHYOLITE

Washington,[19] in Geological Survey Professional Paper 99, gives 21 analyses of rhyolite in which nickel is mentioned. Of these, 14 analyses record "none" for NiO; 3 others show 0.10, 0.04, and 0.03 percent, respectively; 2 contain 0.01 percent; and the average is 0.009 percent. It may be said at this point that the word "none" in an analysis is just about as unsatisfactory as the word "trace." Ordinarily it probably means not more than 0.01 percent, but the nickel content may be anything less than that.

The following are new determinations of nickel in rhyolite:

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Boundary Cone, Oatman district, Ariz. (Bull. 878, p. 10, R)	3,000	2.45	0.0026
2	Piedra rhyolite, Bennett Creek, San Christobal quadrangle, Colo. (Bull. 878, p. 18, G-2)	11,000	2.42	.0024

In view of these results it seems fair to conclude that the average NiO content of rhyolite is about 0.002 percent, a figure considerably less than Washington's average. But if his one high result is excluded, his mean becomes 0.004 percent.

GRANITE

The determinations of nickel in granite reported by Washington resemble those for rhyolite in that 46 out of 57 analyses specify "none" for NiO. Among the analyses listing NiO, three specimens are reported to contain 0.23, 0.15, and 0.03 percent respectively, and two specimens to contain 0.02 percent. The figure 0.23 appears to be exceptional; and if that result is excluded, the average falls from 0.009 to 0.005 percent. These figures are about the same as those for rhyolite.

New tests for nickel were made in granite from the following localities:

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Rockport, Mass. (Bull. 878, p. 29, E)	20-40	2.63	0.0025
2	Idaho batholith, Mayfield Creek, Casto quadrangle, Idaho. (Bull. 878, p. 26, B)	5,800	2.65	.0017

The average for granite is 0.002 percent of NiO, about the same as for rhyolite and less than the older figure.

DACITE

Washington, in 14 analyses of dacite reported no nickel in 9, 0.06 in 2, and 0.08, 0.03, and 0.02 percent of NiO in 3 others—an average of 0.017 percent. The average MgO content is 1.37 percent.

Three new determinations of nickel in dacite gave the following results:

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Mount Lassen, eruption of May 22, 1916. (Bull. 878, p. 12, E)	10,000	2.62	0.0095
2	5 miles northwest of Riddle, Oreg. (Bull. 591, p. 198, C)	2,500	2.70	.0008
3	Silver Peak Range, Esmeralda County, Nev. (Bull. 591, p. 163, E)	5,500	2.42	.0002

The dacite of the Mount Lassen eruption is distinctly higher in nickel than specimens from the other two localities and may represent material from greater depth. However, the average of the three new determinations, 0.0035 percent of NiO, is considerably lower than Washington's average and probably of the right order.

GRANODIORITE

Washington, in listing 12 analyses of granodiorite, reported no NiO in 7, a trace in 3, and 0.20 and 0.19 percent in 2—an average of 0.033 percent. The two high figures, both by Melville, are so exceptional that they must be discarded, leaving an average of "trace."

New determinations are as follows:

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	1¼ miles west of Haystack Mountain, Livingston quadrangle, Montana. (Bull. 591, p. 110, A)	9,000	2.69	0.0095
2	East fork of Rock Creek, Anaconda Range, Mont. (Bull. 591, p. 111, B)	9,000	2.68	.0027
3	Silver Wreath mine, Boise County, Idaho. (Bull. 591, p. 115, J)	3,000	2.71	.0012
4	About 5 miles north of Yellow Pine, Valley County, Idaho. (Bull. 878, p. 27, E)	7,000	2.71	.0011
5	Near Silver Lake, Eldorado County, Calif. (Bull. 591, p. 183, B)	7,300	2.70	.0017
6	Paradise Range, Nev., near brucite deposit. (Bull. 878, p. 32, J)	5,800	2.70	.0070

These results average 0.0039 percent of NiO, which differs appreciably from the average of the older determinations. The individual results, however, are more nearly of the same order, a "trace."

TRACHYTE

The average NiO content for 16 analyses of trachyte reported by Washington is 0.018 percent, including 7 with "none." The average of 5 new determinations given in the following table is considerably lower, only 0.0039 percent.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Goldroad mine, 1¼ miles east of Mohave, Ariz. (Bull. 591, p. 157 K)	2,500	2.55	0.0053
2	Same locality as No. 1. (Bull. 591, p. 157 L)	2,500	2.63	.0086
3	Near Lahaina, Maui. (Bull. 591, p. 211, G, or P. P. 88, p. 27)	100	2.87	.0018
4	Gold Mountain, Humboldt Range, Rochester district, Nevada. (Bull. 878, p. 31 C)	6,000	2.63	.0008
5	Deep Creek, Gold Hill quadrangle, Utah. (Bull. 878, p 40, D-2)	5,400	2.51	.0032

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[19] Washington, H. S., Chemical analyses of igneous rocks published from 1884 to 1913, inclusive, with a critical discussion of the character and use of analyses: U. S. Geol. Survey Prof. Paper 99, 1917.

SYENITE

Washington's average for the NiO content of syenite is 0.024; and for the MgO content, 1.20 percent. The following determinations are new:

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Hueco Tanks, El Paso County. Tex. (Bull. 591, p. 60, V)	4,500	2.46	0.0014
2	Northwest of Gem, Idaho. (Bull. 591, p. 115, O)	4,000	2.75	.0016
3	Burkettville, Knox County, Maine. (Bull. 591, p. 26, B)	300	2.88	.058
4	South side of Clear Creek, near Soda Creek, Idaho Springs, Colo. (Bull. 591, p. 127, A)	8,000	2.65	.0019
5	Near Merriman mine, 3 miles east of Organ, N. Mex. (Bull. 591, p. 151, F)	5,300	2.69	.0029

The average of NiO in these five samples of syenite is 0.0132 percent. The rock from Burkettville, Maine, however, seems to be exceptionally high in nickel; and if it is excluded, the average falls to 0.0020 percent, a much lower figure than Washington's. The norm of the rock from Maine shows some olivine. This rock comes from a low altitude; and, considering erosion, it may represent material from even a lower altitude than its present position.

LATITE

In 10 analyses of latite, Washington reported no NiO in 6, a trace in 2, and 0.06 and 0.04 percent, respectively, in the remaining 2—an average of 0.01 percent, but a wide spread. The rock with 0.06 percent was from Victoria and contained 4.03 percent of MgO and had olivine in the norm.

New determinations are tabulated below:

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Portland mine, Cripple Creek district, Colorado. (Bull. 591, p. 121, S)	7,000	2.60	0.013
2	Southeast of Devil's Lake, Cannibal Plateau, Uncompahgre quadrangle, Colorado. (Bull. 591, p. 134, A–2)	12,000	2.77	.0005
3	Same locality as No. 2. (Bull. 591, p. 134, B–2)	12,000	2.75	.0042
4	Nellie Creek, Lake City quadrangle, Colorado. (Bull. 591, p. 135, C)	10,000	2.69	.0015
5	Near head of Middle Fork of Cimarron Creek, Ouray quadrangle, Colorado. (Bull. 591, p. 136, A)	11,500	2.65	.0012
6	East slope of Trout Creek, San Cristobal quadrangle, Colorado. (Bull. 591, p. 139, I)	10,000	2.45	.0013
7	Superior mine, Bonanza district, Colorado. (Bull. 878, p. 13, B–3)	11,000	2.69	.0021
8	East slope of Caldwell Mountain, Conejos quadrangle, Colorado. (Bull. 878, p. 15, E)	10,500	2.59	.0006
9	Head of Willow Creek, eastern part of Creede quadrangle, Colorado. (Bull. 878, p. 16, H)	8,800	2.68	.0015
10	Bear Creek in northwestern part of Del Norde quadrangle. Colorado. (Bull. 878, p. 17, D)	10,500	2.48	.0004
11	South side of Saguache Creek, Saguache quadrangle, Colorado. (Bull. 878, p. 18)	8,400	2.58	.0012

The average of the 11 new determinations of NiO in latite is 0.0025 percent. Excluding the first, which is exceptionally high, the average is 0.0014 percent. Neither of these figures differs much from the average of the other rocks so far considered.

MONZONITE

Out of 14 analyses of monzonite, Washington reported no NiO in 5, a trace in 6, and 0.09, 0.10, and 0.07 percent, respectively in 3—an average of 0.019 percent. The rock containing 0.07 percent was from Scotland and had 12.48 percent MgO, olivine being in the norm.

New determinations were made on the following specimens:

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	About 4 miles west of Nederland, Colorado. (Prof. Paper 94 and Bull. 591, p. 126, C–2)	10,300	2.78	0.0014
2	Near Reipetown, Nev. (Bull. 591, p. 161, A–2)	7,000	2.80	.0006
3	Dike half a mile northeast of Tungsten, Nederland district, Colorado. (Bull. 878, p. 18, I)	8,000	2.71	.0014
4	Lower tunnel of Yellowstone Pine mine, 1 mile east of Wall Street, Colo. (Bull. 878, p. 23, N)	7,000	2.71	.0004
5	1 mile north of Kelly, Magdalena district, New Mexico. (Bull. 878, p. 36)	7,500	2.82	.0089

The average for the five samples of monzonite tested is 0.0025 percent of NiO, a figure essentially the same as that found for latite.

ANDESITE

In the 45 analyses of andesite listed by Washington, NiO is reported as "none" in 26 and as "trace" in 8; and the average of all is 0.0076 percent of NiO. The highest figure is 0.07 percent in andesitic ash from St. Vincent, West Indies. This rock, however, may represent material from a low altitude that should be high in nickel.

The following are new determinations:

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Ridge west of east fork of Woodfern Creek, San Cristobal quadrangle, Colorado. (Bull. 591, p. 139, J)	11,000	2.72	0.0014
2	Hill northwest of Vindicator Mountain, Goldfield district, Nevada. (Bull. 591, p. 159, B)	5,900	2.46	.0010
3	Naches Valley, near Sand Creek, Snoqualmie quadrangle, Washington. (Bull. 591, p. 204, B)	3,100	2.57	.0011
4	Ravine south of Kaupo Gap, crater of Haleakala, Maui. (Bull. 591, p. 211, H)	1,000	2.88	.0006
5	From central plateau, east of Hat Mountain, Lassen National Park, Calif. (Bull. 878, p. 12, K)	7,000	2.70	.0031
6	North of the Saguache River, near head of Spanish Creek, Cochetopa quadrangle, Colorado. (Bull. 878, p. 14, A–2)	11,000	2.69	.0016
7	Carnero Canyon, Del Norte quadrangle, Colorado. (Bull. 878, p. 20, A)	8,000	2.78	.0042
8	Upper floor on north slope of Santa Clara Canyon, Abiquiu quadrangle, New Mexico. (Bull. 878, p. 33, A)	10,000	2.82	.0117
9	Point Farfan, across the Canal from Balboa, Panama. (Bull. 878, p. 39, E)	100	2.57	.0013
10	Boring in Bermuda. (Bull. 878, p. 11)	−910	2.99	.013

The average of the 10 determinations is 0.0039 percent of NiO, a figure appreciably less than Washington's average for andesite.

DIORITE

In 48 analyses of diorite in which nickel was determined, Washington reported "none" in 15. The highest figure is 0.09 percent of NiO, which was found by W. H. Melville in a sample from Electric Peak, Yellowstone National Park; and the average of all is 0.017 percent of NiO.

In the following 11 new determinations of nickel in diorite the average is only 0.0022 percent of NiO.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Burra Burra mine, Ducktown, Tenn. (Bull. 591, p. 54, A-2)	1,700	2.78	0.0013
2	North of Haystack Mountain, between Blue and Mud Lakes, Mont. (Bull. 591, p. 111, G)	8,000	2.84	.0069
3	Quarry half a mile southwest of Cable mine, Philipsburg quadrangle, Montana. (Bull. 591, p. 111, C)	7,000	2.80	.0005
4	Wellington mine, Breckenridge district, Colo. (Bull. 591, p. 128, E)	10,000	2.83	.0008
5	East side of Trout Creek, San Cristobal quadrangle, Colorado. (Bull. 591, p. 140, N)	10,000	2.84	.0019
6	2 miles north of Kelvin, Ray district, Arizona. (Bull. 591, p. 153, D)	2,000	3.02	.0006
7	Minnesota mine, Shasta County, Calif. (Bull. 591, p. 169, L)	1,500	2.87	.0008
8	Jumbo Basin, Copper Mountain, Prince of Wales Island, Alaska. (Bull. 591, p. 207, A-2)	1,700	2.76	.0006
9	Cocovi Island, Bay of Panama. (Bull. 591, p. 214, O)	20	2.52	.0008
10	Southeast of Buckle Lake, Summitville quadrangle, Colorado. (Bull. 878, p 20, C)	10,500	2.78	.0075
11	Sec. 9, T. 8 S., R. 43 E., Baker County, Oreg. (Bull. 878, p. 37, H)	3,900	2.85	.0027

PHONOLITE

In 11 analyses of phonolite, Washington reported no nickel in 5, a trace in 2, 0.04 percent of NiO in 3, and 0.05 percent in 1—an average of 0.015 percent of NiO.

Only one sample was available for a new determination.

Locality	Altitude (feet)	Specific gravity	NiO (percent)
Mine Creek, 4 miles north of Nashville, Tenn. (Bull. 878, p. 11, A)	500	2.96	0.0010

SHONKINITE

Washington reported nickel in several analyses of shonkinite. With these the writer has grouped a number of analyses of rocks closely related to shonkinite in chemical composition, although they were classified by Washington under other or unusual names, making altogether a group of 28. Washington reported no NiO in only 6 analyses, a trace in 10, and from 0.01 to 0.07 percent in the remainder—an average of 0.016 percent.

The three new determinations for shonkinite tabulated below give an average 0.028 percent of NiO.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Walsen dike, at intersection with Walsenburg-Gardner road, Walsenburg quadrangle, Colorado. (Bull. 878, p. 19, B-2)	6,250	2.86	0.028
2	Dike near Walsenburg-La Veta road, Colorado. (Bull. 878, p. 19, C-2)	6,500	2.87	.019
3	Wildcat Gulch, Uncompahgre quadrangle, Colorado. (Bull. 878, p. 21, G)	8,100	2.97	.038

BASALT

Washington reported on nickel in 182 analyses of basalt. Two of these, 0.75 and 0.41 percent of NiO, probably represent segregations, but they serve to offset 41 specimens reported as containing "none" and 27 reported as having a "trace," giving an average for all of 0.039 percent of NiO.

The 21 new determinations tabulated below give an average of 0.037 percent NiO.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	8 miles east-northeast of North Rattlesnake Butte, Apishapa quadrangle, Colorado. (Bull. 591, p. 123, D)	5,700	3.04	0.042
2	Top of Breeze Mountain, 4 miles southeast of Craig, Colo. (Bull. 878, p. 22, H)	6,990	2.82	.035
3	South rim of Barilla Mesa, Colfax County, N. Mex. (Bull. 591, p. 150, J)	8,450	2.80	.016
4	Headwaters of Little Ash Creek, Bradshaw Mountains quadrangle, Arizona. (Bull. 591, p. 155, C)	4,500	2.93	.011
5	6 miles north of Silver Peak, Nev. (Bull. 591, p. 163, G)	4,900	2.76	.018
6	1½ miles from Franklin Hill, Plumas County, Calif. (Bull. 591, p. 177, M)	5,000	2.93	.011
7	West peak of the Dardanelles, Alpine County, Calif. (Bull. 591, p. 195, H)	8,000	2.81	.021
8	2 miles south-southeast of Naches Pass, Snoqualmie quadrangle, Washington. (Bull. 591, p. 204, D)	4,500	2.99	.042
9	Rim of caldera of Kilauea, Hawaii. (Bull. 591, p. 212, K)	3,600	3.09	.053
10	East branch of Makaweli Canyon, Kauai. (Bull. 591, p. 212, L)	1,400	3.15	.140
11	Post-Pahala basalt, pahoehoe on floor of Makanao Valley, at southwest end of Pakua graben fault, Hawaii. (Bull. 878, p. 25, A)	1,400	3.17	.174
12	Mauna Loa aa flow, cut on Government road at south boundary of Waiakea National Forest. (Bull. 878, p. 25, E)	290	[a] 3.09	.049
13	Reservoir at Piihonua, Mauna Loa pahoehoe flow. (Bull. 878, p. 25, F)	900	[a] 3.05	.013
14	National Park quarry on Hilo road 1 mile from observatory, Kilauea pahoehoe flow. (Bull. 878, p. 25, G)	4,000	[a] 3.05	.015
15	Halemaumau, splash from lava lake, 1917. (Bull. 878, p. 25, H)	3,600	[a] 2.85	.016
16	Halemaumau, splash from lava lake, 1919. (Bull. 878, p. 25, I)	3,600	[a] 3.05	.015
17	Halemaumau, pahoehoe from northeast edge of floor of Kalauea Crater, 1919. (Bull. 878, p. 25, J)	3,600	[a] 2.90	.014
18	Halemaumau, pahoehoe from south edge of floor of Kilauea Crater, 1919. (Bull. 878, p. 25, K)	3,600	[a] 3.06	.021
19	Flow, sec. 24, T. 25 S., R. 4 W., Douglas County, Oreg. (Bull. 878, p. 38, D)	1,300	2.89	[b] .015
20	Younger basalt from Cupola Rock, 10 miles west of Three Sisters Mountains, Oreg. (Bull. 878, p. 38, G)	3,000	2.86	.015
21	Border facies, Stillwater complex, Mont. (Supplied by H. H. Hess; laboratory No. D-1019)	[c] 7,500	3.04	.039

[a] Determination by J. G. Fairchild.

[b] Determination by F. S. Grimaldi.

[c] Geologic evidence suggests that this rock was emplaced at considerable depth, at least 10,000 feet below sea level; hence the altitude might be considered to be −17,000 feet.

DIABASE

The average of 29 determinations reported by Washington is 0.061 percent of NiO; but one relatively high determination, 0.73, is from an exceptional dike in Victoria County, Ontario. Excluding this figure the average for 28 analyses of diabase reported by Washington is 0.037 percent of NiO, a result of the same order as that for basalt.

Only six samples of diabase were available for new determinations of nickel. The individual results are is 0.020.
given below, and the average percentage of NiO found

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Greenstone Cliff, Keweenaw Point, Mich. (Bull. 591, p. 64, A)	620	2.96	0.028
2	"Ashbed" diabase, bed 65, Eagle River section, Keweenaw Point, Mich. (Bull. 591, p. 64, B)	620	2.93	.0090
3	Dike, sec. 29, T. 25 S., R. 4 W., Douglas County, Oreg. (Bull. 878, p. 38, C)	1,000	2.97	.012
4	Analcite diabase, forming part of 80-foot sill, just north from Starvation Wash, T. 26 S., R. 6 E., Emery County, Utah. (Bull. 878, p. 41, A)	6,000	2.92	.034
5	Palisade sill, 700 feet above lower contact, Hudson River, N. J. (Walker, Geol. Soc. America Bull., vol. 51, p. 1080, 1940)	700	2.91	.0038
6	Palisade sill, olivine layer, 60 feet above lower contact. (Laboratory No. D-1624)	60	3.15	.036

GABBRO

New determinations of nickel in gabbro are given in the table below:

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	1 mile east of Preston post office, Connecticut. (Bull. 591, p. 38, K)	250	[a]2.98	[b]0.011
2	Elkhorn mining district, Montana. (Bull. 591, p. 109, H)	6,500	3.05	[b].0022
3	Half a mile northeast of Haystack Mountain, Mont. (Bull. 591, p. 110, D)	10,000	[a]2.98	[b].013
4	Central City quadrangle, Colorado. (Bull. 591, p. 127, D)	9,000	[a]3.06	[b].0049
5	Uncompahgre quadrangle, Colorado. (Bull. 591, p. 134, D-2)	9,000	[a]2.70	.0049
6	Waiale Canyon, near Waimea Canyon, Kauai. (Bull. 591, p. 212, M)	1,200	3.03	.0042
7	Mount McKensie, north of Los Cerillos, N. Mex. (Bull. 591, p. 151, C)	6,500	[a]2.88	.0026
8	Top of Whiteface Mountain, Adirondacks, N. Y. (Bull. 591, p. 38, B)	4,500	2.81	.0018
9	300 feet N. 10° E. of southwest corner Glasgow claim, Profile Gap, Edwardsburg district, Idaho. (Bull. 878, p. 27, D)	7,000	[a]2.75	.0036
10	Duluth, Minn. (Laboratory No. D-1010)	650	3.05	[c].032

[a] Determination by J. M. Axelrod.
[b] Determination by F. S. Grimaldi.
[c] Determination by E. B. Sandell. Personal communication.

The average of the 10 new determinations of NiO in gabbro is only 0.0080 percent, which is much lower than that found in basalt and diabase. It is also much lower than the average, 0.041 percent, of 61 analyses reported by Washington, who gives 36 results ranging from 0.01 to 0.27 percent and 25 containing a "trace" or "none." The differences between the old and the new determinations are comparable to those found in the analyses of diorite. These differences are attributed to the rocks themselves, rather than to any errors in analysis. Most of the rocks analyzed in this study are from the United States, whereas those reported by Washington include rocks from many foreign countries. As samples of foreign rocks were not available, a more comprehensive survey will have to be left for future investigations. It seems probable, however, that the average NiO content in gabbro should be higher than 0.008, though not so high as 0.041 percent—possibly about 0.02. A change in the nickel content of this rock alone would have very little effect on the final figures for relative abundance of nickel, as computed in this paper. According to Daly, gabbro is not an abundant rock. The calculation based on density, given on page 14, includes the full effect of rocks of higher density.

PYROXENITE

Determinations of nickel are reported by Washington in 10 samples of pyroxenite, the average being 0.10 percent of NiO. The 5 new determinations reported below yield an average of only 0.023 percent of NiO.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Prospect Hill, west of Litchfield, Conn. (Bull. 591, p. 37, G)	1,200	3.21	0.011
2	⅓ mile south of Honeybrook, Pa. (Bull. 591, p. 45, S)	700	3.11	.047
3	2 miles north of Libby, Mont. (Bull. 591, p. 113, D)	2,500	3.42	.0068
4	Central City quadrangle, Colorado. (Bull. 591, p. 127, E)	10,300	3.28	.011
5	Same locality as No. 4. (Bull. 591, p. 127, G)	10,200	3.56	.038

PERIDOTITE

Washington reports nickel in 47 analyses of peridotite, which average 0.11 percent of NiO. Two new determinations were made by the writer, the average content of NiO being 0.061 percent.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Stony Point, N. Y. (Bull. 591, p. 41, 1)	100	3.22	0.066
2	Yosemite National Park. (Bull. 591, p. 189, 1)	5,000	3.12	.056

In Kimberlite from South Africa (laboratory No. D-1343) 0.095 percent of NiO was found, and in kimberlite from Murfreesboro, Ark. (laboratory No. D-1345), 0.078 percent.

SEDIMENTARY ROCKS

SANDSTONE

The following new determinations of nickel in sandstone yield an average of 0.0013 percent of NiO, which, on account of the relative minor importance of sandstone, is sufficient for the present purpose. It is evident that nickel has no marked tendency to accumulate in sandstone.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Boscobel, Wis. (Bull. 591, p. 218, C-2)	1,000	2.66	0.0019
2	Red clayey sandstone, east of Spearfish, S. Dak. (Bull. 591, p. 267, B)	4,000	2.71	None
3	Tuscaloosa formation, Russellville district, Alabama. (Bull. 878, p. 65, B)	800	2.67	.0020

SHALE AND CLAY

The average of the following 12 new determinations of NiO in shale and clay is 0.0089 percent, a figure of the same order as the average percentages of NiO in inorganic rocks. This is about what it should be, as shale and clay are the main weathering products of igneous rock, and the percentage of nickel in sandstone and limestone is very small.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Shale, Hermosa, N. Mex. (Bull. 591, p. 256, B)	5,000	2.63	0.0111
2	Diatomaceous shale near Hollywood Country Club. (Bull. 878, p. 63, A-2)	500	2.16	.0074
3	Composite sample of 10 Miocene siliceous shales, southern California. (Bull. 878, p. 63, D)	500	2.23	.0039
4	Composite of 235 samples of river silt, delta of the Mississippi River. (Bull. 591, p. 264)	0	2.58	.0045
5	Composite of 52 samples of terrigenous clay collected on the *Challenger*. (Bull. 591, p. 271, C-2)	−1,000	2.51	.0070
6	Oceanic red clay, composite of 51 *Challenger* samples	−15,000	2.56	.028
7	Swedish kolm. (Bull. 878, p. 64, A-3)	--------	1.76	.020
8	Red glacial till, Oshkosh, Wis. (Bull. 591, p. 266, H)	750	2.58	.011
9	Bentonite, Bighorn Basin, Wyo. (Bull. 591, p. 267, E)	5,000	--------	.0016
10	Hot Springs district, Arkansas (Bull. 591, p. 267, M)	500	2.70	.0031
11	Bauxitic clay, sec. 18, T. 2 S., R. 13 W., Saline County, Ark. (Bull. 878, p. 65, B-2)	500	2.59	.0011
12	Clay residue from limestone, Iowa. (Bull. 878, p. 67)	800	2.65	.0085

A sample of clay material derived from nickeliferous vermiculite collected at Webster, N. C., by C. S. Ross, of the Geological Survey, was found by the writer to contain 11.3 percent of NiO. This is, of course, an unusually large percentage of nickel and is explained by the association of the clay with nickel ores.

LIMESTONE

Only two determinations of nickel in limestone were made, but of these one sample was a composite of 19 separate samples from 18 States and 1 foreign country. The average NiO content is 0.0010 percent.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Bore hole at Key West, Fla. (Bull. 591, p. 229, M-2)	−2,000	2.69	0.0009
2	Composite of 19 samples from 18 States and 1 foreign country	--------	2.75	.0011

METAMORPHIC ROCKS

GNEISS

The first 6 samples of gneiss (one a composite of 33) all proved to be relatively low in nickel, containing an average of only 0.0015 percent of NiO. The seventh, which came from a nickeliferous district but not from the mine itself, is much higher in NiO and suggests a different kind of gneiss.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Composite Becket gneiss from 33 localities in the Sheffield quadrange, Massachusetts (Bull. 591, p. 34, I)	2,000	2.72	0.0012
2	Pochuck gneiss, Greenwood Lake quadrangle, New Jersey (Bull. 591, p. 42, E)	600	3.20	.0025
3	Byram gneiss, 1 mile west of Hibernia, N. J. (Bull. 591, p. 42, F)	900	2.63	.0005
4	Baltimore gneiss, East Branch of the Brandywine, 2 miles north of Downingtown, Pa. (Bull. 591, p. 44, M)	400	2.65	.0004
5	Marquette region, Michigan. NW¼ sec. 35, T. 47 N., R. 26 W. (Bull. 591, p. 62, I)	1,300	2.70	.0010
6	Gneissic pre-Cambrian quartz monzonite, Coldspring tungsten mine, fifth level, 3 miles northeast of Nederland, Colo	7,500	2.67	.0034
7	Hornblende gneiss, Key West nickel area, Nev. (Collected by Ward C. Smith)	4,000	3.11	.014

SCHIST

The average NiO content for the following nine new determinations in schist is 0.0041 percent.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Pine Grove Furnace, South Mountain, Pa. (Bull. 591, p. 44, J)	900	2.75	0.0009
2	Ladiesburg, Md. (Bull. 591, p. 50, F)	500	2.82	.0054
3	Near Ducktown, Tenn. (Bull. 591, p. 54, C)	1,700	2.74	.0021
4	Aragon iron mine, Menominee River, Mich. (Bull. 591, p. 66)	900	2.53	.0036
5	Cripple Creek district, Colorado. (Bull. 591, p. 121, Y)	10,000	2.77	.0062
6	1 mile south of Black Hawk, Central City quadrangle, Colorado. (Bull. 591, p. 126, A-2)	8,300	2.77	.0056
7	Pinal schist, half a mile southwest of Vitoria, Ray district, Arizona. (Bull. 591, p. 154, E)	2,500	2.69	.0021
8	2½ miles S. 60° E. of Jamestown, Colo. (Bull. 878, p. 18, G)	7,500	3.03	.0052
9	Half a mile southeast of Springdale, Colo. (Bull. 878, p. 23, R)	6,600	2.84	.0058

Matveiev [20] reported 0.04, 0.06, and 0.11 percent of NiO in biotite schist from the Tyrol, the Urals, and the Transvaal, respectively.

SLATE

Two determination of nickel in slate were made, and the results are shown below. The average is 0.0074 percent of NiO.

No.	Locality	Altitude (feet)	Specific gravity	NiO (percent)
1	Average sample of "Virginia slate," Mesabi iron district, Minnesota. (Bull. 591, p. 254, A-2)	1,500	2.72	0.0066
2	Cambrian slate near Field, British Columbia. (Bull. 591, p. 258)	4,000	2.82	.0083

MINERALS

ANTHOPHYLLITE

Sahama [21] gives the NiO content of a cordierite-anthophyllite-garnet rock from Finland as less than 0.001 percent. However, in view of the supposed derivation of anthophyllite from olivine in many places, a somewhat higher percentage of nickel would not be surprising.

CHROMITE

Nickel was determined in several samples of chromite. One sample from Casper Mountain, Wyo. (laboratory No. D-996), containing 42.7 percent of Cr_2O_3 and 4.1 percent of MgO, gave 0.13 percent of NiO. Another from Grant County, Oreg. (laboratory No. D-994), containing 51.6 percent of Cr_2O_3 and 13.4 percent of MgO, gave 0.15 percent of NiO. Still another collected by J. W. Peoples from the lowest part of the Stillwater

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[20] Matveiev, K. K., The occurrence of nickel in the biotite schists of the Ural emerald mines and other emerald deposits: Acad. Sci. U. R. S. S. Comptes rendus (Doklady), vol. 14, pp. 123-126, 1937.

[21] Sahama, T. G., Akzessorische elemente in der granuliten von Finnisch-Lappland: Comm. géol. Finlande Bull. No. 115, pp. 267-274, 1935.

complex, Mont. (laboratory No. D-1160), gave the following complete analysis.

	Percent		*Percent*
Cr_2O_3	46.20	MnO	0.01
Al_2O_3	15.60	NiO	.12
Fe_2O_3	8.46	SiO_2	.32
FeO	16.66	TiO_2	.72
MgO	11.67		
CaO	.28		100.04

Chromite from Chester, Pennsylvania, contained 0.10 percent of NiO, according to Dana.[22]

IRON ORE MINERALS

F. J. Pope [23] noted significant percentages of nickel in titaniferous iron ores, and special analyses of different concentrates lead him to conclude that the nickel is present in a spinel cell of the titaniferous ores. In magnetite from a dike in Victoria County, Ontario, Pope found 1.87 percent of Ni+Co, and in titaniferous iron ores from several other different localities he found percentages of nickel ranging from 0.08 to 0.39.

Genth [24] found 0.33 percent of NiO in spinel from Madison County, N. C.

KRYPTOMELANE

Most specimens of kryptomelane,[25] contain little or no nickel. However, one specimen from Oriente Province, Cuba (laboratory No. D-1175), submitted by Charles Park, Jr., of the Geological Survey, was found by Victor North to contain 1.27 percent of NiO.

LIGNITE

Shadlun [26] reports from 3 to 15 percent of nickel in the ash of a peculiar altered lignite occurring near the Novo-Cheremshansky mine, Ural Mountains, Russia. In this connection may be mentioned the well-known fact that nickel is present in petroleum.

NONTRONITE

Three samples of nontronite were analyzed for nickel, but the average percentage of NiO found was only 0.0018. The individual results were as follows:

No.	Locality	NiO (percent)
1	Woody, Calif. (Bull. 878, p. 108, A-2)	0.0014
2	Sandy Ridge, N. C. (Bull. 878, p. 109, D)	.0025
3	Spokane, Wash. (Sample collected by Edward Sampson)	.0015

OLIVINE

The following determinations show the range of nickel content in different samples of olivine. NiO averages 0.23 percent, which clearly indicates that in general if olivine is a constituent of a rock, the presence of nickel may be inferred. In rocks of magmatic origin nickel tends to segregate in the silicate olivine, or as a sulfide. In ore deposits, however, it may be further concentrated as a sulfide, a silicate, or one of the other well-known nickel minerals.

Source of olivine	*Percent of NiO*
Peridotite, Riddles quadrangle, Oreg. (Bull. 591, p. 198, B)	0.26
Elliott County dike, Ky. (Bull. 591, p. 53, C-2)	Trace
Gabbro, west side of Birch Lake, SE¼, sec. 19, T. 63 N., R. 4 W., Minn. (Bull. 591, p. 72 E)	.20
Mauna Loa, flow of 1852. (Bull. 591, p. 213, C)	.34
Meteorite, Kiowa County, Kans. (Bull. 591, p. 274, B-3)	.02
Dunite, Webster, N. C. (Econ. Geology, vol. 23, p. 545, 1928)	.34-.44
Purified sample from Shasta County, Calif. (collected by F. G. Wells; analyzed by Michael Fleischer; laboratory No. D-1181)	.19

POLIANITE

Shadlun [27] has reported the presence of 5 to 9 percent of NiO in polianite from the Novo-Cheremshansky mine.

PYRITE

According to Thomson and Allen [28] nickeliferous pyrite from Ontario contains on the average about one atom of nickel to two unit cells of Fe_4S_8 and has a faint violet color and specific gravity of 4.81.

In faintly tinted pyrite from Pitcher, Okla. (laboratory No. D-1164), carefully selected by E. T. McKnight, of the Geological Survey, the writer found 0.22 percent of NiO. Marcasite was found to contain much less.

SERPENTINE

Serpentine near Orsk in the southern Urals contains from 0.01 to 0.13 percent of NiO.[29]

Serpentine and other related minerals containing nickel from Webster, N. C., have been described by Ross, Shannon, and Gonyer.[30] Among these minerals—talc, actinolite, kämmererite, amphibole, chromite, and vermiculite—the nickel content ranges from very small traces to 0.61 percent NiO, depending on the extent of concentration from the original dunite to the different secondary minerals.

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[22] Dana, E. S., System of Mineralogy, 5th ed., p. 153, 1884.

[23] Investigation of magnetic iron-ores from eastern Ontario. Am. Inst. Min. Eng. Trans., vol. 29, pp. 372–405, 1899.

[24] Genth, F. A., Contributions to mineralogy, XX: Am. Philos. Soc. Proc., vol. 20, pp. 381–404, 1882.

[25] Richmond, W. E., and Fleischer, Michael, Kryptomelane, a new name for the commonest of the "psilomelane" minerals: Am. Mineralogist, vol. 27, pp. 607–610, 1942.

[26] Shadlun, N. A., Nikkel: Akademii͡a nauk, Kommissii͡a po izuchenii͡u estestvennykh proizvodetel'nykh sil Rossii, Estestvennye proizvoditel'nyi͡a sily Rossii, tom. 4, no. 5, 7 pp., 1923.

[27] Shadlun, N. A., Nikkel: Akademii͡a nauk, Kommissii͡a po izuchenii͡u estestvennykh proizvodetel'nykh sil Rossii, Estestvennye proizvoditel'nyi͡a sily Rossii, tom 4, no. 5, 7 pp., 1923.

[28] Thomson, Ellis, and Allen, J. S., Nickeliferous pyrite from the Denison mine, Sudbury district, Ontario: Toronto Univ. Studies, Geol. ser., No. 42, pp. 135–139, 1939.

[29] Bogitch, Basile, Nickel oxide deposits in the Urals: Acad. sci. Paris Comptes Rendus, tome 209, pp. 652–653, 1939.

[30] Ross, C. S., Shannon, E. V., and Gonyer, F. A., The origin of nickel silicates at Webster, N. C.: Econ. Geology, vol. 23, pp. 528–552, 1928.

TALC

Genth found 0.23 percent of NiO in talc from Webster, N. C.,[31] and 0.16 percent of NiO in the same mineral from Delaware County, Pa.[32]

THE NICKEL CONTENT OF THE EARTH'S CRUST

METHODS OF CALCULATION

As stated in the introduction, figures for the nickel content of igneous rocks published heretofore are largely arbitrary averages of available determinations without reference to the type of rock, its origin, or relative abundance. Of course such averages have a value as preliminary estimates. Some investigators, in order to save time by making only a single analysis, have prepared "standard mixtures" of many samples. Thus the mixture used by Hevesy,[33] in determining the relative abundance of columbium, tantalum, zirconium, and hafnium in the igneous rocks of central Europe, consisted of 133 samples of granite, 9 of quartz diorite, 35 of chlorite, 82 of gabbro and norite, and 23 of highly ferromagnesian rocks. The rocks in this composite were collected by Osan.

It would seem that first consideration should certainly be given to the relative abundance of the different types of rock. This method was used by Knopf,[34] who employed figures computed by Daly for the percentage distribution of the main types of igneous rocks; however, both Daly and Knopf considered only the areal surface distribution of such rocks, rather than the distribution with respect to depth. The latter is difficult to evaluate, but either some attention should be paid to it or the figment of a 10-mile crust should be abandoned. An attempt is made in this paper to take into account the distribution of different kinds of rocks with respect to depth.

RESULTS BY OLDER METHODS

The earliest published estimate of the relative abundance of nickel in the earth's crust appears to be that of Clarke,[35] who states it is less than 0.01 percent of metallic nickel. Vogt[36] in 1898 calculated 0.005 percent of nickel. These low figures are caused partly by the inclusion of too many analyses of the more siliceous rocks. In 1924 Clarke and Washington[37] found 0.018 percent of nickel, or 0.020 for the igneous rocks alone. Fersman,[38] Berg,[39] and Vernadsky[40] obtained practically the same figures as Clarke and Washington.

The following table contrasts the results of two sets of calculations—one based on the average percentage of NiO in various rocks as computed by the writer from Washington's tables;[41] the other, based on the averages of new determinations reported by the writer in this paper. Daly's figures[42] for the areal distribution of different kinds of igneous rocks are used in both calculations; but with Washington's data the total is 0.016 percent of NiO, or about 0.012 of Ni; whereas with the writer's new averages the result is 0.011 percent of NiO, or about 0.008 of Ni.

Percentage of nickel in average igneous rock

(1)	(2)	From Washington's analyses			From Wells' analyses		
		(3)	(4)	(5)	(6)	(7)	(8)
Rock	Relative abundance	Number of analyses	Average NiO content (percent)	Integrated NiO content (percent) (2)×(4)	Number of analyses	Average NiO content (percent)	Integrated NiO content (percent) (2)×(7)
Andesite	0.2380	45	0.008	0.00190	9	0.004	0.00095
Granite	.2315	57	.009	.00208	2	.002	.00047
Basalt	.2072	182	.039	.00808	21	.037	.00767
Rhyolite	.1280	21	.009	.00115	2	.002	.00026
Granodiorite	.1216	12	Trace	--------	6	.004	.00049
Gabbro	.0222	15	.048	.00106	10	.008	.00018
Diorite	.0180	48	.017	.00030	11	.002	.00004
Diabase	.0160	28	.037	.00059	4	.020	.00032
Dacite	.0053	15	.017	.00009	2	.003	.00002
Peridotite	.0043	47	.110	.00047	2	.061	.00026
Syenite	.0038	17	.024	.00009	5	.013	.00005
Anorthosite	.0031	--------	--------	--------	--------	--------	--------
Quartz monzonite	.0010	10	.012	.00001	--------	--------	--------
	1.0000	--------	--------	0.01582	--------	--------	0.01071

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[31] Genth, F. A., The minerals of North Carolina: U. S. Geol. Survey Bull. 74, p. 61, 1891.

[32] Genth, F. A., Contributions to mineralogy, XX: Am. Philosophical Soc. Proc., vol. 20, pp. 381–404, 1882.

[33] Hevesy, Georg von, Chemical analysis by X-rays and its applications, p. 270, New York, McGraw-Hill Book Co., 1932.

[34] Knopf, Adolph, The composition of the average igneons rock: Jour. Geology, vol. 24, p. 620, 1916.

[35] Clarke, F. W., The relative abundance of the chemical elements: Philos. Soc. Washington Bull., vol. 11, p. 135, 1889.

[36] Vogt, J. H. L., Ueber die relative Verbreitung der Element, besonders der Schwermetalle, und ueber die Concentration des urspünglich fein vertheilten Metallgehaltes zu Erzlägerstatten: Zeitschr. prakt. Geologie, Band 6, pp. 225–238, 314–327, 377–392, 413–420, 1898; and Band 7, pp. 10–16, 1899.

[37] Clarke, F. W., and Washington, H. S., The composition of the earth's crust :U. S. Geol. Survey Prof. Paper 127, p. 34, 1924.

[38] Fersman, A. E., Geokhimiñ, tome 1, p. 142, Leningrad, 1933.

[39] Berg, G., Neue Versuche zur Festellung der relative Verbreitung seltener Elemente: Zeitschr. prakt. Geol., Band 33, pp. 73–79, 1925.

[40] Vernadsky, W. J. Geochemie, translated by E. Kordes, p. 21, Leipsig, 1930.

[41] Washington, H. S., Chemical analyses of igneous rocks published from 1884 to 1913, inclusive, with a critical discussion of the character and use of analyses: U. S. Geol. Survey Prof. Paper 99, 1917.

[42] Daly, R. A., Igneous rocks and the depths of the earth, p. 35, New York, McGraw-Hill Book Co., 1933.

The new average is considerably lower than that based on the older data. The difference is traceable mainly to the writer's lower figures for the nickel content of andesite, granite, basalt, rhyolite, and gabbro. The table is presented chiefly for comparsion and summary, as farther on in the paper (see p. 17) the amount of nickel in the 10-mile crust is computed by other methods, which in general yield higher figures.

The preceding table reveals in a striking way the extreme dependence of the calculated average on the analyses used as well as on the relative abundance of different kinds of rocks. Rather wide variations appear in some of the analytical results. For example, the writer's figure for the nickel content of gabbro is much lower than Washington's, but the final effect of this difference is small on account of the small quantity of gabbro. In contrast, the lower figures for granite and andesite have an appreciable effect. The figure that counts most is that for basalt. These results show, at least, the relative amount of nickel in the different kinds of rocks. It is clearly more abundant in the ferromagnesian rocks, especially in the high-magnesium or olivine-bearing rocks. The calculation can easily be corrected as further data become available.

FACTORS INFLUENCING NEW CALCULATIONS

DENSITY OF ROCKS AND NICKEL CONTENT

As shown by the determinations of nickel on previous pages, the nickel content of igneous rocks is more or less proportional to the magnesium content. Consequently the nickel content is also related to the density of the rocks; and insofar as this relation can be evaluated, it will assist in the determination of the amount of nickel in the 10-mile crust. Only the fresh silicate rocks are considered, not the ores or segregations.

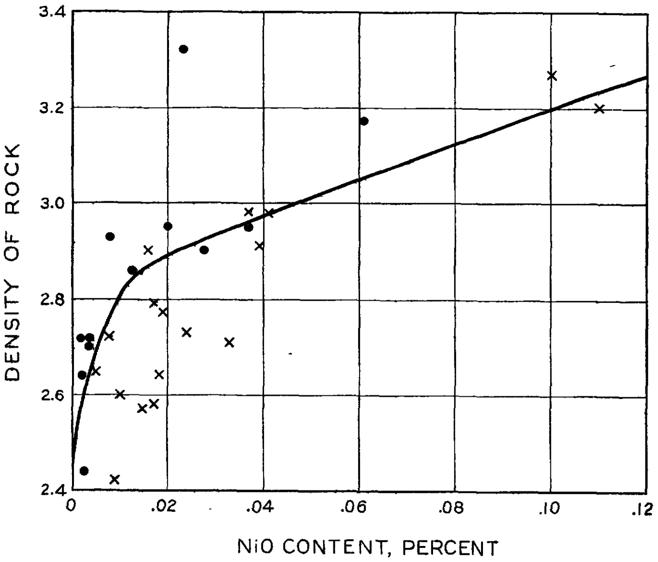

FIGURE 1.—Relation of nickel content to density of rock. Black dots, author's determinations; crosses, Washington's determinations.

The relation between the average nickel content of the igneous rocks in which nickel has been determined by the author and the average density is shown in the table following. A number of the average determinations of nickel by the writer and by Washington are plotted against the density in figure 1. Washington's nickel averages for the lighter rocks are all higher than the writer's, but those for the heavier rocks are generally of the same order. The curve clearly indicates an increasing nickel content with increasing density, a relation somewhat independent of the kind of rock; and the nickel content increases rapidly for densities greater than 2.83, approximately. This progressive increase is one of the most important features brought out in the study, and it leads definitely to higher estimates of nickel in the deeper rocks and in the suboceanic rocks.

Average MgO and NiO content and average density of various igneous rocks

Rock	MgO (percent)	NiO (percent)	Density
Rhyolite	0.05	0.0025	2.44
Granite	.23	.0021	2.64
Dacite	1.08	.0035	2.58
Granodiorite	1.48	.0039	2.70
Trachyte	.89	.0039	2.64
Syenite [1]	2.71	.0132	2.86
Latite	2.00	.0025	2.60
Monzonite	2.13	.0025	2.76
Andesite	3.42	.0039	2.72
Diorite	3.00	.0022	2.72
Phonolite [2]	.54	.0010	2.96
Shonkinite	9.57	.028	2.90
Basalt	8.33	.037	2.96
Diabase	7.54	.020	2.95
Gabbro	5.22	.0080	2.93
Pyroxenite	13.43	.023	3.32
Peridotite	16.93	.061	3.17

[1] One rock with exceptionally high figures included in the average of five.
[2] One rock only.

DISTRIBUTION OF DIFFERENT KINDS OF MATERIAL IN THE EARTH'S CRUST

Clarke and Washington [43] compute the mass composition of the 10-mile crust of the earth on the following percentage of distribution of matter:

Atmosphere	0.03
Hydrosphere	7.00
Shale	3.72
Sandstone	.70
Limestone	.23
Igneous rock	88.32

Of course, as far as nickel is concerned, the atmosphere and hydrosphere require merely a small allowance in the final mathematical calculation, as they contain no nickel. The sedimentary rocks contain some nickel but are negligible because they form only a small proportion of the 10-mile crust. The chief problem is to evaluate

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[43] Clarke, F. W., and Washington, H. S., op. cit., p. 34.

the percentage of the different kinds of igneous rocks in the crust.

The figures for the areal distribution of igneous rocks computed by Daly have already been used in calculating a preliminary estimate for the relative abundance of nickel. It is rather remarkable that the amount of nickel calculated from Daly's figures is very nearly the same as that obtained by simply averaging all available determinations of nickel. The writer feels, however, that attention should also be given to the distribution of different kinds of rocks with respect to depth, as well as to their distribution over continental and oceanic areas.

It is not the intention to speculate here about the composition of the earth at great depths, a subject that has been discussed by Williamson and Adams.[44] There seems to be general agreement that at some depth the constituents merge into a basaltic layer, and farther down even into one of peridotitic or semimetallic composition. With this change in composition must go an increase in the percentage of nickel. The main question is whether these changes are recognizable within a 10-mile crust, either on the continents or below the oceans. Two lines of evidence may be considered briefly.

Evidence from earthquake waves.—The fact that the velocity of earthquake waves increases with depth, indicates the presence in depth of peridotite, which is the only rock having a composition that will give a velocity as high as that observed. After considering this matter Bowen [45] stated:

> The conclusion most commonly reached is that there is a granitic layer variously estimated at from 6 to 25 kilometers in thickness, which gradually changes through intermediate to basic rocks, and these give place rather abruptly to an ultrabasic layer at a depth anywhere from 37 to 60 km. The geologic evidence as obtained in the deepest eroded sections indicates a preference for the larger of these figures.

Bowen also wrote:

> We have seen that basaltic substance would give rise by selective fusion to nonbasaltic liquid and that, at a time when there was enough liquid to render its intrusion possible, the liquid would be considerably more salic than basalt.

It appears from these views that the physical, geologic, and petrologic evidence all points in a general way to the existence of a basaltic substratum. It is also suggested by Bowen that with increasing depth the composition of the upper granitic layer should change more or less progressively to that of basalt or peridotite.

Evidence from isostasy.—Another guide is the theory of isostasy, which is based on considerations of the relative density of the rocks. It is generally recognized that the rock masses under the oceans are on the average more dense than those forming the continental segments and that the density of these masses varies inversely with the altitude of the surface.[46]

Many writers have assumed also that density increases more or less uniformly with depth. This greater density would represent in part a decrease in the percentage of quartz and orthoclase but mainly an increase in the percentage of plagioclase and possibly also in the proportions of pyroxene and olivine. The particular problem of the distribution of the different kinds of rocks in a 10-mile crust is difficult because of the uncertainty as to whether any property, such as density, can be assumed to vary regularly and continuously with depth, or whether a stepwise variation is more probable. It is a general practice for purposes of calculation and averaging, to assume uniform variation, although some objections to it may be raised.

UNCERTAINTIES OF EXTRAPOLATION

The density-altitude gradient arrived at by Washington [47] was obtained by considering the densities of rocks actually available for measurement and by assuming that rocks from certain Pacific islands represented the composition of the earth's crust at the oceanic depths involved. This gradient is shown in figure 2, a. If extrapolated linearly, however, it leads to an impossibly high density at a depth of 10 miles. A lower gradient, figure 2, b, would be obtained by using Washington's

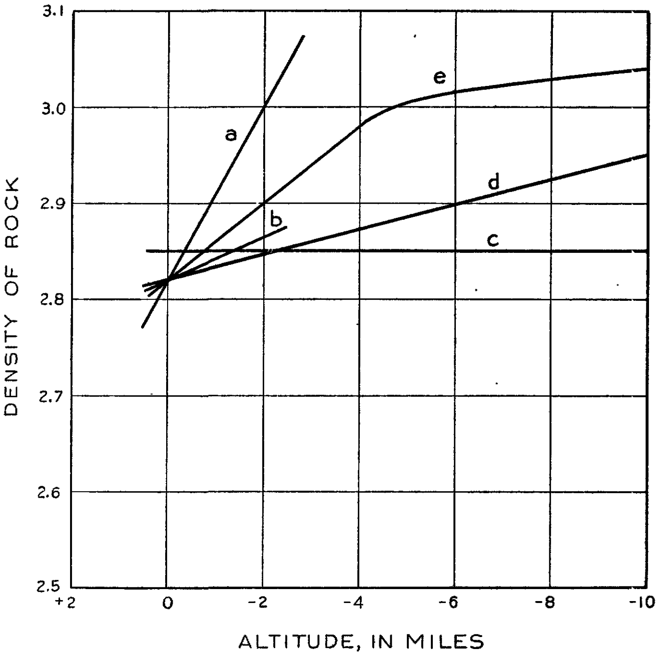

FIGURE 2.—Density-altitude gradients.

a, Washington's gradient based on Pacific island rocks.
b, Gradient based on Washington's densities for Atlantic island rocks.
c, No gradient (uniform density).
d, Uniformly increasing gradient.
e, Upper part of an S-shaped gradient extending to a depth of 37 miles.

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[44] Williamson, E. D., and Adams, L. H., Density distribution in the earth: Washington Acad. Sci. Jour., vol. 13, p. 413, 1923.

[45] Bowen, N. L., The evolution of the igneous rocks, p. 305, Princeton University Press, 1928,

[46] Washington, H. S., Isostasy and rock density: Geol. Soc. America Bull., Vol. 33, pp. 375–410, 1922.

[47] Washington, H. S., Isostasy and rock density: Geol. Soc. America Bull., vol. 33, pp. 375–410, 1922.

densities for Atlantic island rocks, but even this gradient is too steep if it is assumed to continue uniformly to the basaltic substratum. One may well question whether the rocks of the oceanic islands are really typical of the ocean bottoms and should be used to determine a density gradient, or whether they are outpourings from far greater depths than the upper part of the ocean bottoms.

The density distribution commonly assumed for great depths rests mainly on observations of the velocity of earthquake waves. Williamson and Adams,[48] considering all the factors involved, assume that the density and ferromagnesian content of rocks must increase with depth, although the increase need not necessarily be regular. They deduce the existence of a layer that corresponds roughly in composition to a peridodite of 3.3 density, and that begins at a depth of about 37 miles and extends possibly to 1,000 miles. They say nothing concerning changes in composition in the ferromagnesian layer with depth, and we are not concerned with that here, but they refer to the outer layer as material that changes "more or less gradually from granitic to something more basic than a gabbro."

The average density of the igneous rocks at the surface is of fundamental significance in estimating the nickel content of the 10-mile crust. Williamson and Adams[49] consider the average density of the igneous rocks at the surface to be 2.8, but allowing for a small proportion of sedimentary rocks they assume the surface density to be 2.7. Inasmuch as the sedimentary rocks play out well within 5 miles and their nickel content can be estimated separately, a density gradient based on the igneous rocks is particularly needed in this problem. The density calculated by the writer from Daly's average igneous rock is 2.73. As a compromise, 2.76 will be used here for the average density of continental igneous rocks at sea level. This figure falls between Washington's calculations[50] for the water-free rocks and the analyzed specimens.

The density selected, it may be noted, refers to continental igneous rocks, but from the isostatic relations it is easy to calculate that corresponding suboceanic rocks would have a density of approximately 2.90. This is an increase in density of 0.14, which must obtain whatever the absolute densities may be. The density of the average igneous rock of the whole upper rocky crust would thus be about 2.85 (taking account of the relative areas of land and sea). The theory, tacitly assumed in previous methods of estimating the relative abundance of the elements, is that rock of essentially the same composition extends downward for at least 10 miles.

Several reasons may be advanced, however, for assuming the existence of a density gradient even in the 10-mile crust. Segregation by gravity is a common process. There may be a stratum, then, characterized by a particular average density, for example, a batholith or a sill, in which the density is greater at the bottom than at the top. Again there may be above or below the first, another sill in which similar or overlapping ranges of density will be found. In general, however, broadly speaking, the density probably tends to increase with depth.

Using 2.82 for the density at sea level and 3.3 for the density at 37 miles, a uniformly increasing density gradient would be that shown as figure 2, d. Even this gradient, 0.0129, is steeper than the over-all gradient, 0.0018 per mile, indicated by Williamson and Adams[51] for a depth of 1,000 miles, but it offers a guide for calculating a figure for the nickel content of the 10-mile crust. Such a calculation is made on page 18.

Lastly, if Washington's higher densities for Pacific island rocks and Atlantic island rocks are taken as representative for rocks at these altitudes, an **S**-shaped curve for the density gradient is indicated. This gradient cannot reasonably rise above the mean density of the 37-mile layer, which is almost certainly less than 3.1. The upper part of such as **S**-shaped gradient, figure 2, e, has been assumed and is used as a basis for calculating a maximum nickel content of the 10-mile crust.

ALTITUDE AND NICKEL CONTENT

With the information shown in figures 1 and 2 it is a simple matter to draw curves showing the relation to be expected between nickel content and altitude (or depth below sea level) for any particular density gradient. One such curve is shown in figure 3, based on the uniform gradient, figure 2, d, and the author's determinations plotted in figure 1. It should be noted that this

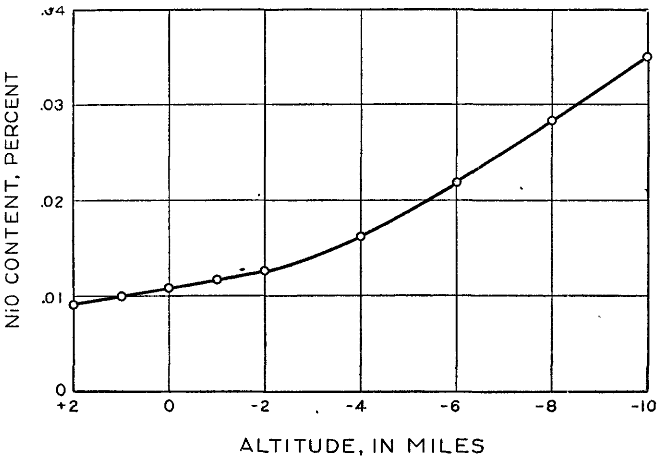

FIGURE 3.—Curve showing increase of nickel content with decrease of altitude, assuming a uniformly increasing density gradient (fig. 2, d).

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[48] Williamson, E. D., and Adams, L. H., Density distribution in the earth: Washington Acad. Sci. Jour., vol. 13, p. 413, 1923.

[49] Williamson, E. D., and Adams, L. H., op. cit., p. 413.

[50] Washington, H. S., Isostasy and rock density: Geol. Soc. America Bull., vol. 33, pp. 375–410, 1922.

[51] Williamson, E. D., and Adams, L. H., op. cit., p. 413.

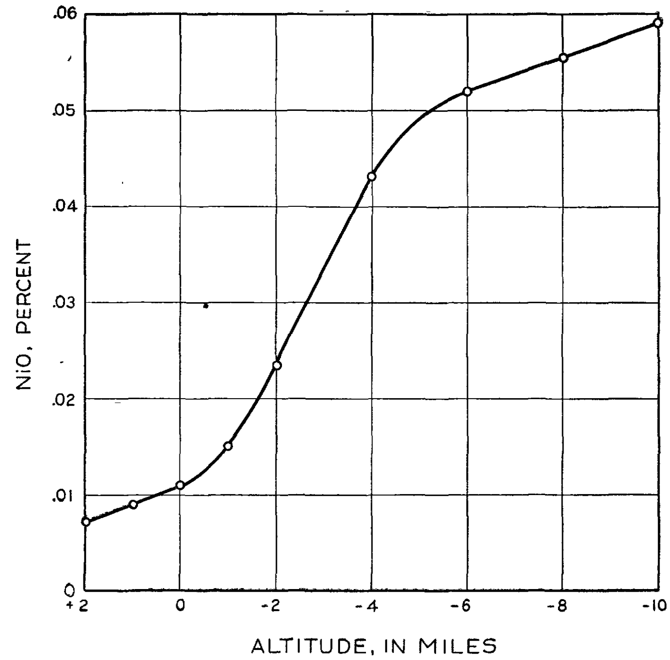

FIGURE 4.—Curve showing increase of nickel content with decrease of altitude, assuming an S-shaped density gradient (fig. 2, e).

is a theoretical rather than a practical relation under certain conditions. The approximate altitude from which each sample came has been recorded, but obviously these figures are not generally the altitude at which the rock was formed. A rock mass may have been elevated, depressed, eroded, or covered by sediments. Further, lavas originate at different depths, and the composition of any one flow represents the magma or differentiate at that depth. For this reason the density rather than altitude has been chosen as a basis of reference. Nevertheless, the altitude has a certain significance because in any given mass, for example a sill, the heavier minerals tend to separate by gravity and are found at lower altitudes than the lighter minerals in the main part of the sill. In the Palisade diabase along the Hudson River only 0.0036 percent of NiO has been found 700 feet above the lower contact, whereas the olivine layer 60 feet above the contact contains 0.034 percent of NiO.

A similar curve based on the S-shaped gradient (fig. 2, e) is shown in figure 4, and corresponding calculations for nickel are given on page 18.

DISTRIBUTION OF SEDIMENTARY AND IGNEOUS ROCKS AT DIFFERENT ALTITUDES

For the final calculations it remains to evaluate the mass of rock in each mile of the earth's outer 10-mile shell. The value for any 1-mile layer differs slightly from 10 percent of the whole on account of the volume of the ocean and the slight increase of density with depth. As already shown the percentage of nickel is found to increase with depth.

Some estimate must be made of the relative proportions of sedimentary and igneous rock. It will be assumed that the sedimentary rocks practically vanish at a depth of 5 miles. Clarke and Washington [52] assume that the sedimentary rocks amount to 5 percent of the whole rocky crust. The proportions of the two kinds of rock as shown in the table below are based on all available evidence and have been adopted for use in this paper. It is quite unnecessary for the purpose of the present study to have an exact figure for the ratio of igneous to sedimentary rock in any one of the layers referred to in the table, as a displacement from one layer to another would have only slight effect on the final estimate of nickel; but the fact that the sedimentary rocks are in the upper layers of the crust throws greater emphasis on the higher percentages of nickel in the lower silicate layers.

Proportions of sedimentary and igneous rock in different layers of the rocky crust

Layer of crust (miles)	Fraction of sedimentary rock	Fraction of igneous rock
Above 0	0.80	0.20
0 to −1	.80	.20
−1 to −2	.13	.87
−2 to −3	.025	.975
−3 to −4	.006	.994
−4 to −5	.002	.998
−5 to −10	None	1.000

The average NiO content found for the sedimentary rocks is 0.0073 percent. This is slightly less than the figure for the igneous rocks, 0.0107 percent. The difference may be either accidental or real. Possibly nickel is retained in intermediate products, or by repeated cycles it may have passed preferentially into the igneous rocks. In any event this difference is of practically no consequence in estimating the nickel content of the crust of the earth because the sedimentary rocks constitute so small a proportion of the 10-mile crust.

NEW CALCULATIONS FOR THE RELATIVE ABUNDANCE OF NICKEL IN THE 10-MILE CRUST

The first of three new calculations of the abundance of nickel is made without reference to a density gradient, but it takes into account the distribution of ocean, igneous rock, and sedimentary material for each mile layer. The distribution of rock and ocean in the various depth zones was estimated by the writer from a graph based on figures given in Murray [53] and other available hydrographic information.[54] The results are shown in the following table. The greater density of the suboceanic rocks throws a greater weight on the percentages of NiO in the deeper layers (see column 3) and this has a slight effect on the integrated NiO content (see column

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[52] Clarke, F. W., and Washington, H. S., op. cit., p. 2.

[53] Murray, John, The ocean, a general account of the science of the sea, p. 87, New York, Henry Holt & Co., 1914.

[54] Clarke, F. W., The data of geochemistry: U. S. Geol. Survey Bull. 770, p. 22, 1924.

5). The NiO content of the sedimentary rocks is assumed to be 0.0073 percent, and that of the igneous rocks 0.0107 percent.

Nickel content of the 10-mile crust, without considering a density gradient

(1) Altitude (miles)	(2) Material	(3) Fraction of the whole crust	(4) Average NiO content (percent)	(5) Integrated NiO content (3)×(4) (percent)
Above 0	Sedimentary	0.011	0.0073	0.0001
	Igneous	.003	.0107	
0 to −1	Ocean	.027		
	Sedimentary	.027	.0073	.0002
	Igneous	.007	.0107	.0001
−1 to −2	Ocean	.024		
	Sedimentary	.006	.0073	
	Igneous	.037	.0107	.0004
−2 to −3	Ocean	.020		
	Sedimentary	.002	.0073	
	Igneous	.054	.0107	.0006
−3 to −4	Ocean	.010		
	Sedimentary	.001	.0073	
	Igneous	.087	.0107	.0009
−4 to −5	Igneous	.110	.0107	.0012
−5 to −6	Igneous	.113	.0107	.0012
−6 to −7	Igneous	.114	.0107	.0012
−7 to −8	Igneous	.115	.0107	.0012
−8 to −9	Igneous	.116	.0107	.0012
−9 to −10	Igneous	.116	.0107	.0012
		1.000		0.0095

The integrated total calculated above, 0.009 percent of NiO, or 0.008 percent of Ni, is considered a minimum estimate for the relative abundance of nickel in the 10-mile crust. It is slightly lower than the writer's average for igneous rocks. The next two more elaborate calculations, however, gave final results that differ appreciably from the figures for the average igneous rock.

The preceding table indicates the relatively small proportion of the earth's crust available for observation either above sea level or slightly beneath the surface of the solid part.

The second calculation has been made on the basis of a uniformly increasing density gradient in the crust. (See fig. 2, d, and fig. 3.) As might be expected, the final result shown in the table below is appreciably higher than that of the calculation based on a uniform NiO content. The total of 0.020 percent of NiO, or 0.016 percent of nickel, is only slightly less than Clarke and Washington's figure.

Nickel content of the 10-mile crust, assuming a uniformly increasing density gradient

[See fig. 2, d, and fig. 3]

(1) Altitude (miles)	(2) Material	(3) Fraction of the whole crust	(4) Average NiO content (percent)	(5) Integrated NiO content (3)×(4) (percent)
Above 0	Sedimentary	0.011	0.0073	0.0001
	Igneous	.003	.0093	
0 to −1	Ocean	.027		
	Sedimentary	.027	.0073	.0002
	Igneous	.007	.0117	.0001
−1 to −2	Ocean	.024		
	Sedimentary	.006	.0073	
	Igneous	.037	.0122	.0005
−2 to −3	Ocean	.020		
	Sedimentary	.002	.0073	
	Igneous	.054	.0130	.0007
−3 to −4	Ocean	0.010		
	Sedimentary	.001	0.0073	
	Igneous	.087	.0150	0.0013
−4 to −5	Igneous	.110	.0177	.0019
−5 to −6	Igneous	.113	.0204	.0023
−6 to −7	Igneous	.114	.0236	.0027
−7 to −8	Igneous	.115	.0268	.0031
−8 to −9	Igneous	.116	.0300	.0035
−9 to −10	Igneous	.116	.0335	.0039
		1.000		.0203

It remains to consider a similar calculation based on the third possibility—the **S**-shaped density gradient, figures 2, e, and 4. The integrated total is 0.042 percent of NiO, or 0.033 percent of nickel, which is certainly a maximum figure, though not entirely impossible.

Nickel content of the 10-mile crust, assuming an S*-shaped density gradient*

[See fig. 2, e, and fig. 4]

(1) Altitude (miles)	(2) Material	(3) Fraction of the whole crust	(4) Average NiO content (percent)	(5) Integrated NiO content (3)×(4) (percent)
Above 0	Sedimentary	0.011	0.0073	0.0001
	Igneous	.003	.0104	
0 to −1	Ocean	.027		
	Sedimentary	.027	.0073	.0002
	Igneous	.007	.0125	.0001
−1 to −2	Ocean	.024		
	Sedimentary	.006	.0073	
	Igneous	.037	.0190	.0007
−2 to −3	Ocean	.020		
	Sedimentary	.002	.0073	
	Igneous	.054	.0285	.0015
−3 to −4	Ocean	.010		
	Sedimentary	.001	.0073	
	Igneous	.087	.0385	.0033
−4 to −5	Igneous	.110	.0463	.0051
−5 to −6	Igneous	.113	.0505	.0057
−6 to −7	Igneous	.114	.0526	.0060
−7 to −8	Igneous	.115	.0545	.0063
−8 to −9	Igneous	.116	.0562	.0065
−9 to −10	Igneous	.116	.0580	.0067
		1.000		0.0422

SUMMARY AND CONCLUSIONS

The percentages of nickel (Ni) in the crust of the earth calculated by previous investigators and by the present writer in the course of this study are as follows:

	Percent
Clarke, 1889	Less than 0.01
Vogt, 1898	.005
Clarke and Washington, 1924	.018
New computations based on—	
(1) Washington's figures for the nickel content of various rocks and Daly's figures for areal distribution	.012
(2) Wells' determinations of the nickel content in various rocks and Daly's figures for areal distribution	.008

New computations based on—Continued.	*Percent*
(3) Average nickel content of the ocean, the sedimentary rocks, and the continental and suboceanic igneous rocks and on the relative amounts of these materials in the crust	.008
(4) Increase of nickel content with depth (uniform density gradient) and relative amounts of ocean, sedimentary rocks, and igneous rocks in the crust	.016
(5) Increase of nickel content with depth (S-shaped density gradient) and relative amounts of ocean, sedimentary rocks, and igneous rocks in the crust	.033

It is difficult to choose the most representative figure for the percentage of nickel in the crust. When the investigation was begun, better methods of analysis were expected to raise the figure, but this expectation was not fulfilled; the writer's determinations of nickel in many common rocks were lower than those of Washington, the average being about 0.008 percent of nickel. On the other hand, computations that included consideration of the probable density gradient in the crust gave higher percentages. With these in view 0.016 is considered a minimum and 0.033 a maximum. The most likely figure appears to be 0.016, which is only very slightly less than Clarke and Washington's figure of 1924.

The general methods used in this investigation will prove valuable in the study of other elements.

At present a comparison of the relative abundance of nickel with that of such elements as zinc, boron, copper, and rubidium, which are of the same order of abundance, is omitted both because the percentage of nickel is not known with exactness and because similar and comparably extensive studies have not been made for the other elements. If the percentage 0.016 is accepted, nickel would be the twenty-fourth element in order of abundance and occupy essentially its present position. If the lower figure, 0.008 percent, involving no extrapolation of any sort is considered to be more comparable to figures for the other elements, nickel would fall to about the twenty-sixth place in order of abundance.

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