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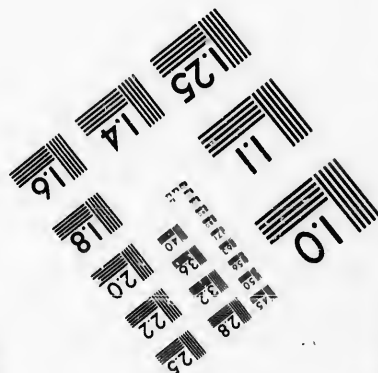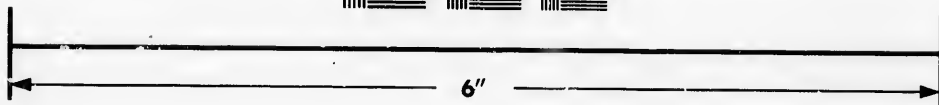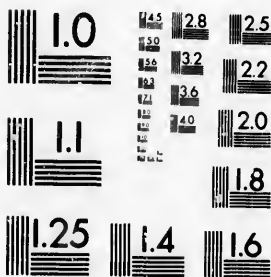# TEST TARGET (MT-3)

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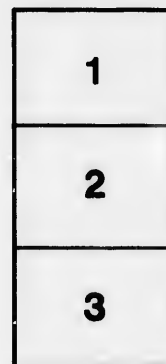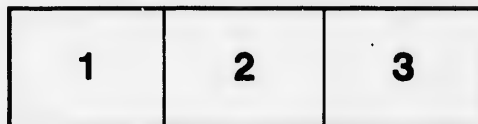
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Investigation of

Magnetic Iron-Ores from Eastern Ontario.

BY

FREDERICK JOHN POPE.

INVESTIGATION OF MAGNETIC IRON-ORES
FROM EASTERN ONTARIO.

BY

FREDERICK JOHN POPE.

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INTRODUCTION.

In the following work a study has been made of magnetic iron-ores from Eastern Ontario, particular attention being devoted to those magnetites which are titaniferous. After discussing the geology of the ore-bodies and tabulating their analyses, several relations existing between their geological associations and elementary constituents are considered.

It has been found that the titaniferous magnetites always carry vanadium, and also that the proportion of vanadic oxide present appears to bear a definite ratio to the titanic oxide. This ratio seems to be so regular that it is suggested that in these ores the two elements exist as a complex inorganic acid.

In order to determine whether, in the precipitation of titanium by the methods ordinarily employed, vanadium acts as an interfering agent, a series of experiments have been made in which definite amounts of titanic and vanadic oxides were subjected to analyses, and it has been found that in the "acetate method" vanadium is partially precipitated.

Further, it has been shown that under certain conditions and with various reagents vanadium will be completely precipitated with ferric iron, while in the case of aluminum the precipitation is more or less incomplete.

In the titaniferous magnetites, nickel and cobalt have been found to be invariable constituents.

Assays were made of the titaniferous magnetites for platinum, but none could be found.

Finally, it has been demonstrated that it is impossible, by magnetic concentration, to more than partially eliminate titanic oxide from titaniferous magnetites.

Investigation of Magnetic Iron-Ores from Eastern Ontario.*

BY FREDERICK J. POPE.

GENERAL GEOLOGICAL ASSOCIATIONS OF THE ORE-BODIES.

THE protaxis of the North American continent consists, as is well known, of a large V-shaped area of Archæan rocks, which lie for the most part in the Dominion of Canada, and occupy an area of not less than 2,031,000 square miles. The western limit of this area extends from Lake Superior in a north-westerly direction to the Arctic Ocean, the southern is found along the Lower St. Lawrence as far as Labrador. A minor area, spoken of as the Adirondack region of northern New York, has a somewhat broken connection with the main body in a narrow band of igneous rock, which crosses the Upper St. Lawrence where it leaves Lake Ontario. The ancient crystallines are also presumably beneath all the later sediments, but the above brief description outlines their principal exposures.

This great rock complex consists, for the most part, of a series of gneisses, which present great variations in both structure and composition. In certain sections areas of gneisses of the general composition of granite, and remarkably uniform in character, prevail. They consist largely, if not exclusively, of crystalline rocks in which a banding or foliation has been induced by pressure. These rocks constitute the basal member of the Laurentian system, and by later writers have been referred to as the Ottawa gneiss.

In other and quite extended areas gneisses, regarded by many as composed of altered sediments, are associated with crystalline limestones, quartzites, and much injected igneous matter. To this series the term Grenville has been applied.

Both of these series of gneisses are penetrated by various igneous masses, of which the most important are great intrusions of several members of the gabbro family, such as anorthosites, norites, pyroxenites, and gabbros proper; the whole forming the Norian series of Hunt.† These rocks are for the most

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part homogeneous, but in some instances exhibit that irregular
structure so characteristic of gabbros—a condition brought
about by a variation either in the size of the grains or in the
relative proportions of the constituents from place to place.

The whole of this area is more or less productive of economic
minerals, but the deposits are not uniformly distributed; some
occur in a restricted region or in some special geological rela-
tions, while others may prevail over large areas and with vari-
ous geological associations.

Magnetite is one of the commonest minerals, and one of the
most abundant of the ores. It occurs not only as an accessory
constituent in both the gneisses and gabbros, but by itself forms
beds of such considerable extent and thickness that, prior to
the development of the Lake Superior ranges, this region
afforded a considerable supply for American furnaces. These
magnetic iron-ore bodies may be classified, according to their
associations, into three groups corresponding to the three series
of crystalline rocks already referred to, viz.:

Ore-bodies where the magnetite occurs in lenses or as im-
pregnations in schistose or gneissic belts. In most of these in-
stances limestone is either altogether absent, or only occurs at
some distance from the deposit.

Ore-bodies occurring in belts of crystalline limestone imme-
diately at their contact with the harder gneissic and schistose
members of the series.

Ore-bodies, titaniferous in character, occurring entirely in
the anorthosites and basic gabbros.

Magnetic iron-ore bodies having the above geological asso-
ciations are found in the counties of Renfrew, Lanark, Leeds,
Frontenac, Hastings, Victoria, and Peterboro in Eastern Onta-
rio. A number of these have been examined, and in the present
paper some of the relations existing between their geological
associations and elementary constituents are considered.

MAGNETITES OCCURRING IN GNEISSES AND SCHISTS.

The ore-bodies of this type exhibit a tendency to lineal
arrangement, parallel with the foliation. The individual bodies
may be separated by barren rock, or by rock richly impregnated
with disseminated magnetite. In this latter case variations in
the proportion of magnetite may afford all gradations between

the extreme of a magnetite-bearing rock and an ore with a small intermixture of bisilicate minerals. The different gneisses, schists, etc., associated with the ores are the more or less metamorphosed products of various igneous types, and can best be described by reference to particular occurrences.

I. *Paxton Mine.*—The Paxton mine is located on lot 5, concession 5, of Lutterworth, Victoria county. The country-rock is a reddish, granitic gneiss, containing many small amphibolite bands. The gneiss has the usual granitic elements and has suffered considerable squeezing. Hornblende and mica are very subordinate and occasionally quartz is so predominant as to give the rock the characteristics of a quartzite. The ore-body conforms to the strike of the gneiss but is irregular in width. In one of the main openings it is 40 feet wide. This, however, is not all iron-ore, since—as is the case with so many of the iron-ore deposits in these Laurentian rocks—the ore itself is mixed with a large proportion of various ferruginous silicates, such as hornblende, pyroxene and garnet. The garnet, which is present in considerable amount, occurs in irregular masses, no crystal forms being observed. In color it is dark, reddish-brown, resembling those varieties which have been regarded as titaniferous. Chemical analysis, however, failed to detect even a trace of titanic oxide.

II. *Seymour Mine.*—The Seymour ore-bed is situated on lot 11, concession 5, Madoc township, Hastings county. The deposit occurs in a fine-grained orthoclase gneiss. The contact between the magnetite and associated rock is for the most part formed by 15 to 18 inches of decomposing hornblende schist, while thin belts of the same composition cut the ore-body diagonally at short irregular distances. The ore is black, fine-grained, and not only magnetic, but in some instances possesses polarity.[*] A large portion of the ore is solid and free alike from rock and pyritic impurities. When it is less pure, radiating green actinolite, in disseminated nodules, appears to be the principal accessory. Green and colorless fluor spar, associated in minute pockets with calcite and quartz, is prevalent, its occurrence appearing to be related to the distribution of the hornblende schist. Uraninite occurring in small quantities in some of the minute fissures, has been noted by Prof. Chapman.

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[*] *Report of the Bureau of Mines*, Ontario, 1892, p. 37.

III. *Robertsville Mine.*—This ore-body occurs on lots 3 and 4, concession 9, Palmerston township, Frontenac county. The country-rock is a typical hornblende gneiss containing a little feldspar, some augite, and a little secondary quartz. It is evidently either a metamorphosed diorite or diabase. The magnetite occurs in irregular masses and although the division between the ore and the wall-rock is distinctly defined by the contrast of color, yet there is no actual separation between them, the two breaking like one rock.

Magnetites Occurring at the Contact of Crystalline Limestones with Gneisses and Schists.

These magnetite deposits are associated with gneisses and schists of various types, which generally strike to the N. and N.E., and have an almost invariable dip to the eastward at high angles. Some of these types may be metamorphosed sediments, but the majority are undoubtedly the metamorphic product of various igneous rocks, the more basic predominating. Bands of crystalline limestone occur among these gneisses, and with them are found deposits of magnetic iron-ore. The limestones are always highly crystalline and vary from a nearly pure marble to those plentifully intermingled with various silicates—a result of the metamorphism. On account of their relatively slight resistance to pressure they have been thinned out, here and there along the strike, by squeezing. The result of this on the ore-bodies is to make them pinch and swell along the contact; and, in some instances, what undoubtedly were originally parts of the same ore-mass are now separated by considerable distances.

IV. *Black Bay Mine.*—This ore-body is located about two miles north of Calabogie, Renfrew county. The ore occurs along the contact of a metamorphosed diorite and a crystalline limestone. Disseminated through the ore, and particularly where it is in contact with the walls, there is considerable hornblende and less augite. The crystalline limestone is particularly free from bisilicates and other secondary products, but in thin sections exhibits the effects of considerable crushing. The dioritic gneiss is for the most part composed of a hornblendic element, the feldspar being quite subordinate. Considerable augite is present; chlorite and garnet are common.

V. *Glendower Mine.*—On lot 3, concession 6, Bedford township, Frontenac county, a band of crystalline, dolomitic limestone is in contact with a coarse-grained metamorphosed pyroxenite. Near the contact, but entirely within the limestone, a large bed of hard, compact magnetite, associated with much hornblende, occurs, which in former years afforded a very considerable output. For some distance from the surface the ore is quite free from sulphur. At a certain depth, however, pyrite* is found, but usually in concretionary masses, and seldom impregnating the magnetite sufficiently to detract from its value. A short distance from the main deposit the limestone is traversed by a great number of parallel bands of magnetite, so numerous and extensive as to have afforded profitable exploitation in an open cut. Intercolated between these bands of ore, serpentine occurs in both massive and fibrous forms. The limestone is coarsely crystalline, usually graphitic, and in many places is very impure because of the abundance of bisilicates, hornblende predominating. Garnet and vesuvianite crystals are also plentiful.

VI. *Dufferin Mine.*—The Dufferin mine is situated near Malone, Hastings county. The ore, which appears as a series of larger and smaller overlapping lenses, occurs in an impure crystalline limestone at some distance from its contact with a gneissic band. The lenses follow the foliation of the limestone, which is banded and contorted. The ore is considerably impregnated with hornblende and actinolite.

VII. *Howland Mine.*—This ore-body occurs on lot 26, concession 4, Snowdon township, Victoria county. The deposit follows the contact of a hornblendic gneiss and a narrow band of limestone. The ore is fine grained, and has associated with it much green hornblende and epidote. Near the surface it is somewhat pyritic, but with increasing depth the sulphur lessens. The gneiss presents little banding, but under the microscope the effects of considerable crushing are exhibited by the various components. The feldspar in particular is much shattered, and has afforded considerable scapolite as an alteration product. This secondary scapolite is equally abundant with green hornblende, the two constituting nearly the entire rock. Some

* W. G. Miller. Ontario Mining Institute, Oct., 1895.

mica is present and titanite is plentiful, particularly in the immediate vicinity of the hornblende. At a distance of several hundred yards from the mine, and where the metamorphic changes are not so marked, augite is more abundant than the hornblende, and the texture is typically gabbroic.

The limestone is finely crystalline, graphitic, and often set with little scales of phlogopite. Irregularly dispersed through it are bunches of various silicates, hornblende predominating.

MAGNETITES OCCURRING IN BASIC ROCKS OF THE GABBRO TYPE.

These rocks present the usual differences found in gabbros, due to variations either in the size of the grains or the relative proportions of the constituents from place to place. They pass insensibly by the increase or decrease of plagioclase into anorthosites, pyroxenites, and gabbros proper. The magnetic, titaniferous ore-bodies which these igneous rocks contain, do not, as a rule, have well defined walls, and may be considered as particularly basic phases of the gabbro. J. H. L. Vogt,[*] the eminent Norwegian geologist, has regarded similar Scandinavian deposits as excessively basic segregations of fused and cooling magmas.

VIII. *Chaffey Mine.*—The Chaffey iron-mine is situated near Newboro, in the county of Leeds. The ore, which is titaniferous, occurs in and near the margin of an extensive gabbro mass in the form of several elongated, approximately parallel lenses. Between the gabbro wall-rock and the ore-body there is no sharply defined contact. The ore near its boundary gradually becomes leaner and leaner, finally fading away in a matrix of the country-rock. The ore, which is fine grained, contains, besides an admixture of pyroxenic matter, a little hornblende, a few green spinels, and a small proportion of sulphur in the form of disseminated grains of pyrite.

A dark gray color characterizes the usual appearance of the gabbro, which for the most part is granitoid in texture. Near the ore-body, however, the gneissoid structure is quite marked. The plagioclase is usually subordinate to the more abundant dark silicates, consisting of augite, diallage, and original hornblende.

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[*] Vogt, " Bildung von Erzlagerstätten," *Zeits. für praktische Geol.*, 1893.

IX. *Pine Lake Ore-Body.*—This ore-body is situated on lot 35, concession 4, of Glamorgan township, Victoria county. The containing-rock is a dark, medium-grained gabbro, which appears in the form of an elongated lens of variable width penetrating the gneisses and schists. From place to place the rock varies greatly in the proportion of its constituents. In many instances the feldspar is more abundant than the dark silicate, but in the vicinity of the ore augite is so predominant that a thin section under the microscope exemplifies a typical pyroxenite. Reddish-brown allotriomorphic augites are seen to compose the major portion, the remainder consisting mostly of grains of amphibole, the product of uralitization. In addition there is a little titaniferous magnetite, irregular in outline and in every instance surrounded by a rim of uralite. Accessories, such as apatite, chlorite, olivine, titanite, etc., have not been observed; the only minerals other than the bisilicates and magnetite present being a very little pyrite and a few irregular masses of kaolinized plagioclase. Near the ore-body the pyroxenite has yielded to dynamic metamorphism, as is shown by several gneissic and amphibolite bands.

The Pine Lake magnetite, similarly to that in the Chaffey mine, affords no well-defined contact with the country-rock. The whole ore-body is more or less impregnated with pyroxenic elements, and its boundaries are marked only by a gradual passage of the one into the other.

X. *Eagle Lake Mine.*—The Eagle Lake iron-mine is situated in Bedford township, Frontenac county. The ore-body occurs in and near the margin of a gabbro mass where it is in contact with the characteristic gneiss of this region. The gabbro has the typical granitic texture, with a very light-colored feldspar slightly in excess of the pyroxene and secondary hornblende. Magnetite in small corroded masses is frequent, being most abundant in the pyroxene or around its margin. No olivine has been observed, the only accessory being a few scales of biotite situated on the edge of the pyroxene. Fair exposures of the ore have been made at several places, but the beds are extremely irregular, pinching and swelling for a considerable distance, with a strike N.E. and S.W. The magnetite itself is titaniferous, perfectly homogenous in thin sections under the microscope, and beautifully crystalline. Apatite, which occurs

associated with much of the magnetite, both in the form of grains, crystals, and large masses, causes a large proportion of the ore to be worthless. On the other hand, where macroscopic apatite fails the ore is practically free from phosphorus.

XI. Four miles north of Millbridge, Hastings county, a considerable area of gabbroic rock rises above the general level to a height of about 150 feet. The rock presents the usual variations in the relative proportions of its constituents; and in one of the particularly basic phases, due to a preponderance of augite and diallage, there is an extensive deposit of titaniferous magnetite. As is usual with iron ore-bodies found in gabbros, there is no sharp definition between the ore and the rock, the one passing into the other by inappreciable gradations. No large masses of homogeneous ore were observed, all parts of the ore-body being more or less impregnated with augite.

XII. In the township of Horton, county of Renfrew, just west of the Ottawa river, there is a considerable area of a dark gray gabbro, containing several small deposits of titaniferous magnetite. One of these is situated in the sixth range of Horton. Here the magnetite is homogeneous throughout and presents a fairly well defined boundary with the gabbro wall-rock. The gabbro is of uniform texture, the feldspar and augite being in about equal proportions. The feldspar is broadly twinned, presents the extinction angles of anorthite, and has the dusted appearance so characteristic of the plagioclase in anorthosite.

The above completes the descriptions of the magnetic iron ore-bodies which have been taken as typical of the ore-bodies occurring in the three different geological associations to which reference has been made. On the following page are tabulated the analyses of these ores.

METHOD FOR ESTIMATING TITANIUM IN TITANIFEROUS MAGNETITES.

The determination of titanic acid has always presented many difficulties, not only because of the tediousness of the operations, but also because of the inaccuracies of the results. When titanic acid is precipitated by boiling in a dilute sulphuric acid solution after the iron has been reduced the results are generally low. Thus, as is well known, phosphoric acid, which is generally present in greater or less amounts, interferes

Analyses of Ores.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
Fe_2O_4	41.23	61.21	57.04	56.43	55.21	51.47	63.23	46.67	39.27	62.39	37.35	29.40
FeO	26.54	30.63	24.21	29.32	27.62	28.31	26.72	22.10	21.73	26.93	28.82	29.78
Cr_2O_3			0.32								.12	
MnO	1.63	.22		.08	.54	.88	.17	.11	.37	.45	.31	.22
NiO				.23				.23	.27	.22	.26	.43
CoO								.31	.07	.05	.04	.10
Al_2O_3	6.44	1.67	.41	1.62	.75	1.87	.21	.09	4.61	.67	5.01	3.20
SiO_2	18.10	4.13	8.31	7.44	9.88	4.41	3.26	4.45	10.77	1.47	10.37	7.82
P_2O_5		.02	.03	.04	.02	.03	.01	7.52	.02	.03	.09	.11
S	.05	.06	.17	.22	.16	.23	.08	.07	.11	.06	.04	.06
TiO_2			.13					.82	13.52	6.41	8.17	17.23
V_2O_3	2.38	.17	2.36	1.22	3.15	2.33	2.46	10.21	.52	.23	.29	.63
MgO	.31	.60	.14	1.83	.09	.41	.12	.35	2.34	.33	4.23	5.67
BaO	2.82		4.23	.33	.43	6.51	3.73	3.13	.07			
CaO	.42	.11	.18		.11	.27		2.17	4.84	.72	4.40	3.42
Na_2O	.10							.52	.31		.57	.61
K_2O	.34	.09	1.50	.17	1.21	3.27	.33	.22	.24		.12	.17
CO_2	.79											
Moisture		.47	.59	.37	.54	.62	.48	.37	.44	.31	.47	.38
	100.55	99.38	99.42	99.20	99.81	100.61	100.80	99.34	99.50	100.55	100.65	99.26

with the determination by partially preventing the precipitation of titanic acid from its boiling sulphuric acid solution.   There are also mechanical losses in the above method, due to the adhesion of the precipitate to the sides of the beaker, and to the finely divided condition of the precipitate.

The volumetric determination of titanic acid as described by Wells and Mitchell* appears to obviate most of the difficulties, but since titaniferous ores usually have associated with them more or less vanadium,† the results so determined are liable to error.   In brief, their method is as follows : The ore is digested with hydrochloric acid, then with sulphuric; any insoluble residue is fused with potassium disulphate.   The melt from the fusion is dissolved in water, added to the solution obtained from digestion, and the whole diluted to one litre.   200 c.c. of this solution is reduced with hydrogen sulphide, and after eliminating the excess of hydrogen sulphide, is titrated with potassium permanganate.   Another 200 c.c. is reduced by zinc and titrated with the same standard permanganate.   In each case precautions are taken to prevent oxidation by the air.   The difference between the permanganate used in the latter case and that consumed by the iron alone represents the amount corresponding to the titanic acid.

In the hydrogen sulphide reduction, in the above method, the vanadium present would be reduced to hypovanadic sulphate (V_2O_4. x SO_3), and upon titration the results for iron would be too high, since each molecule of V_2O_4 present would require as much of the standard for oxidation as two molecules of FeO.   On the other hand, in the reduction of the iron and the titanium by means of zinc, the vanadium present in the original solution as vanadic sulphate (V_2O_5. x SO_3) would be reduced to hypovanadious sulphate (V_2O_2 x SO_3‡).   Consequently to oxidize the vanadium from this hypovanadious condition to the vanadic, three times as much permanganate will be necessary as was required for oxidation from the hypovanadic condition to the vanadic in the titration of iron.   Thus the results for both the iron and titanic oxide will always be too high, the amount of error for the latter being twice that of

* Jour. Am. Chem. Soc., 17, 878.   † This article, page 30.
‡ Roscoe and Schorlemmer, vol. ii., Metals, part ii., 1880.

the former; and since, in titaniferous ores, vanadium may be present to the extent of over one-half of one per cent. (see page 31), this cause for error is considerable.

Another method for the determination of titanic acid, which is based upon Gooch's experiments* in connection with the separation of the oxides of titanium and aluminum, is that described by Blair.† By this method quite satisfactory results may be obtained, but, as usually described, several possible sources of error and annoyance are not mentioned. In the following description of this "acetate method" some of these will be considered:

One gramme of the finely pulverized ore intimately mixed in a large platinum crucible with 12 grammes of potassium disulphate and 2 grammes of sodium fluoride is gradually heated by a low flame until the disulphate is melted. Heating is continued, keeping the mass just liquid and the temperature at the point at which slight fumes of sulphuric anhydride are given off when the lid of the crucible is raised, until all the particles of ore have disappeared.

Generally, at high temperatures, part of the sulphuric oxide, liberated by decomposition of the pyrosulphate, attacks the crucible, and, as a result, the removal of platinum is subsequently necessitated. By not raising the temperature higher than just intimated, contamination of the melt by platinum is either obviated or minimized. When the ore is completely decomposed, remove the flame, and, as the melt cools, incline the crucible in different directions, so that the fused mass may solidify well up on the sides. When cool, add 2 to 3 c.c. concentrated sulphuric acid, and carefully heat until the mass is just liquid. Discontinue heating, and place a platinum rod in the solidifying melt. When cold, fuse the mass where it is in contact with the crucible, and remove it by means of the platinum rod to a beaker containing 150–200 c.c. of a 5 per cent. solution of sulphuric acid. In the beaker also place the crucible and cover, and add 50 c.c. of sulphurous acid. Gently warm, but do not raise the temperature of the beaker and its contents beyond that which can be comfortably endured by the palm of the hand. The heat greatly facilitates solution, while

* *Am. Acad. of Arts and Sciences*, 1884–85, p. 435.
† *The Chemical Analysis of Iron*, 3d edition.

the proportion of sulphuric acid present prevents precipitation
of titanic acid at this temperature. Since silica has been re-
moved by means of the sodium fluoride, the melt should com-
pletely dissolve to a clear solution. The solution is cooled and
neutralized with ammonia until the precipitate which forms dis-
solves with difficulty. A portion of the liquid is next tested
by means of hydrogen sulphide for platinum, and, if its pres-
ence is detected, the whole solution is subjected to the action
of the gas until the metal is precipitated. After removing the
platinum, or if no platinum is found, the solution is directly
treated with 10 c.c. of sulphurous acid, 20 grammes of sodium
acetate (in solution), and one-sixth the total volume of acetic
acid (sp. gr. 1.04 = 49 per cent. of absolute acid). The solu-
tion is heated to boiling, the titanium being precipitated in a
flocculent condition. Boiling is continued for two or three
minutes. If filtered immediately, the filtrate, upon evapora-
tion, is sometimes found to contain traces of titanic acid; this,
however, may be obviated by digesting the previously boiled
precipitate on the steam bath for half an hour.

* "Experiments to determine the amount of acetic acid necessary to prevent
the precipitation of alumina from a boiling solution of the acetate indicate that
amounts of the absolute acid in excess of 5 per cent. by volume of the solution
are adequate to the purpose, and that the addition of sodic acetate in reasonable
amounts does not sensibly affect conditions. . . . . The small apparent losses to
be observed in some of the determinations in which a large excess of acetic acid
was employed is probably explicable by the tendency of the precipitate to change
its consistency as the amount of free acid increases, and, in very acid solutions,
to show an inclination to adhere in small amounts, but quite persistently, to the
vessel in which the precipitation takes place."

After allowing the precipitated titanic acid to settle, filter,
wash with hot water containing 5 per cent. of acetic acid, and
finally with hot water. The washed precipitate, after drying,
instead of being white, is generally dark-colored, and is always
more or less contaminated with various impurities, as iron,
alkali sulphates, alumina, phosphoric acid, vanadic acid, etc.
By some it is thought that the small quantity of iron present in
the precipitate is carried down in the ferrous condition. It is
also possible that during the filtering a little of the iron be-
comes oxidized and is precipitated as basic acetate. As referred

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* Gooch, *Am. Acad. of Arts and Sciences*, new series, vol. xii., p. 441.

to by Gooch,[*] titanic hydrate, like aluminum hydrate, has a tendency to occlude the sulphates of the alkalies, the amount carried down by the former in most instances being quite considerable. As is well known, alumina or phosphoric acid, if present in the original sample, will be found in small quantities in the precipitate. On page 23 of this article it is demonstrated that vanadic acid is also partially precipitated with the titanic acid. In order to eliminate these impurities from the titanic oxide, the precipitate is fused with sodium carbonate (avoid presence of potassium carbonate) and a little sodium nitrate, in order to obtain a soluble phosphate, vanadate, and aluminate of sodium; the titanium, at the same time, is converted into insoluble sodium titanate, and the iron into insoluble ferric oxide. A liberal amount of the flux and an hour's fusion with the strong flame of a blast-lamp are necessary to effect these changes completely. After fusion, the melt is boiled with a solution of sodium carbonate, filtered and washed with water containing a little sodium carbonate. The insoluble sodium titanate and ferric oxide are collected on a filter, dried in an air-bath, and transferred to a platinum crucible. The filter paper is burned on a platinum wire, and the residue also added to the crucible. The contents of the crucible are fused with a little sodium carbonate, and the cooled mass treated in the crucible with sulphuric acid, heat being gradually applied until fumes of sulphuric anhydride are evolved. After cooling, the liquid or pasty mass is dissolved in a mixture of 100 c.c. water and 20 c.c. sulphurous acid. Then, after neutralizing with ammonia until the precipitated titanic acid dissolves with difficulty, 5 to 8 grammes of sodium acetate (in solution) and 25 c.c. of acetic acid (sp. gr. 1.04) are added. The solution is boiled for several minutes; digested at a temperature just below boiling on the steam-bath for half an hour; the precipitated titanic hydrate filtered; washed with hot water containing 5 per cent. of acetic acid, and finally with hot water; ignited and weighed as titanic oxide (TiO_2).

Method for Estimating Vanadium in Titaniferous Magnetites.

Ten grammes of the finely pulverized ore are thoroughly mixed with 50 grammes of sodium carbonate and 6 grammes

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[*] Gooch, *Am. Acad. of Arts and Sciences*, new series, vol. xii., p. 441.

of sodium nitrate. The mixture is added in small quantities
to a platinum crucible, each addition being thoroughly fused
before the next is added. In this way the infusible ferric ox-
ide is scattered throughout the melt instead of being agglom-
erated in a single large mass, which happens if the whole mix-
ture is fused at one time. After all is added and fused, the
whole mass is subjected for an hour to the highest temperature
which it is possible to obtain from two blast-lamps. The melt
is digested in boiling water until the carbonates, etc., are dis-
solved, and the ferric oxide thoroughly disintegrated. A second
fusion of the residue is found to be necessary in order to sep-
arate all the vanadium. After combining the aqueous extracts,
alcohol is added to reduce the manganese, after which the
greater part of the alkali is neutralized with perfectly colorless
nitric acid, the solution yet remaining slightly alkaline. Free
carbon dioxide is eliminated by boiling, care being taken to
keep the solution alkaline. During the neutralization and sub-
sequent boiling the bulk of the alumina and silica is precipi-
tated. Filter, and to the filtrate add nitric acid, drop by drop,
until just acid. The solution is again rendered slightly alka-
line by the addition of a few drops of sodium carbonate, boiled
for a few minutes, and again filtered. To the filtrate, still
slightly alkaline, barium nitrate is added. The precipitate con-
sisting of barium vanadate and barium carbonate (also barium
chromate, phosphate, etc., if these elements are present), is col-
lected on a filter-paper, and the filter-paper with its contents is
removed to a beaker and digested with dilute sulphuric acid
for some time. After filtering, the solution which contains the
vanadium as vanadic acid is concentrated to about 100 c.c.
The solution is rendered alkaline with 2 or 3 c.c. of ammonia;
heated to boiling for a few minutes to facilitate the conversion
of the vanadic acid into ammonium metavanadate; solid am-
monium chloride is added until it dissolves with difficulty, and
this is followed by 200 c.c. of a mixture of alcohol and ether
(1 : 1). The ammonium metavanadate almost immediately be-
gins to crystallize out, and after standing three or four hours in
a cool place, may be filtered. The precipitate is first washed
with a strong solution of ammonium chloride which has been
rendered alkaline with ammonia and which contains alcohol.
A final washing is made with the mixture of alcohol and ether.

The dried precipitate is ignited in a porcelain crucible, two or three drops of nitric acid added, re-ignited and weighed. Since, however, the titaniferous ores may contain small amounts of chromium and phosphorus, traces of the oxides of these elements may contaminate the vanadic oxide.* In order to obviate this probable error the vanadic oxide thus obtained is dissolved in sulphuric acid (1:1) and reduced by SO_2 after diluting. The sulphurous acid converts $V_2O_5 . x SO_3$ into $V_2O_4 . x SO_3$, which is perfectly unchanged in acid liquors, so that the excess of SO_2 can be removed by boiling in a current of carbon dioxide without danger of oxidation. After elimination of the sulphurous acid the solution, which should now have a volume of about 50 to 100 c.c., is titrated at a temperature of about 70–80° C. with a $^N/_{100}$ solution of potassium permanganate. As shown by Hillebrand,[†] at temperatures near boiling, chromium, if present, is oxidized, thus making the vanadium result too high. The phosphoric acid almost invariably present in smaller or larger amounts does not affect the result.

The coloration obtained by the permanganate generally disappears after a short time, but is reproduced by the addition of another drop. In every case the first appearance of the pink color is the indication that all the vanadium is oxidized. In solutions at a temperature near boiling (chromium absent) the first appearance of pink is permanent.

"One or two checks are always to be made by reducing again in a current of sulphur dioxide gas, boiling this out in a current of carbon dioxide again, and repeating the titration."[‡]

PREPARATION OF PURE VANADIC OXIDE.

Before proceeding with the precipitations of vanadium, subsequently described, it was found necessary to prepare pure vanadic oxide, since the various samples of vanadic acid and ammonium metavanadate at my disposal were found to leave an insoluble residue after digestion with hydrochloric or sul-

* Tungsten and molybdenum, if present in the ore, would also be found in the ignited vanadic oxide. In the ores examined neither could be detected. Recently W. F. Hillebrand (*Am. Jour. of Sci.* 1898, p. 209) has shown that molybdenum occurs in trace in many acidic rocks, but appears to be absent from basic types, such as gabbro.

† *Am. Jour. of Sci.*, 1898, p. 209.   ‡ *Ibid.*

phuric acid. Since in their occurrence the various minerals of vanadium, from which vanadic oxide of commerce is prepared, may have associated with them minerals containing tungsten, arsenic, copper, lead, bismuth, zinc, chromium, and phosphorus, these elements were particularly suspected as impurities.

Ammonium metavanadate (marked C. P.) was taken and eliminated from such of these elements as were present as follows: 100 grammes of the salt were dissolved in hot dilute sulphuric acid (water one part, acid two parts), an insoluble residue remaining. After cooling, diluting and filtering, the residue was found to consist of barium sulphate and a little silica. Tungsten if present would have been precipitated as yellow WO_3,[*][†] insoluble in hot sulphuric acid. The filtrate, after partially neutralizing with ammonia, was reduced with sulphurous acid and treated with a current of hydrogen sulphide. There was no precipitate, showing the absence of arsenic, copper, molybdenum,[‡] and bismuth. A portion of the solution was then made alkaline with ammonia, and the passage of hydrogen sulphide continued through it without the formation of any precipitate, indicating the absence of iron, alumina, titanic acid, zinc, etc. The other part of the solution, after the hydrogen sulphide was removed by boiling, aided by a current of carbon dioxide, was cooled and a portion tested[§] for phosphoric acid, after neutralizing with ammonia, by adding ammonium nitrate, a little nitric acid, and finally molybdic solution. No phosphorus was detected. The remainder of the solution was oxidized by potassium chlorate, then made strongly alkaline with ammonia and heated. Excess of pure ammonium chloride was added and the whole allowed to cool. The precipitated ammonium metavanadate was filtered and washed with a strong ammonium chloride solution until washings ceased to give a reaction for sulphuric acid. After drying in an air-bath at 110° C. the crystalline vanadate was transferred to a porcelain dish and heated in a gas muffle for two hours, the inside of the muffle being at a dull red heat.

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[*] Desi, *Jour. Am. Chem. Soc.*, 19, 213.
[†] Dammer, *Handbuch der anorganische Chemie, vol. iii.*, 706.
[‡] Fresenius, *Zeit. für Analyt. Chemie*, 35, 77–86.
[§] Holverscheit, *Chem. Central Blatt*, 1890, 1, 977.

Testing Purity of the Vanadic Oxide.—Different amounts were heated in a porcelain crucible until fused. In each case the resulting steel-gray crystalline mass was found to weigh exactly the same as the amount of vanadic oxide taken, indicating the absence of moisture and ammonia.

Further, different amounts were dissolved in sulphuric acid, reduced by a current of sulphur dioxide, and the excess of sulphur dioxide removed by boiling with carbonic acid. The solution was diluted with hot water and titrated with a standard potassium permanganate solution. The number of cubic centimetres of permanganate consumed was in each instance found to be the same as the calculated theoretical quantities. These results showed the vanadic oxide to consist of V_2O_5, and not a mixture of V_2O_4 and V_2O_5 as is claimed by many.[*]

Precipitation of Vanadium with Titanium in the "Acetate Method."

In the ordinary methods described for the estimation of the various constituents of iron-ores, the probable occurrence of vanadium is occasionally referred to, but no intimation is given as to where it may be identified in the usual schemes of analysis, or whether its presence will interfere with the correct determination of other elements. Recently W. F. Hillebrand[†] has pointed out that

"In the regular course of analysis vanadium will be weighed with alumina, ferric oxide, titanic acid, etc., since it is precipitated by both ammonia and sodium acetate in the presence of these and other metals; hence the alumina percentages in nearly all rock analyses heretofore made are subject to correction for the vanadium the rock may have held. . . . All determinations of iron are likewise affected by its presence."

In the analysis of the titaniferous ores vanadium was found contaminating the titanic acid precipitate obtained in estimating titanium according to the "acetate method" described by Blair,[‡] and referred to on page 17 of this article. In order to ascertain if vanadium is carried down with the tita-

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[*] Read, *Jour. of the Chem. Soc.*, 65, 313 ; Poggendorff's *Annalen der Physik und Chemie*, 22, 1 ; Watt's *Dictionary of Chemistry*, vol. iv., 849 ; *Jour. Amer. Chem. Soc.*, xx., No. 6, June, 1898.

[†] *Jour. Am. Chem. Soc.*, xx., No. 6, June, 1898.

[‡] *The Chem. Analysis of Iron*, p. 178.

nium completely or according to some ratio, vanadic oxide
and titanic oxide were mixed in different proportions and fused
with potassium disulphate. To the melt 2–3 c.c. of concen-
trated sulphuric acid were added. After re-fusing and cooling,
the cake was dissolved in 150 c.c. of water, the operation being
hastened by gently warming. The solution was cooled, and
after diluting, the usual traces of platinum (from the crucible)
were precipitated by hydrogen sulphide. The filtrate was
partly neutralized with ammonia until the precipitated titanic
hydrate redissolved with difficulty. To the solution were then
added 50 c.c. of strong sulphurous acid, 20 grammes of sodium
acetate (in solution), and one-sixth the total volume of acetic
acid (sp. gr. 1.04). The temperature was raised to boiling and
continued for several minutes. After digesting on the steam-
bath for half an hour the precipitated titanic acid was filtered,
washed with dilute acetic acid, dried, ignited and weighed.
The following are the results:

	Grammes of TiO_2 Taken.	Grammes of V_2O_5 Taken.	Molecular Ratio.	Weight of TiO_2 Precipitate.
I. { A	.4000	.9136	1 : 1	.4129
{ B	.4000	.9136	1 : 1	.4111
II. { A	.4000	.2316	4 : 1	.4071
{ B	.4000	.2316	4 : 1	.4092
III. { A	.4000	.0579	16 : 1	.4047
{ B	.4000	.0579	16 : 1	.4060
IV. { A	.4000	.0145	64 : 1	.4038
{ B	.4000	.0145	64 : 1	.4019

From the foregoing results it is to be observed that the vana-
dium is only partially precipitated, that the amount carried
down by the titanic acid depends somewhat upon the relative
proportions of titanic oxide and vanadic oxide present, and that
there does not appear to be any definite ratio between the
amount of vanadium present and the quantity precipitated.
The discrepancies in the results obtained, even when the same
quantities were used, suggested a variation due to the slight
differences of conditions. Accordingly Experiment II. was
repeated under the following conditions. In the first instance
the amount of free acetic acid was restricted to about one-
twentieth the total volume, while in another it equaled half
the volume. In the first case the amount of titanic acid ob-

tained weighed 0.4141 gramme, and in the latter, 0.4033 gramme, showing that the amount of vanadium precipitated depends upon the amount of free acetic acid, being less when the acid is present in great excess.

PRECIPITATION OF VANADIUM IN THE PRESENCE OF IRON.

(*a*) By Ammonia.

As previously remarked, Hillebrand has intimated that vanadium will appear in the ammonia precipitate of iron. He has also shown how in the dissolved precipitate the two may be estimated volumetrically, by means of a standard solution of potassium permanganate, the combined result being expressed in terms of iron. From this combined result the previously estimated proportion of the vanadium can be deducted, leaving the correct iron value of the sample. Having ascertained, however, that the precipitation of the vanadium with the iron is not always complete, the following experiments were made in order to determine the conditions under which it is wholly precipitated.

Experiment I.—To 0.3000 gramme of ferric oxide in a hydrochloric acid solution, was added 0.0855 gramme of vanadic oxide (molecular ratio 4:1). The solution was heated and a little potassium chlorate added. After again heating ammonia was added in slight excess beyond that required for precipitation, and the whole boiled for several minutes. The filtrate contained free ammonia, and when tested gave strong reactions for both iron and vanadium. The precipitate was washed with both cold and hot ammonia water of various strengths. In each case the washings gave reactions for iron and vanadium, the quantity present being greater the stronger the ammonia solution used. Washed with hot or cold distilled water the washings were likewise found to contain iron and vanadium. The addition of a little ammonium chloride to the wash-water, however, prevented this removal of iron and vanadium from the precipitate. On the other hand, ammonium chloride wash-water containing free ammonia was found to remove both iron and vanadium from the precipitate.

Experiment II.—The same course was followed as in Experiment I. except that boiling was continued until ammonia ceased to be evolved. The filtrate gave no reaction for iron or

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vanadium. The precipitate was washed with water containing
a little ammonium chloride, and then dissolved in as little hy-
drochloric acid as possible. Hydrochloric acid was used to dis-
solve the precipitate rather than sulphuric, since, in the subse-
quent reduction by SO_2, it was found impossible in a sulphuric
acid solution to reduce all the ferric iron. The dissolved pre-
cipitate was nearly neutralized with ammonia; reduced by SO_2
(the excess of SO_2 being removed); diluted with boiling water
to about 500 c.c., and, after the addition of 5–7 c.c. of " pre-
ventive solution "* titrated with standard permanganate, 24.6
c.c. being consumed. Separately the quantity of iron taken re-
quired 19.7 c.c. and the vanadium 4.9 c.c. of the standard, the
two quantities combined, or 24.6 c.c., being the same as that
required by the precipitate.

This experiment was repeated several times, and in each case
the results obtained were approximately the same as the cal-
culated.

Experiment III.—To 0.3000 gramme of ferric oxide in a hy-
drochloric acid solution was added 0.0855 gramme of vanadic
oxide which had been reduced by SO_2. The solution was
heated to boiling and ammonia added, the precipitate appear-
ing black, probably due to the presence of vanadyl oxide.
Boiling was continued until ammonia ceased to be evolved.
The filtrate when tested showed the presence of a very consid-
erable amount of vanadium, but did not give a reaction for iron.

From the foregoing experiments it is to be observed that for
the complete precipitation of vanadium in the presence of iron
by ammonia, free ammonia must be eliminated before filtering,
and that the vanadium should be present in the vanadic and
not in the hypovanadic condition. Since, however, the agen-
cies which oxidize the iron will oxidize the vanadium, loss of
the latter element because of a low state of oxidation is highly
improbable in the ordinary course of analysis.

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* The name " preventive solution " has been used by Dr. E. H. Miller (*Notes
on Quantitative Analysis for Electrical Engineers*, p. 19) instead of the confusing term
" titrating solution " for the solution used to obviate the errors due to chlorine
when titrations are made with potassium permanganate in a hydrochloric acid so-
lution.

The solution is made by dissolving 160 grammes of manganese sulphate in
1750 c.c. of water, then adding 330 c.c. of phosphoric acid, 1.7 sp. gr., and 320 c.c.
of concentrated sulphuric acid, 1.82 sp. gr.

Further, since by itself iron is completely precipitated by ammonia, it may be inferred that it is some compound of iron and vanadium (probably a ferric vanadate) soluble in ammonia, which carries a part of the former into the filtrate in the presence of free ammonia. That the two are chemically combined in the precipitate is also suggested by the fact that if vanadium were precipitated by the ammonia as ammonium metavanadate, considerable of the vanadium would remain in solution, as the metavanadate would be quite soluble under the conditions of temperature and dilution maintained in the experiments.

(*b*) In Basic Acetate Precipitation.

To a hydrochloric acid solution containing 0.3000 gramme of ferric oxide and 0.0855 gramme of vanadic oxide a little potassium chlorate was added and the solution boiled. After cooling, the solution was carefully neutralized with sodium carbonate solution until a drop of the diluted carbonate solution gave a slight permanent precipitate. The precipitate was dissolved by a drop of dilute hydrochloric acid. After diluting to 800 c.c., 10 grammes of sodium acetate (in solution) were added, and the solution heated to boiling, boiling being continued for one minute. After filtering, neither iron nor vanadium could be detected in the filtrate. The precipitate was washed with dilute ammonium chloride, dried, ignited, dissolved in hydrochloric acid, reduced (by SO_2), and finally titrated with potassium permanganate, using the "preventive solution." The following results were obtained:

								C.c. of $KMnO_4$ Calculated.	C.c. of $KMnO_4$ Required.
(1),	.	.	.	.	.	.	.	24.6	24.62
(2),	.	.	.	.	.	.	.	24.6	24.57
(3),	.	.	.	.	.	.	.	24.6	24.60

From these results it is to be observed that when the ordinary conditions are followed the precipitation of vanadium with iron in the basic acetate precipitation is complete.

(*c*) By Ammonium Succinate.

The same quantities of ferric oxide and vanadic oxide were used as in the basic acetate precipitations referred to above. Oxidation and neutralization were also similarly effected.

Experiment I.—The neutral solution of the mixed oxides was diluted to 300 c.c., ammonium succinate added, and the

precipitate, which immediately formed, was filtered without warning. The filtrate was found to contain considerable of both iron and vanadium. When the precipitate was washed with hot or cold water, the washings were found to give reactions for both vanadium and iron; but when a dilute solution of ammonium chloride was used, neither could be detected.

Experiment II.—Repeated Experiment I., and, in addition, heated to boiling, and boiled for two minutes before filtering. The filtrate gave strong reactions for iron and vanadium.

Experiment III.—Repeated Experiment II., but in this instance boiling was continued for ten minutes. Iron or vanadium could not be detected in the filtrate. The precipitate was washed with ammonium chloride, dried, ignited, dissolved in hydrochloric acid, and, after reduction (with SO_2), titrated with potassium permanganate, using the "preventive solution." The following results were obtained:

	C.c. of $KMnO_4$ Calculated.	C.c. of $KMnO_4$ Required.
(1), ...	24.6	24.60
(2), ...	24.6	24.60
(3), ...	24.6	24.58

Experiment IV.—In this instance the volume was restricted to 100 c.c.; otherwise, the same conditions were followed as in Experiment III. The filtrate was found to contain a very considerable proportion of both iron and vanadium.

From the above results it is to be observed that vanadium is completely precipitated with iron by ammonium succinate under the following conditions. After careful neutralization, the solution must be diluted so that its volume is about 750 c.c. for every gramme of the mixed oxides present; the precipitate should be boiled eight to ten minutes; the wash-water should contain a little ammonium chloride.

(*d*) By Sodium Benzoate.

Using sodium benzoate as a precipitant instead of ammonium succinate, the experiments, as described under (*c*), were repeated, and with approximately the same results.

(*e*) By Caustic Potash.

Experiment I.—A hydrochloric acid solution containing 0.3000 gramme of ferric oxide and 0.0855 gramme of vanadic

oxide (molecular proportions 4 : 1) was neutralized until slightly acid. One or two grammes of potassium chlorate were added, and the solution boiled for a few minutes. After cooling, caustic potash solution was added in slight excess of that required to effect complete precipitation. Without warming, the solution was filtered. The filtrate gave strong reactions for both iron and vanadium.

Experiment II.—The quantities of ferric oxide and vanadic oxide used, also the preliminary conditions, were the same as in Experiment I. The solution, however, was heated to boiling before the addition of the caustic potash, which was added in considerable excess. After precipitation, boiling was continued for two or three minutes. The filtrate gave strong reactions for iron and vanadium.

Experiment III.—Repeated Experiment II., using a large excess of caustic potash, and boiled vigorously for one hour. The filtrate contained both iron and vanadium in large quantities.

From the foregoing experiments it is to be noted that vanadium is not completely precipitated with iron by caustic potash, the ferric vanadate (?) being soluble in excess of the precipitant. It is also to be observed that the separation of vanadium as soluble alkaline vanadate from iron cannot be effected by boiling the two in a strong alkaline solution.

PRECIPITATION OF VANADIUM IN THE PRESENCE OF ALUMINUM—BY AMMONIA.

Experiment I.—0.1913 gramme of alumina and 0.0855 gramme of vanadic oxide (molecular ratio, 4 : 1) were brought together in a hydrochloric acid solution and boiled. After cooling, ammonia was added in slight excess of that required for complete precipitation. The reddish-yellow precipitate was found to contain both vanadium and aluminum, while the filtrate, which retained the reddish-yellow tint characteristic of free vanadic acid, was also found to contain both of these elements.

Experiment II.—Quantities and conditions the same as in Experiment I.; but instead of working in the cold the solution was brought to boiling. Just before coming to a boil the reddish-yellow color of both the precipitate and the solution began

to disappear. After a few minutes boiling the precipitate became white, and the solution, which still contained free ammonia, became colorless. After filtration, both the precipitate and the solution were found to contain vanadium, the major portion being in the latter.

Experiment III.—Quantities and conditions similar to Experiments I. and II. The solution was boiled until all the free ammonia was expelled. Just as the last traces of ammonia were being eliminated, both the solution and the precipitate began to assume a faint yellowish tinge, which intensified, with prolonged boiling, to a deep reddish-yellow. Boiling was continued for half an hour, the color still remaining. After filtration, the solution was found to contain nearly all of the vanadium and traces of alumina. On the other hand, the precipitate was found to contain nearly all the alumina and also a small quantity of vanadium; the latter could not be removed by washing twenty-five times with boiling water.

From these experiments it is to be observed that vanadium is only partially precipitated by ammonia in the presence of aluminum, and also that the precipitation of aluminum is incomplete in the presence of vanadic oxide. In this respect the influence of aluminum differs from that of iron, since, in the presence of the latter, as has been shown, vanadium, as well as the iron, can be completely precipitated by ammonia.

OCCURRENCE OF VANADIUM IN TITANIFEROUS MAGNETITES.

In review of the analyses (p. 15) of the magnetic iron ores previously described, it may be noted that vanadium invariably appears as a constituent of those ores which are titaniferous. A number of non-titaniferous ores besides those described were examined for this element, but in no instance was it detected. The first few examinations of the non-titaniferous ores, however, yielded traces of vanadium, but in unappreciable amounts.

In the *Journal of the Franklin Institute* (November 19, 1889) Professor E. F. Smith reports the occurrence of vanadium in caustic potash. Donath* also reports finding as much as 0.16 per cent. of vanadic oxide in a sample of commercial

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* Dingler's *Polytechnisches Journal*, 240, 318.

caustic soda. These facts suggested that the constant trace of vanadium, which the non-titaniferous ores yielded, might be due to its occurrence in the carbonate used in the fusion rather than in the ore itself. Accordingly a blank analysis was made, using the same amount of alkali carbonate as before. The same trace of vanadium was obtained. This trace, when dissolved and treated in alkali solution with hydrogen sulphide, gave approximately the same intensity of ammonium sulpho-vanadate coloration as had been obtained from the treatment of the ore.

That vanadium is an invariable constituent of titaniferous minerals, as rutile, brookite, anatase, titanite, etc., has frequently been noted. From the analyses (p. 15), however, it is to be observed that an approximate ratio appears to exist between the percentage of titanic oxide and vanadic oxide present in these titaniferous ores, thus:

Number of Ore.	Percentage of TiO_2.	Percentage of V_2O_5.	Ratio of TiO_2 to V_2O_5.
VIII	10.21	.35	29 : 1
IX	13.52	.52	26 : 1
X.	6.41	.23	28 : 1
XI	8.17	.29	28 : 1
XII	17.23	.63	27 : 1

The following analyses of five Adirondack titaniferous magnetites, made by the U. S. Geol. Survey for Prof. J. F. Kemp (to whom I am indebted for their presentation), appear to corroborate this ratio:

	Percentage of TiO_2.	Percentage of V_2O_5.	Ratio of TiO_2 to V_2O_5.
1	18.82	.62	30 : 1
2	13.07	.50	26 : 1
3	10.55	.34	31 : 1
4	16.45	.61	27 : 1
5	15.66	.55	28 : 1

From the foregoing analyses it appears that in the titaniferous magnetites, vanadic and titanic oxides follow a ratio approximating 1 : 28. From the regularity manifested in the

proportion of vanadium to titanium it is possible that in the titaniferous ores these two elements are related to each other in a manner analogous to that existing in the complex, inorganic acids which have been studied by Gibbs, Marignac, and others.

In these complex, inorganic acids we find one oxide related to another in a definite ratio, regular series following with gradations in content of one of the acidic oxides to the other; for example, in the phosphomolybdic acids the ratio of P_2O_5 to MoO_3 varies in different compounds from $1:10$ to $1:48$. In some of these acids, ratios of 10, 32, 36, 44 and 48 molecules of MoO_3 to one of P_2O_5 seem to constitute acids which are more or less definite. That titanium is capable of combining with other acidic oxides to form complex inorganic acids is shown by the phosphotitanates. On the other hand, Gibbs has shown "that V_2O_5 may form combinations with a number of molecules of tungstic or molybdic teroxide analagous to phosphotungstates, or phosphomolybdates." Thus from our knowledge of the complex, inorganic acids and from the proportion of V_2O_5 to TiO_2 in these ores, it would seem that a complex, inorganic acid containing vanadic and titanic oxides (vanadotitanate), in which the ratio approximates $1:28$, exists in these titaniferous magnetites. Or it may be possible that a complex, inorganic acid containing a less amount of titanic oxide than that expressed in the ratio of $1:28$ exists, and that the additional titanic oxide, indicated by analyses, occurs combined with iron as iron titanate.

OCCURRENCE OF NICKEL AND COBALT IN TITANIFEROUS MAGNETITES.

Of the magnetites examined it has been found that nickel and cobalt are universal constituents of those ores which are titaniferous, while the non-titaniferous magnetites of the region have not, so far as examined, been found to contain any. Both metals are always present, the nickel invariably greatly in excess of the cobalt, but apparently with no relation.

In addition to the magnetites previously described the following titaniferous ores were subjected to partial analyses and yielded the following results:

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Metallic Ni and Co, .	.39	.27	.32	.68	.11	.17	.08	.10
TiO_2, . .	12.01	9.70	18.30	7.70	8.60			
Metallic Fe, .	58.20	61.20	56.40	64.20	—	—	—	—
S, . . .	0.13	.08	.1	.14	—	—	—	—

Localities.—I. Newfoundland. II. North shore of Lake Superior. III. Minnesota. IV. Glamorgan, Victoria county. V. Ivigtut,* Norway. VI., VII., VIII. Adirondacks, N. Y.

From these analyses it may be inferred that the occurrence of nickel and cobalt in titaniferous magnetites is general and not peculiar to the ores of the region particularly discussed.

The presence of nickel in an ore rich in titanium has been recorded in the analysis of the titaniferous magnetite of Cumberland, R. I. This deposit occurs in a peridotite, and by some the nickel has been regarded as being combined in the olivine. The gabbros, pyroxenites, etc., in which the ores already referred to occur, are olivine free and without evidence of its alteration products. Hence, in these instances, we cannot regard the nickel as isomorphous with iron in olivine.

Further, in its most abundant American occurrence nickel is found as a constituent of pyrrhotite, and in this association is believed to exist as a sulphide. Review of the analyses, however, shows us that the titaniferous magnetites are very low in sulphur, and in several cases the total sulphur present is insufficient, on the basis of a sulphide combination, to account for even the small percentage of nickel present. In these instances, then, we must look for a different combination for at least a part, if not all, of the nickel. Since, however, nickel in many of its combinations affords compounds analogous with those of zinc, iron, etc., we might assume that in these ores it occurs as an oxide.

Cutting the limestones, gneisses, and gabbros, over the area under consideration, we find a great abundance of dikes. Many observers, as Sir Wm. Logan, Vennor, Prof. Harrington, and others, have noted their occurrence, and many have been described. Recently† Prof. W. G. Miller and R. W. Brock, School of Mining, Kingston, referring to a basic dike located along the Rideau canal, have drawn attention to the fact that it contains nickel. Acting upon this suggestion, a number of

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* Purchased sample. † *Canadian Record of Science*, Oct., 1895.

dikes from Eastern Ontario, together with several from the Adirondack region, N. Y., have been examined for nickel, the results being as follows:

	I.	II.	III. Per Cent.	IV.	V.	VI.	VII. Per Cent.	VIII. Per Cent.	IX. Per Cent.
Ni and Co,	trace.	trace.	.09	none.	none.	trace.	.07	.73	.51

I. From Bedford township, Frontenac county. This dike is evidently an altered diabase. The bisilicate is a secondary hornblende. A few irregular masses of magnetite are present but no olivine was observed.

II. From Adam's bay along the Rideau canal. In thin sections it presents the characteristics of a diorite. A little magnetite is present, but no olivine.

III. From Dungannon, Hastings county. Typical diabase. No olivine is present.

IV. From Dungannon, Hastings county. A diorite.

V. From near Jay, Essex county, N. Y. A camptonite.

VI. From Clinton county, N. Y. A typical diabase containing a little olivine.

VII. From Franklin county, N. Y. An olivine diabase.

VIII. From Lutterworth, Victoria county. This dike is an olivine free diabase containing a little hypersthene and considerable magnetite in irregular grains.

IX. From Snowdon, Victoria county. The same as VIII.

From the analyses we observe that only two of the dikes examined carry more than a trace of nickel and cobalt. These two dikes are olivine free, while others containing this bisilicate have only traces of the two metals. These facts corroborate the previous opinion that nickel (also cobalt) is present in these titaniferous ores, in a combination other than that of olivine.

Examined in thin sections, these two dikes present no characteristics distinguishing them from the diabase dikes containing only traces of nickel and cobalt, other than a slightly greater proportion of magnetite. In order to ascertain if the nickel and cobalt in these two dikes are intimately associated with the magnetite, 600 grammes of the Lutterworth dike (crushed so as to pass through a 40-mesh sieve) were subjected to magnetic concentration, using a current of 0.5 amperes. The magnetic heads weighed 36 grammes. A comparison be-

tween the quantities of iron, sulphur, silica, nickel and cobalt present in the dike and in the concentrates is afforded by the following analyses:

											Dike.	Concentrates.
Fe,	.	.	.	.	.	.	.	.	.	.	15.71	32.60
S,	.	.	.	.	.	.	.	.	.	.	.21	.15
SiO$_2$,	.	.	.	.	.	.	.	.	.	.	45.13	40.50
Ni and Co,	.	.	.	.	.	.	.	.	.	.	.73	1.87

These analyses show not only that the proportion of iron is increased in the concentrates, but also that of the nickel and cobalt, while at the same time the proportion of sulphur is somewhat lessened. From these results it may be inferred that between the magnetite (which is titaniferous) in these dikes and the nickel and cobalt, there is an intimate association. These results would, therefore, support the theory (page 33) that in the titaniferous ores nickel (also cobalt) occurs as the oxide of a spinel molecule.

Although the percentage of nickel so far obtained in these titaniferous magnetites is small, yet there is reason for believing that magnetites may be found containing a higher percentage of this metal than those already examined. In this connection it is to be remembered that some of the Canadian pyrrhotites, which are also believed to be of igneous origin, contain amounts of nickel which make them valuable as ores, while others contain the metal in only traces.

These titaniferous ore-bodies, although occurring in enormous masses in Canada and various localities in the United States, have so far baffled economic reduction, and by many are regarded as beyond present metallurgical methods. In a recent paper,* formulating the results of experiments carried on in a small experimental furnace at Buffalo, A. J. Rossi claims to have obviated the difficulties. But whatever may be the opinion of metallurgists regarding the possibility of smelting these ores, there appears to be a general appreciation of the special qualities of the metal obtained from them. The superior quality of such iron has been thought by some metallurgists to be due to the absence of phosphorus; others regard it as due to the presence of titanium. In a general manner it may be said that if it is due to the presence of titanium, very small quantities of

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* *The Iron Age*, February 6 and 20, 1896.

this substance are then sufficient to secure these results. "In our blast-furnace tests we have not been able to obtain more than a few hundredths to one-tenth of 1 per cent. of titanium . . . . and still the qualities of the pig metal and iron were exceptionally good."*

The fact that iron produced from titaniferous ores is of a very high quality may have some connection with the occurrence of nickel in these ores. Even a very small percentage of nickel in an iron-ore would be of value if the total nickel present could be extracted along with the iron in smelting, as the resulting alloy might be used directly in the production of nickel steel. In this connection a sample of pig-iron—the product of Mr. Rossi's experiments on titaniferous ores at Buffalo—was examined for nickel, and found to contain 0.11 per cent. Samples of the ore, however, upon which Mr. Rossi's experiments were made, I have not been able to secure. Consequently, I have not been able to ascertain what proportion of the nickel in the ore is extracted with the iron in a blast-furnace operation. However, in order to arrive at some idea regarding this important question, 100 grammes of the Lutterworth dike, pulverized to 100-mesh and fluxed according to Percy's minimum charge, were fused in a brasque-lined crucible. A small button of iron was obtained. Analyzed, it was found to contain 11.6 grammes of iron and 0.58 gramme of nickel and cobalt. The calculated amounts of these metals (based upon the analyses at bottom of this page)† present in the 100 grammes would be 13.7 grammes of iron and 0.73

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* *The Iron Age*, February 6 and 20, 1896.

† Analysis of Lutterworth dike :

Ni and Co, ...	0.73
FeO, ...	13.11
Fe₂O₃, ...	5.22
CaO, ...	10.32
MgO, ...	5.78
Na₂O, ...	1.01
K₂O, ...	.87
SiO₂, ...	44.91
TiO₂, ...	1.84
Al₂O₃, ...	14.41
S, ...	.12
Moisture, etc., ...	1.13
	99.45

gramme of nickel and cobalt. From these results it may be inferred that nickel would be as easily reduced and collected in a blast-furnace as iron.

Examination of Titaniferous Magnetites for Platinum.

The occurrence of platinum in igneous and metamorphic rocks of the general type met with in association with the titaniferous magnetites, previously described, suggested the possibility of the metal being present in the ores. In almost all of the hitherto described platinum localities the associated rocks have been peridotites, or serpentines which are themselves altered peridotites or pyroxenites. Thus, at Tagilsk and Biserk, Russia, the platiniferous area is completely bounded by serpentine rocks, while in California the placers containing platinum are always in close proximity to serpentine.

Recently, Emmens* found platinum to the extent of 0.25 per cent. in the nickel oxide manufactured by the Orford Copper Company from Sudbury matte. The pyrrhotite and chalcopyrite from which the matte was produced are regarded as constituting a basic segregation in a more or less metamorphosed diabase or gabbro.

These facts suggested that platinum might be present in the segregated titaniferous magnetites occurring in gabbros, and containing a small proportion of nickel. Two hundred grammes of ore from the Pine Lake (p. 13), Horton (p. 14), and Chaffey (p. 12) ore-bodies, respectively, were assayed for this metal, but in no instance could the faintest trace be detected.

The Elimination of Titanic Oxide from Titaniferous Magnetite by Magnetic Concentration.

Many have suggested and some have claimed the possibility of reducing titanic oxide in titaniferous magnetites by magnetic concentration. Nothing definite regarding such a concentration appearing in the literature at my disposal, a number of experiments were conducted to ascertain if such a separation might be effected. The experiments were made with a Wetherell magnetic concentrator at Newark, N. J. The ore in each case was crushed so as to pass through a 40-mesh but not through a 60-mesh.

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* *Min. Industry*, 1892, vol. i., p. 377.

I. *Eagle Lake Ore.*—As already remarked, the ore is characteristically homogeneous, even thin sections under the microscope failing to exhibit any foreign constituent. The first attempt to effect a separation was made, using the current from a single small dry cell. Every particle of ore was picked up by the magnet. Other attempts were made having the current further reduced, but as long as the current was of sufficient strength to enable the magnet to attract a single particle, every particle within the field was picked up. Thus, for this ore, no separation whatever could be effected.

II. *Pine Lake Ore.*—This ore has already been described as being impregnated with more or less augite, and contains 13.52 per cent. of titanic oxide and 43.38 per cent. of metallic iron. The sample treated weighed 380 grammes. The results obtained are shown in the following table:

	Sample.	Current.	Weight of Hea's.	Per Cent. of TiO$_2$.	Per Cent. of Fe.
			Grammes.		
I....	Ore.	Single dry cell.	272.0	18.10	56. 45
II....	Tailings from I.	2 amperes.	17.3	1.62	......
III....	Tailings from II.	5 "	7.8	1.41	......
IV....	Tailings from III.	10 "	3.1	1.29	......
V ...	Tailings from IV.	15 "	2.0	1.35	......
VI....	Tailings from V.	17 "	13.1	1.30	......
	Final tails............		64.0	1.19	5.33
	Lost............		17.0		

From the above it is to be observed that as a result of the magnetic concentration the percentage of metallic iron has increased from 43.38 per cent. in the ore to 56.45 per cent. in the heads, but at the same time the titanic oxide has increased from 13.5 per cent. to 18.1. Fractionally expressed, the metallic iron has increased by $\frac{10}{33}$, while the titanic oxide has increased by $\frac{11}{33}$. From this close relation in the increase of percentage, it may be inferred that in this ore the titanic and iron oxides are at least intimately associated, if not chemically combined.

III. *Chaffey Ore.*—This ore, which is fine-grained, contains a small amount of pyroxene and of pyrite. A sample containing more than the average quantity of pyrite was selected, in order to more readily ascertain the proportion of sulphur which would

be eliminated by the magnetic concentration. A current of 0.25 amperes was used.

							Ore. Grammes.	Heads. Grammes.	Tails. Grammes.
Weight,	.	.	.	.	.	.	720	640	73
							Per cent.	Per Cent.	Per Cent.
Fe,	.	.	.	.	.	.	53.0	56.1	27.0
TiO$_2$,	.	.	.	.	.	.	7.4	5.0	29.9
S,	.	.	.	.	.	.	1.5	1.3	2.8
SiO$_2$,	.	.	.	.	.	.	7.0	6.2	14.6

From these results it is to be observed that the magnetic concentration of this ore has effected a partial removal of silica, sulphur, and titanium, while the proportion of metallic iron has been slightly increased. The fact that the tails, which constitute only one-ninth of the original sample, contain two-fifths of the whole titanic oxide is particularly noteworthy. This would show that at least a portion of the titanium occurs in this ore in a non-magnetic combination, and since the sample treated would not pass through a 60-mesh, it would also indicate that this non-magnetic titaniferous combination forms particles of considerable size. From this it may be inferred that in some titaniferous ore-bodies, where the conditions of temperature and pressure at the time of segregation differed from those under which the Chaffey ore-body was formed, these titaniferous particles might be larger, and thus permit of a more complete magnetic elimination of the titanic oxide. On the other hand, in those cases where the proportion of titanium cannot be reduced by magnetic concentration it is probably due to the fact that the titaniferous constituent of the ore exists in such small particles that it is held mechanically by the magnetic portion.

Besides the three general occurrences of magnetite previously cited, there are also found along shore lines, in various parts of the world, siliceous sands containing a greater or less proportion of heavy black grains, which consist chiefly of iron minerals. The proportion of these minerals to the whole mass of sand is generally very small. In places, however, the action of moving water has effected a concentration of the heavier ferruginous constituents, giving rise to accumulations of so-called iron sands. Such beds are at present forming in various localities, as along the shores of the Lower St. Lawrence, the

Mediterranean, the Baltic, Lake Superior, etc. The source of the minerals comprising these beds is easily traced to the various crystalline rocks which, by their disintegration, have given rise to the siliceous sands. Hence, as might be expected, these "iron sands" contain iron in the various ore combinations found in the different crystalline rocks, as hematite, magnetite, ilmenite, etc. Some of these sands are completely magnetic and non-titaniferous. On the other hand, others, by means of a magnet, can be separated into a magnetic portion which is free from titanium and a non-magnetic part which is chiefly titanic iron. Thus an "iron sand" from the north shore of Lake Superior, when treated with a small hand-magnet, yielded grains quite free from titanium, and which were evidently pure magnetite. The remaining black grains were found to contain 47.8 per cent. of titanic oxide.

Many of the schists and gneisses found in Archæan areas are believed to be metamorphosed sediments or beach deposits, and the iron ore-bodies which they contain are regarded as having a similar genesis. If the original "iron sand" which afforded these ore-bodies contained both magnetite and titaniferous iron, the resulting ore would undoubtedly be titaniferous; and if the metamorphism had not been too pronounced, the ore might, when crushed, be resolved by means of a magnet into a magnetic and non-magnetic portion. Probably some of the titaniferous ores, in which the proportion of titanic oxide is reported to have been largely reduced by magnetic concentration, have had such an origin.

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1898–99. University Fellow in Chemistry, Columbia University.

Published Papers.

"Volumetric Estimation of Lead." *Journal of the American Chemical Society*, August, 1896. Vol. XVIII.

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