



GEOLOGICAL
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DEPARTMENT OF ENERGY,
MINES AND RESOURCES

PAPER 69-54

THE FERRIDE ELEMENT CONTENT OF
TITANIFEROUS MAGNETITE IN CANADA

(Report and 1 table)

E. R. Rose

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ABSTRACT

The term titaniferous magnetite is defined, and historical progress in the knowledge and utilization of titaniferous magnetite is summarized. The distribution and nature of titaniferous magnetite deposits in Canada is outlined and reference is made to the general geology and mineralogy. Much new analytical data on the ferride element content of titaniferous magnetite is shown in Table I. Comparisons made between the analyses of natural titaniferous magnetite (crude potential ore material) with those of magnetic concentrates made from them, give a measure of both the grade and relative ease of concentration of most of the occurrences. The high metal content of the magnetic concentrates made from many samples of titaniferous magnetite deposits suggests that they should be given consideration as sources of materials from which iron, titanium, and vanadium, as well as other elements and minerals might be recovered.

THE FERRIDE ELEMENT CONTENT OF TITANIFEROUS MAGNETITE IN CANADA

INTRODUCTION

Scope and Acknowledgments

The purpose of this paper is to indicate the chemical and mineralogical composition of a large number of titaniferous magnetite deposits in Canada, to outline their geological setting, and thus to suggest a measure of their industrial potential. A number of analyses of samples taken from titaniferous magnetite deposits in Canada and of magnetic concentrates made from the samples are recorded in Table I. The field work and most of the analytical work on which this report is based was done for the Geological Survey of Canada; the samples were collected and magnetic concentrates made from them by the writer; chemical analyses were done over a period of years by J. A. Maxwell, S. Abbey, K. Hoops, S. Courville, G. Bender, J. L. Bouvier, P. Gauthier and R. Beaulne, spectrographic analyses by W. H. Champ, J. P. Malone, K. A. Church and the late W. F. White, and X-ray fluorescence analyses by G. Lachance, all of the Analytical Laboratories of the Geological Survey of Canada. A number of chemical analyses were gathered from the literature, and several were done in the Analytical Chemistry Subdivision of the Mineral Science Division of the Mines Branch, under W. L. Chase and W. R. Inman, Chief Chemist. The manuscript has been critically read by D. R. E. Whitmore.

A Geological Survey Economic Geology series report, on the Geology of Titanium and Titaniferous Deposits in Canada (Rose, 1969), gives additional information and detail on this subject and it is recommended as a companion volume. Titaniferous magnetite forms an important part of titanium occurrences in Canada. Much new information on the composition of titaniferous magnetite in Canada is given in this account.

Although only selected references are given the selections listed lead the reader by way of their respective bibliographies back into a long story of investigation and discovery, of success and failure, and of effort and progress. It is upon this foundation that the present paper is based.

Terminology

The term titaniferous magnetite may be used in restricted mineralogical sense to describe titanium-bearing magnetite (i. e. titanian magnetite and titanomag-
netite), or with broader geological connotation, to refer to a body of rock that has a

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large content of these minerals, in much the same way that the term dolomite has been used to refer both to the mineral and rock. This usage has no doubt developed because it is virtually impossible visually to distinguish titanium-bearing magnetite from non-titanian magnetite in the field, except perhaps through mineral and rock associations, and striated crystals, and also because there is commonly no sharp difference between titaniferous magnetite deposits and their host rocks. Not only is the titanium content of magnetite variable without visible expression, and this is true also for the other ferride elements (Fe, Ti, V, Cr, Mn, Co, Ni), but the main components (Fe, Ti and O) combine in various proportions to form a series of mix-crystals that form complex intergrowths of Fe - Ti oxide minerals which in turn are not identifiable in the field and only with difficulty in the laboratory. Ferrian ilmenite, one end member of this mineral series, commonly occurs with titanomagnetite, both as a fine-grained intimate intergrowth within the magnetite and as separate grains, and although these separate grains are essentially ilmenite (titanic iron) they are in places sufficiently magnetic to pass as magnetite.

In the broad geological sense titaniferous magnetites may be described as occurrences or deposits of titanium-bearing magnetites in rocks. They consist mainly of mixtures of titanian magnetite, titanomagnetite, ferrian ilmenite, ilmenite, ilmenite-hematite, hemo-ilmenite, magnetite-ilmenite, ulvöspinel, and other members of an oxy-solid solution series of iron-titanium oxide minerals, and they are commonly disseminated through a mafic igneous rock or concentrated in more massive segregations within such a rock, but they may also occur in the heavy dark sands and sandstones derived from other rocks by weathering, erosion and sedimentation. Because of the mineralogical complexity the geological definition is useful, and the term titaniferous magnetite is used here as a general mineralogical term to include titanian magnetite and titanomagnetite, as well as a general geological term. In this account titanian magnetites are arbitrarily considered to carry from 0.1 to 1 per cent Ti, grading into titanomagnetites that carry from 1 to 15 per cent Ti and from them into mixtures with ulvöspinel, ilmenite-hematite, and more rarely some rutile, that carry from 15 to 20 per cent or more titanium. These are the main ore minerals of titaniferous magnetite deposits.

With increasing ilmenite and titanium content titaniferous magnetite deposits grade into ilmenite deposits that range from about 20 to 45 per cent titanium. The term 'low titanium magnetite' is used to describe magnetite carrying less than 1 per cent Ti. Magnetite that carries less than 1 per cent Ti may find use as an ore of iron, although current blast furnace practices in North America restrict the use of iron ores containing more than 0.1 per cent Ti.

Historical Résumé

Progress in the utilization of the world's titaniferous magnetite deposits, as well as of those in Canada, presents a rather unimpressive record. It has generally been considered uneconomic to use them as iron ore, and their trace elements have been widely considered as deleterious. Some of these elements, especially titanium and vanadium could be regarded as assets rather than liabilities as processes were developed to recover them. The following résumé reviews briefly some of the limited progress made to date in this direction and points the way to further progress.

The presence of a new element, "menachite" (titanium) was first suspected in 1790 by McGregor in the new mineral "menachanite" (ilmenite) in sands from Cornwall, England, but it was not until 1910 that relatively pure titanium metal was isolated and prepared in the laboratory by Hunter. In the eighteenth century and earlier both ilmenite and titaniferous magnetite were mined on a small scale for iron

in Asia and Europe, and later in America, before it was recognized that they carried titanium. The most enduring of these mining and smelting operations appears to have been at Taberg in Sweden, in the Egersund district of Norway, and in the Ilmen Mountains, a branch of the Urals, in Russia, as well as at Sanford Lake in New York State (1840-1856) preceding the modern operation there. Some ilmenite from Norway was successfully smelted in England, in the 1800s, and in 1859-61 Robert Mushet attempted to develop processes using titanite pig metals and alloys to purify steel in England.

In Canada, an iron deposit near Newboro, Ontario, reported by Alexander Murray of the Geological Survey of Canada in 1852, was opened in 1858 and a small tonnage of titaniferous magnetite was shipped as good quality iron ore from the Matthews and Chaffey pits via the Rideau Canal to the United States for smelting (Hunt, 1866). Some excellent quality iron is reported to have been produced in 1867-68 from furnaces at Moisie, Quebec, using titaniferous magnetite recovered from both sand and bedrock in Sept Iles Bay area, and at St. Urbain, Quebec, in 1873-74, from furnaces using ilmenite (titanic iron) as ore (Dulieux, 1915). Experimental work by Haanel (1907) and Stansfield (1916) and others indicated the feasibility of smelting some Canadian titaniferous ores. Extensive and interesting studies and experiments on the utilization of the St. Charles titaniferous magnetites were carried out in 1924 by the Federal Mines Branch (Robinson, 1926) and by the Quebec Department of Mines in 1941-42 (Bourgoin, 1943), and some good quality pig iron castings were made. The feasibility of the utilization of St. Charles titaniferous magnetites once again was indicated.

In 1830 a new element was first definitely identified by N. G. Sefstrom in pig iron made from titaniferous magnetite ore of Taberg, Sweden, and was named vanadium by him, although it had been previously suspected in another form by M. del Rio in Mexico in 1801. Subsequently some attempts were made to recover vanadium from titaniferous magnetite in Sweden, Norway, England and Germany, and more recently it has been commercially recovered from titaniferous magnetite at Otanmäki, Finland, in the Russian Urals, and from the Bushveld Complex near Steelport in South Africa. In Japan, vanadium is recovered from the waste sulphuric acid used in the manufacture of titanium dioxide (DeHuff, 1966).

The titanium pigment industry, based on ilmenite, had its start on a small scale in Norway in 1918, and since 1942 the National Lead Company has been mining titaniferous magnetite deposits from which both magnetite (titanomagnetite) and ilmenite are recovered and used, at Sanford Lake (Tahawus) in New York State, magnetite (titanomagnetite) as iron ore, ilmenite as a source of TiO_2 for pigment (Osborne, 1944; Elliott, 1959). As additional sources of TiO_2 for the pigment industry, large ilmenite-hematite deposits at Lac Allard, Quebec, were opened in 1954 by Quebec Iron and Titanium Corporation, and others at Tellnes, Norway, in 1957 by National Lead Company (Stamper, 1965).

Since the turn of the century numerous extensive experiments have been carried out in the United States, Germany, Russia, South Africa, Canada and New Zealand, many of which have indicated the feasibility of making good quality iron and steel using titaniferous magnetite ore and recovering vanadium as well (Goodwin, 1921; Harris *et al.*, 1924). Although titaniferous magnetite is being smelted commercially now in both Finland (Otanmäki), the U. S. S. R. (Kachkanar Mountain), and the Republic of South Africa (Highveld Steel and Vanadium Corp. Ltd., Witbank, South Africa) this is not yet being done in America.

The deposit being mined in the U. S. S. R. is believed to hold millions of tons of low-grade titaniferous magnetite that averages about 17% Fe, 0.06% V, and 0.6% Ti, from which a concentrate carrying 53% Fe, 0.24% V, and 2.4% Ti can be made. In South Africa, weathered parts of the Bushveld Complex hold millions of tons of

vanadium-bearing titaniferous magnetite carrying up to 0.96% V. This magnetite is pre-reduced in coal-fired kilns that feed electric furnaces in which first titanium, and then vanadium, is slagged off and recovered. The remaining hot metal is converted into steel using the basic oxygen process (DeHuff, 1966). A steel plant is also being built at Glenbrook, New Zealand, based on iron sands at the mouth of Waikato River. New Zealand's iron sands are probably derived from andesitic and basaltic flows of Tertiary and Quaternary age. Titanomagnetite containing about 55% Fe, 5.4% Ti and 0.28% V, and ilmenite are the main ore minerals in the sands.

The use of titanium metal has been spurring since 1960 in the United States, and the demand is likely to increase. Rutile is the main ore mineral used in production of titanium sponge and metal, but upgraded ilmenite is now being considered as a possible alternative ore, despite certain disadvantages (Metals Week, Dec. 30, 1968). It should be recalled that ilmenite concentrate may be a by-product derived from titaniferous magnetite.

Considering the size and metal content of the world's titaniferous magnetite deposits, their development has been very slow. This is particularly true of titaniferous magnetite deposits in Canada, where they are not only abundant, but ranking in size and grade with the better foreign occurrences. As indicated in Table I, most of the large titaniferous magnetite deposits in Canada hold more than 25 per cent combined iron and titanium, which can be concentrated generally to more than 60 per cent Fe and Ti, along with traces (1 - 0.01%) of vanadium, chromium and manganese, and faint traces (0.01 - 0.001%) of cobalt and nickel. Other possible by-product mineral concentrates in places include apatite (phosphorus), rutile, pyrochlore, zircon, monazite, garnet and artificial sand.

GEOLOGY

Distribution and Nature of Occurrences

Figure 1 shows the location and distribution of the samples of titaniferous magnetite deposits listed in Table I. Their geology, mineralogy, geochemistry, and their typical close spatial association with gabbroic and anorthositic intrusions are discussed at length elsewhere (Gross, 1967; Rose, 1969). More than 100 large bedrock deposits of titaniferous magnetite are known at present and many other deposits will yet be found in Canada. Representatives of these deposits occur in most of the provinces, but they are most abundant in Quebec where more than 50 are known (Rose, 1963; Gross, 1967). Most of the deposits hold more than a million tons of magnetite-ilmenite (titanomagnetite) intergrowths, and many contain more than 10 million tons of titaniferous magnetite averaging more than 20 per cent Fe and 5 per cent Ti. Several of them are measurable in billions of tons of such material. A few are of much higher grade, but these are for the most part of smaller size. About 90 per cent of the deposits are associated with gabbro-anorthosite intrusions within the Canadian Shield and they range from Archean to Grenville in age; 6 or 7 deposits in British Columbia are of possible Mesozoic age and related to basic phases of Coast Range intrusions; 2 in the Eastern Townships of Quebec are of Paleozoic (Ordovician?) age associated with ultramafic intrusions, and 2 more are of Mesozoic (Cretaceous?) age associated with Montereian basic alkaline intrusions; and 1 near East Sooke on Vancouver Island is related to a gabbro-anorthosite intrusion of Tertiary age (Rose, 1967). In addition, consolidated beds of dark titaniferous magnetite-bearing sandstones of Cretaceous age are exposed along the front ranges of the Rocky Mountains near Burmis and Dungarvan in Alberta (Mellon, 1961), and unconsolidated dark magnetic sands of Pleistocene and Recent age occur at widespread localities along the north shore of the St. Lawrence River (Mackenzie, 1912) and the Pacific coast of British Columbia.

Regardless of age or provenance all of the titaniferous magnetite deposits in Canada and elsewhere carry traces or faint traces of the ferride elements as well as major iron and titanium, and these are held largely within the titanomagnetite and ilmenite-hematite grains in these rocks. The presence of high titanium content in magnetite is a good indication not only that the magnetite was derived from a mafic rock, but also that it is likely to be vanadium-bearing as well. Moreover, low titanium magnetite deposits are characteristically also low in vanadium (Rose, 1958) and as yet these are the only magnetite deposits in Canada that have been, and are being, extensively mined. On the other hand, some of the titanomagnetite associated with basic anorthositic rocks is sufficiently low in titanium in places that it should be given serious consideration as a source of concentrating iron ore (Rose, 1960). As a rule the titanomagnetite in these occurrences will carry traces of vanadium, and will be intergrown with ilmenite-hematite at least some of which will be mechanically separable from the titanian magnetite, as indicated in Table I. This indicates the possibility of making both a low-titanium and high-titanium concentrate from some of these titaniferous magnetite occurrences. After the removal of the titanomagnetite from the raw sample, the less magnetic ilmenite-hematite may be separated from the non-magnetic gangue by high intensity magnetic or electrostatic methods, by gravity, or by flotation, leaving an artificial sand tailings composed mainly of feldspar and pyroxene. Extensive concentration tests by the Mineral Processing Division of the Mines Branch are very informative in this regard.

Analytical Data

Table I gives the ferride element content of 82 samples of crude titaniferous magnetite from 63 occurrences in Canada, compared directly with that of the magnetic concentrate made by hand from each sample. Most of the samples consist of composites of carefully chosen representative material (selected samples), a number are chip or grab samples, each several pounds in weight, and a few are composite averages of bulk samples or drill core analyses from private company data, as indicated in Table I. The crude samples consist generally of titanian magnetite, titanomagnetite, ilmenite-hematite, ferrian ilmenite, titanhematite, spinel, ulvöspinel, rutile, feldspar, pyroxene, garnet, apatite, biotite-phlogopite, pyrite, chalcopyrite, pyrrhotite, epidote, zoisite, chlorite, and other accessory minerals, whereas the magnetic concentrates consist largely of titanomagnetite or titanian magnetite, and less commonly of ferrian ilmenite and ulvöspinel, along with minor amounts of adhering or entrapped pyroxene, feldspar and other minerals. The ferride element content of the magnetic concentrate thus largely reflects the composition of its main component, titanomagnetite or titanian magnetite. A single analysis is not usually representative of a given deposit, many of which vary considerably both across and along strike as well as down dip. The analyses shown in Table I are intended to be as representative as possible of the deposits under these circumstances, but they should be regarded only as guides. Additional information on the location and nature of the deposits listed is given by Rose, (1969).

Interpretation of Data

The total ferride element content of these samples of crude titaniferous magnetites of various types and ages from across Canada, shows a range from 9.2 to 68.6 per cent, compared to a range from 58.3 to 73.5 per cent for magnetic concentrates made from them. Iron, averaging 34.7 per cent in the crudes and 61.9 per cent in the concentrates, is most abundant, ranging from 7.5 to 65.5 per cent in the crude material, and from 43 to 72.2 per cent in the concentrates. Titanium comes next, averaging

4.9 per cent in the crudes and 4.3 per cent in the concentrates, ranging from 1.1 to 16.8 per cent in the crudes and from 0.1 to 18.7 per cent in the concentrates. Titanium is followed by manganese, chromium and vanadium. Of these, vanadium averages highest in the concentrates at about 0.4 per cent, ranging from 0.01 to 0.5 per cent in the crudes, and from 0.1 to 1.3 per cent in the concentrates. Chromium ranges from 0.001 to 2.5 and 5.7 per cent in the crude, and from <.001 to 1.0 per cent in the concentrates, but chromium is much more abundant in the ferrian chromites and chromian magnetites associated with ultrabasic rocks, which are not well represented here, as they are not truly representative of titaniferous magnetite. If more of these were included the chromium content and range would be increased. Manganese ranges from 0.001 to 3.8 per cent in the crudes, and from 0.005 to 3.0 per cent in the concentrates. Manganese is high in magnetic concentrates from the Oka, Quebec, and Nemegos, Ontario carbonatites, and is also slightly enriched in hematite-bearing occurrences, such as ilmenite-hematite lodes in anorthosite. Cobalt and nickel contents are generally low except in certain magnetites associated with ultrabasic rocks which are represented here by samples from Puddy Lake, Ontario and Bloc Range, Quebec. Cobalt ranges from <.001 to 0.015 per cent in the crudes, and from 0.001 to 0.027 per cent in the concentrates; nickel ranges from <.001 to 0.2 per cent in the crudes, and from 0.001 to 1.85 per cent in the concentrates.

In general, the average ferride element content of these samples, 40 per cent, is increased to 67 per cent in the concentrate; iron is raised from 34.7 to 61.9 per cent, vanadium from 0.15 to 0.37 per cent, and cobalt only slightly, whereas titanium is lowered from 4.9 to 4.3 per cent, manganese from 0.5 to 0.3 per cent, chromium from 0.4 to 0.1 per cent, and nickel only slightly. More than one-half of the samples carry less than 30 per cent Fe, but more than four-fifths of the concentrates carry more than 60 per cent Fe, and several of the concentrates carry more than 70 per cent Fe. Half of the ores carry more than 5 per cent Ti, half of the concentrates carry less than 2 per cent Ti, and one-fifth (15) of the concentrates carry less than 1 per cent Ti. One-half of the concentrates carry more than 0.3 per cent V, and 10 per cent (6) of the concentrate samples carry 1 per cent or more vanadium. Chromium and manganese are both in amounts less than 0.3 per cent in most of the samples, and less than 0.1 per cent in most of the concentrates. Cobalt and nickel are both less than 0.01 per cent in most of both the ore samples and concentrates.

In detail, some of the lowest iron samples yield remarkably high iron concentrates, many of which are also low in titanium. Several of these concentrates also carry significant amounts of vanadium, and a few others are notable for their chromium, manganese, or nickel contents. Of the 35 samples which carry less than 30 per cent Fe (about half the group), 11 yield concentrates carrying more than 70 per cent ferride elements, and 35 yield concentrates carrying more than 60 per cent ferrides; of these, 2 gave more than 70 per cent Fe and 35 gave more than 60 per cent Fe, 11 gave less than 1 per cent Ti, 21 less than 2 per cent Ti, 25 less than 3 per cent Ti, and 8 more than 5 per cent Ti. Out of 38 samples comprising the other half of this group of ores with more than 30 per cent Fe, 4 concentrates gave more than 70 per cent Fe, 27 more than 60 per cent Fe, 34 more than 50 per cent Fe, and 4 more than 40 per cent Fe, 10 gave less than 1 per cent Ti, 17 less than 2 per cent Ti, 20 less than 3 per cent Ti and 18 more than 5 per cent Ti. In all there were 60 out of 73 concentrates each of which gave more than 60 per cent Fe, 22 of which gave less than 1 per cent Ti, and 14 of which gave more than 0.5 per cent V. The low content of 0.1 per cent Ti was found in only 2 of the magnetic concentrates both of which carried more than 65 per cent Fe. The high content of more than 1 per cent V was found in 6 of the concentrates each of which carried more than 58 per cent Fe, and in these the titanium content ranged from 0.1 to 9 per cent.

The general lower content of Ti, Cr, Mn and Ni shown by the magnetic concentrates, and their general higher content of V and Co, as compared to the raw samples, is a reflection of the crystal chemistry of these elements, conditioned by the geological environment from which the samples were taken. The smaller ions such as V, Cr, Fe⁺³, and Ti tend to concentrate in the compact oxide minerals that crystallize before the less compact silicate and sulphide minerals in which the larger ions Fe⁺², Mn, Co and Ni are accommodated. The smaller ions prefer the compact spinel structure of magnetite to the less compact rhombohedral structure of hematite. Thus V, Cr, Fe⁺³ may be expected to concentrate in magnetite, whereas Ti, Fe⁺², and Mn, and to a lesser extent Co and Ni, should prefer ilmenite-hematite. Cr departs slightly from this since it is also concentrated in early non-magnetic spinels that do not concentrate in the magnetic extract. There are insufficient analyses of Co and Ni, and the differences are so slight, that it is not possible to judge if they depart from their norms in these samples.

CONCLUSION

Titaniferous magnetite deposits associated with deep-seated anorthositic intrusions, and derived sands, form a large untapped reservoir of Fe-Ti-V oxide minerals and ferride elements in Canada. Some of the deposits are amenable to separation and concentration by mechanical methods into oxide-rich and oxide-poor components, and further, by high intensity magnetic separation, into high iron-vanadium (titanomagnetite), and high titanium (ilmenite-hematite) concentrates.

The high metal content which it is possible to obtain in magnetic concentrates made from many titaniferous magnetite occurrences in Canada, suggests that they should be seriously considered as multi-product sources of the ferride elements. The recovery of iron, titanium, and vanadium, merits particular attention. By adaptation of modern mineral dressing and metallurgical processes it should be possible to commercially recover a number of mineral products from titaniferous magnetite deposits in Canada.

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