

GEOLOGICAL
SURVEY
OF
CANADA

DEPARTMENT OF ENERGY,
MINES AND RESOURCES

PAPER 70-7

SOME CANADIAN OCCURRENCES OF MAGHEMITE

(Report and 4 figures)

C. R. McLeod

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CONTENTS

	Page
Abstract	v
Introduction	1
Maghemite from Steep Rock Lake	1
Polished section study	2
X-ray data	2
Analytical results	3
Other occurrences	4
Baffin Island	4
Labrador geosyncline	5
Other localities	5
Conclusions	10
Acknowledgments	11
References	12
Table I. Analyses of Davis tube magnetic concentrate, Steep Rock 'buckshot' iron ore	3

Illustrations

Figure 1. Photomicrographs of Steep Rock maghemite	6-7
2. Photomicrographs of maghemite development in magnetite from Baffin Island	6-7
3. Photomicrographs of maghemite from Baffin Island and Wabush Lake area	8-9
4. Photomicrographs of maghemite and magnetite from Knob Lake area and braided maghemite veinlets in magnetite pseudomorphous after hematite from Godey Creek, British Columbia	8-9

ABSTRACT

Maghemite has been found in samples from the lateritic 'buckshot' ore bands of the Steep Rock Lake iron deposits. Partial chemical analysis of a magnetic concentrate gave 84.42 per cent Fe_2O_3 , 0.36 per cent FeO , and 2.8 per cent H_2O . The maghemite has a cell edge of $8.33 \pm .01$ A, and an average Vickers microhardness of 920.

Oxidation of magnetite to maghemite is relatively common but not abundant in magnetite-bearing iron ores and iron-formations from a variety of geological environments. Maghemite forms as a rim on magnetite grains, or as irregular linear or cloud-like masses within them.

There is apparently some relationship between maghemite development and polarmagnetism of samples.

SOME CANADIAN OCCURRENCES OF MAGHEMITE

INTRODUCTION

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is a metastable mineral, generally formed by the oxidation of magnetite or dehydration of lepidocrocite ($\gamma\text{-FeOOH}$), but also found in some lavas where it may have formed from low-temperature hydrothermal solutions. The history of its discovery and recognition has been reviewed by Mason (1943).

Maghemite can be changed to hematite ($\alpha\text{-Fe}_2\text{O}_3$), the more stable form, by heating, but is not known to form from it. It has an inverse spinel structure similar to that of magnetite but with a defect lattice, one-ninth of the iron positions being vacant. The X-ray diffraction pattern is similar to that for magnetite, but the cell dimension may vary from 8.30 to 8.35 Å, or larger, depending on the ferric-ferrous iron ratio. Basta (1959) considered the oxidation of magnetite to maghemite a continuous process, conceivably with consequent variations in optical and physical properties from one to the other.

In reflected light maghemite is normally isotropic and bluish grey in colour. The bluish cast, more readily discernible with oil-immersion objectives, and the irregularity with which it forms aid in distinguishing it from martite.

Walker (1931), from analyses of eight lodestones, found that they contained a considerable excess of Fe_2O_3 over the formula of magnetite, and concluded the excess was in the form of ferromagnetic ferric oxide. About one-half of the samples studied in this investigation were found to be weakly to moderately polarmagnetic (used in this paper as indicating the ability to attract ferromagnetic material).

MAGHEMITE FROM STEEP ROCK LAKE

Samples of 'buckshot' ore, a pisolitic clay, laterite-like material from underground workings of the Errington Mine of Steep Rock Iron Mines Limited, were collected by G.A. Gross, Geological Survey of Canada, through the courtesy of D. Mulder, company geologist. Similar material from the same area was submitted by R.A. Riley, Ontario Department of Mines, who requested assistance in identifying suspected maghemite.

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Crushed material from both samples was treated in a solution of dilute hydrochloric acid and stannous chloride and water-washed to remove much of the clay-size fraction. The strongly ferromagnetic material was removed from the residues with a hand magnet, and the magnetic concentrates were mounted and polished for optical study. A similar concentrate was hand ground using an agate mortar and pestle, and a magnetic concentrate obtained from the powder with a Davis tube magnetic separator. A portion of this concentrate was submitted for chemical and spectrographic analyses. As seen under a stereo-microscope, the Davis tube concentrate consisted of a slightly reddish, dark brown mineral of low lustre.

Polished Section Study

The magnetic pisolites separated for study in polished section were generally subspherical to oval, ranging in size from 0.1 mm to 8 mm. Most fragments have an outer rind of goethite, some porous and earthy, others more dense and compact, with both types commonly containing tiny hematite crystals. Crude concentric banding may be evident in the outer part of the pisolites, but the cores usually consist of intimately intergrown maghemite, hematite, and goethite. Both hard and earthy varieties of hematite are common. The pisolites may be similar to those found in limonite deposits in northwestern Australia described by Harms and Morgan (1964). Some of these, from both near and well below the present surface, contained maghemite, that they considered may have been formed by the dehydration of lepidrocrocite. Matsusaka and Sherman (1961) found magnetism in some Hawaiian soils was due to maghemite, and Sherman *et al.* (1969) reported maghemite in the outer shell of ferruginous and ferruginous bauxitic nodules from tropical latosols of the Hawaiian Islands. They considered the nodules were formed by the process of induration in which the hydrated amorphous hydroxide and oxides are dehydrated to their crystalline oxide form.

As observed in polished section (Fig. 1A), the Steep Rock Lake maghemite is isotropic and grey with a slight bluish cast which is more pronounced in oil than in air. Compared with it, the goethite is a darker grey, and the hard hematite a lighter shade of grey. The intimate association of maghemite with hematite and goethite makes it difficult to delineate grain boundaries, partly because of the colour similarity, but also because of the strong internal reflection of the fine-grained hematite and goethite, which tends to mask anisotropism. Porosity is high resulting in poor polishing characteristics.

Microhardness determinations of the Steep Rock maghemite indicated an average Vickers hardness of 920 (886-944). Most values were within the range of 894-988 reported for maghemite by Bowie and Taylor (1958). Measurements were made with a Leitz Miniload Tester using a load of 25 grams.

X-ray Data

Material taken from two of the pisolites in the polished sections and submitted for X-ray diffraction identification resulted in patterns indicating the presence of minerals with the structures of magnetite and hematite. Cell edge of the mineral with the magnetite structure was determined as $8.32 \pm .01$ Å. Material from the Davis tube magnetic concentrate was

ground to a fine powder under acetone, and the X-ray diffraction patterns obtained from it were similar to those above, the mineral with the magnetite-like structure having a cell edge of $8.33 \pm .01 \text{ \AA}$. Cell edges for gamma Fe_2O_3 reported in the literature range from 8.30 \AA (Newhouse and Glass, 1936) and 8.322 \AA (Hägg, 1935) to 8.394 \AA for magnetite-maghemite in solid solution (Basta, 1959), whereas Basta (1957) has shown the cell edge of magnetite to be 8.396 \AA .

Analytical Results

Results of chemical and spectrographic analyses of the Davis tube magnetic concentrate are listed in Table I.

TABLE I.

Analyses of Davis tube magnetic concentrate,
Steep Rock 'buckshot' iron ore (weight per cent)

<u>Chemical</u> ¹		<u>Spectrographic</u> ²					
FeO	0.36	Si	0.41	Mn	0.11	V	0.096
Fe ₂ O ₃	84.42	Al	3.0	Sr	0.0048	Ni	0.013
H ₂ O	2.8	Ca	0.81	Ba	0.005	Cu	0.0047
		Mg	0.033	Cr	0.30	Co	0.014
		Ti	2.2	Zr	0.15	Sc	0.011

1. Analyst: J. L. Bouvier, Geological Survey of Canada

2. Analyst: F. C. Hill, Geological Survey of Canada

The FeO content may be attributable to magnetite, although none was recognized in the polished sections examined, or it may be combined with some of the titanium. The titanium content and relatively high aluminum are in accordance with the anomalous content of these metals in the 'buckshot' facies reported by Jolliffe (1966), in which kaolinite and gibbsite were identified.

Small, elongated (commonly less than 10×4 microns), strongly anisotropic inclusions were observed within the maghemite (Fig. 1B). Electron microprobe analyses were performed by A. G. Plant and G. R. Lachance of the Geological Survey of Canada. Iron values were obtained by direct comparison to a hematite standard (69.9% Fe), and titanium to a rutile standard (60% Ti). Measurements were made with an electron beam bombarding an area about 1 micron in diameter. Electron beam scanning showed that there were many small grains ($<5\mu$) with a high content of titanium. Nine different spots have an average of 45.3 per cent Ti ranging from 37.9 to 49.5 per cent. Iron was not measured at every position, but the iron content of these grains showed an antithetical relationship with the

titanium, typical values being 47.4, 46.3, and 43.8 per cent Ti with 13, 15, and 19 per cent Fe respectively. The impact of the beam causes a reaction halo on these grains.

Readings at 11 different spots on a single larger grain showed Ti content averaging 58.4 per cent, ranging from 55.9 to 59.4 per cent. The average iron content of this grain from readings at 11 spots (not exactly the same positions as for the titanium analyses) is 1.9 per cent Fe, ranging from 1.2 to 2.6 per cent Fe.

Hematite in the sections showed no detectable titanium, but measurements made at several spots on maghemite indicated it contains from 0.6 to 1.2 per cent Ti.

OTHER OCCURRENCES

Partial oxidation of magnetite to maghemite has been recognized in nearly one-half of some 300 polished sections representing iron ores and iron-formations from a variety of geological environments in Canada. Maghemite development is generally accompanied by martitization, which in some cases may have preceded maghemitization, yet in other cases has apparently superceded it. Specular hematite and goethite are frequently associated with oxidized magnetite. David and Welch (1956) pointed out the importance of moisture in the formation of maghemite by the oxidation of magnetite, and in its stability. Although goethite development is usually associated with the iron oxides, it has also been noted rimming pyrite grains. However, maghemite has been recognized in close proximity to pyrite and marcasite that show no obvious effects of oxidation.

Baffin Island

Initially, maghemite development was observed by the writer in a sample of magnetite and hematite, collected by G.A. Gross in 1964, from the No. 1 deposit of Baffinland Iron Mines Limited, in the Mary River area of northern Baffin Island. Gross (1966) considered that these deposits were formed during a period of volcanism in a sedimentary environment, subjected to metamorphism, with later oxidation of some components in preglacial time. Subsequent microscopy studies have shown maghemite to be present in at least 36 other polished sections representing samples collected by Gross and G.D. Jackson from several localities in the Mary River area. One-half of the samples were found to be polarmagnetic.

In the Baffin Island polished sections, maghemite occurs as minute rims along crystal edges of magnetite (Fig. 2A), frequently following mutual magnetite boundaries. It also occurs irregularly within magnetite crystals, ranging in development from fine sharp lines to cloud-like masses. The irregularity with which it usually forms aids in distinguishing it from martite (Figs. 2A, 2B, 3A).

A series of diamond indentation hardness measurements of the magnetite showed an average Vickers hardness of 961 (935-980), using a load factor of 25 grams.

Labrador Geosyncline

Maghemite was identified optically in 13 polished sections of samples from the central and southern parts of the Labrador geosyncline. Eight of the samples were polarmagnetic.

In the Wabush Lake area in the southern division of the geosyncline, Gross (1968, p. 110) reported widespread oxidation and leaching attributed to preglacial weathering, one of the effects being martitization of some of the magnetite. This deep weathering was notably more extensive in deposits south and east of Wabush Lake, and two polished sections of samples from the property of Wabush Iron Company Limited were found to contain maghemite.

One sample consisted of hematite-quartz iron-formation with minor magnetite, chiefly as isolated grains. Most of the magnetite showed effects of oxidation, commonly with a core of remnant magnetite surrounded and cut by maghemite or maghemite and hematite (Fig. 3B). The hematite associated with maghemite is chiefly martite, its development following the octahedral parting planes of the magnetite, and this section is unusual in that some maghemite development also follows the magnetite parting planes.

The other section that was examined from the deposit consisted chiefly of magnetite showing maghemitization gradational from the crystal edges inward. The edges are the typical bluish grey maghemite colour, and magnetite remaining in the interiors of crystals has a brownish appearance, but the boundary between is indistinct. This gives the impression that oxidation was gradual, and incomplete, the product seen representing an intermediate stage in the oxidation of magnetite to maghemite.

Gross (1968) reported magnetite or martite pseudomorphous after magnetite to be widely distributed in all ore types of the Knob Lake iron range. Four samples from the Wishart deposit typically show magnetite partly oxidized to martite, with fine to well-developed maghemite present. One section illustrated the difference in optical properties that may be associated with maghemite development, with a zone or halo of lighter coloured bluish 'magnetite' on either side of fine normal bluish grey maghemite veinlets (Fig. 4A), the remnant (apparently unoxidized) magnetite having a normal brownish appearance. The blue magnetite phase presumably represents an intermediate stage in the oxidation of magnetite to maghemite.

Two samples of magnetite-hematite-quartz iron-formation from the Carol East deposits of Iron Ore Company of Canada both show maghemite development around individual magnetite crystals. Maghemite has also been observed in samples from the Boulder Lake, Mount Reed, and Lac la Bouille areas.

Other Localities

A fine, braided network of maghemite veinlets in magnetite was observed in a polarmagnetic sample from Godey Creek, near Merritt, B. C. The sample was collected by D. F. Sangster from magnetite veins 2 to 3 inches wide in Triassic volcanic rocks. Most of the magnetite is fairly coarse-grained and apparently pseudomorphous after hematite, with remnant hematite usually present as cores of individual pseudomorphs. Maghemite is concentrated as thin braided veinlets that envelop fine-grained magnetite

Figure 1. Photomicrographs of Steep Rock maghemite.
A. Part of ferromagnetic pisolite showing maghemite (mgh), hematite (hem) with intergrown maghemite, and goethite (goe) rim of pisolite. x128 oil. B. Part of area shown in A. Arrows indicate titanium-rich inclusions in maghemite. x615 oil.

Figure 2. Photomicrographs of maghemite development in magnetite, Baffin Island samples. A. Irregular maghemite in and around magnetite (dark grey) grains, with two areas of hematite (h). x615 oil. B. Fine, irregular maghemite (upper) and 'straight-line' martite (lower) development in magnetite. x615 oil.

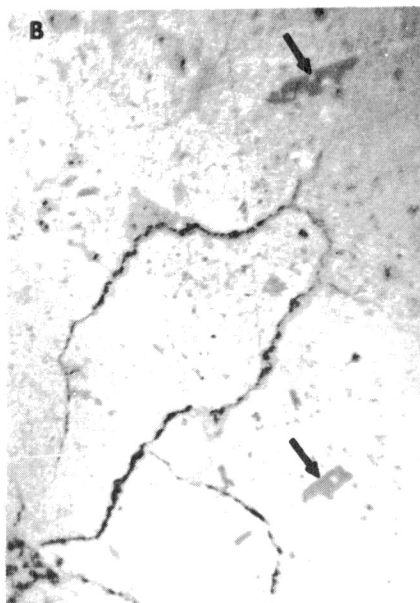
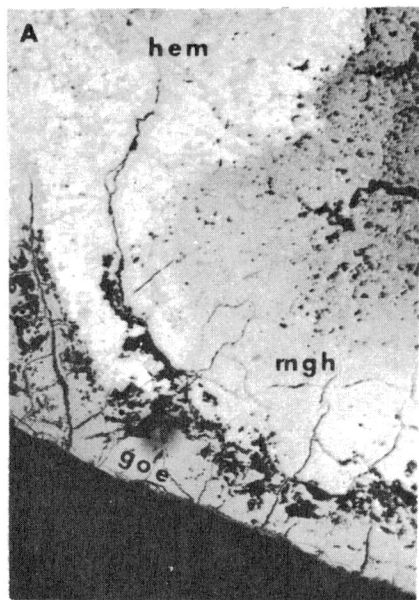


FIGURE 1

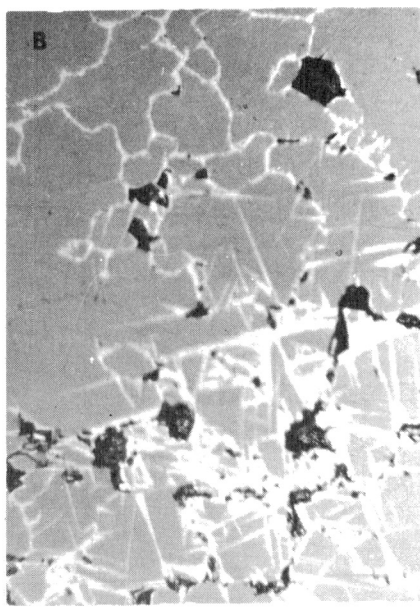
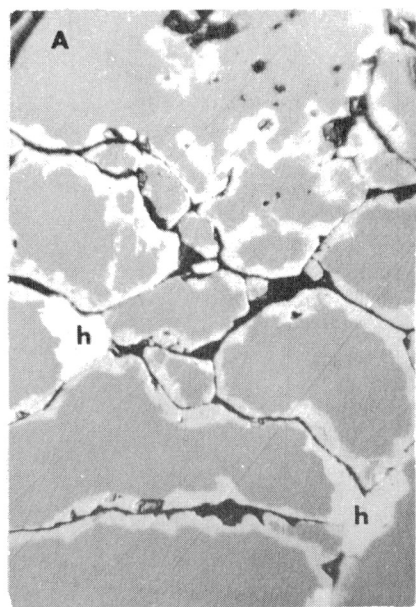


FIGURE 2.

Figure 3. A. Irregular maghemite (centre) and regular martite development, chiefly around periphery of magnetite (dark grey) crystal. Baffin Island. x275 oil. B. Maghemite (medium grey) formed by oxidation of magnetite (dark grey) with some conversion to martite (light grey). Wabush Lake area. x615 oil.

Figure 4. A. Cluster of magnetite crystals partly oxidized to maghemite (irregular, white, chiefly in interior of magnetite crystals), and martite (short, straight, white, near edges of crystals). Note intermediate phase surrounding maghemite (contrast exaggerated photographically). Wishart Mine area. x250 oil. B. Braided maghemite veinlets in and around fine-grained magnetite. White, corroded grain is remnant hematite in magnetite pseudomorphous after hematite. Godey Creek, B. C. x615 oil.

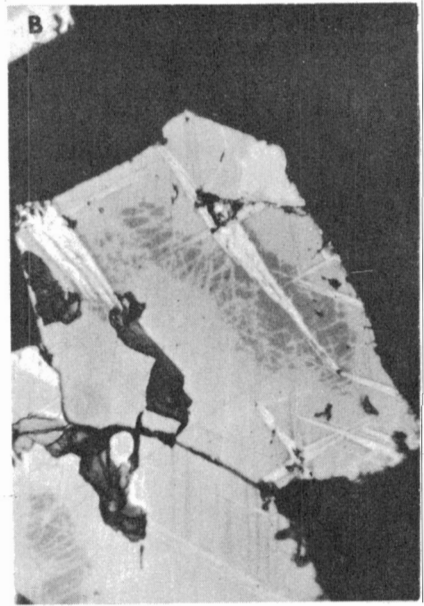
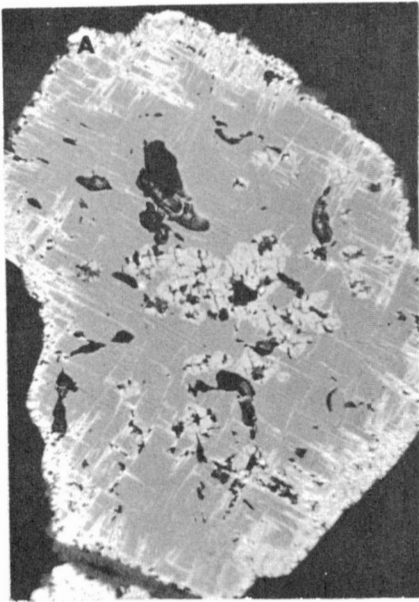


FIGURE 3.

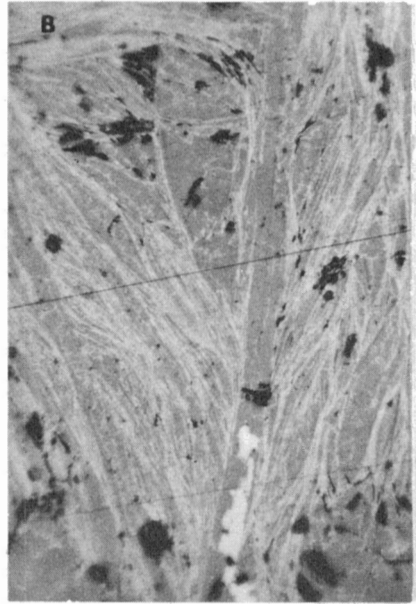
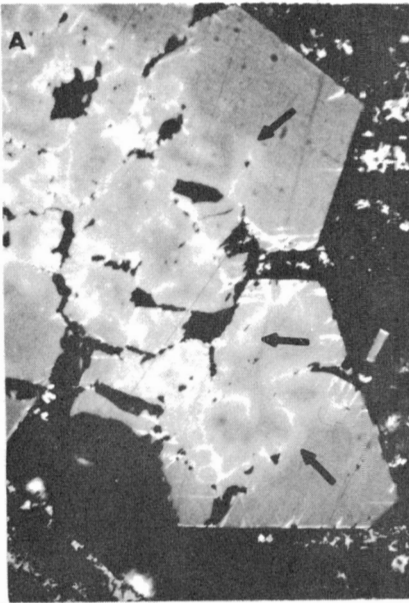


FIGURE 4.

interstitial to pseudomorphic magnetite (Fig. 4B), the latter showing considerably less maghemite development.

Maghemite was noted in a polarmagnetic sample of colloform magnetite from the Shamrock-Blackjack deposit in northern Vancouver Island. However, other fairly strongly polarmagnetic colloform magnetite samples from the Kingfisher pit of Empire Development Company Limited and from the property of Nimpkish Iron Mines Limited showed no evidence of maghemitization. Sangster (1964) described the geology of these deposits and provided the samples for study. The polarmagnetism of these samples may be attributable to the radiating structure produced by long, blade-like magnetite crystals, characteristic of the colloform magnetite described by Stevenson and Jeffery (1964).

Fine maghemite development has also been recognized in samples of magnetite-bearing iron-formations from Moose Mountain Mine, Capreol; from the Boston iron range, near Kirkland Lake; from the Temagami iron ranges, near Cobalt; from the Kapiko iron range in the Briarcliffe Lake area; from the Bruce Lake area, north of Kenora; from the Shebandowan area and the Kaministikwia iron range in the Lake Superior region; from Errington Township in the Geraldton area; and from Proctor Township in the Elliot Lake area. Maghemite (probably titanian maghemite) was also seen in titaniferous magnetite samples from the Roberval area, Quebec, and from the Haliburton and Rainy Lake areas of Ontario.

Electron microprobe analyses of three polished sections of samples from Baffin Island, and the Wabush and Knob Lake areas of the Labrador geosyncline, showed that the magnetite in these sections is free from titanium. This supports the conclusion of van Rensburg (1966), that titanium is not required for the oxidation of magnetite to maghemite, or to martite, either directly or via the maghemite phase.

About one-half of the specimens in which maghemite was identified were found to be polarmagnetic. Polarmagnetism was determined rather crudely by testing polished sections or hand specimens with pieces of iron wire about 1/2-millimetre diameter and 3 to 15 millimetres long. Several of the samples in which polarmagnetism was not detected contained extremely fine maghemite; others had only minor magnetite, and consequently little maghemite. Seven samples were found to be polarmagnetic, but maghemite was not identified in them. No attempt was made to investigate the possible significance or implications of maghemite with respect to its effect on the reversal of rock magnetism.

CONCLUSIONS

The strongly ferromagnetic fraction separated from the 'buckshot' bands of the Steep Rock Lake iron deposits consisted largely of ferric iron as would be expected if the material was maghemite, although some hematite impurity is recognized. The ferrous iron detected is insufficient to produce the strongly ferromagnetic character of the fraction. Cell dimensions measured from X-ray patterns of the magnetic fraction support the conclusion that it consists chiefly of maghemite. The titanium present occurs partly in maghemite, but the greater part of it is apparently concentrated in anisotropic inclusions within the maghemite. Results of analyses and optical examination suggest the inclusions may be similar to alteration products of

ilmenite described by Temple (1966). No lepidocrocite was identified in the samples examined, but the environment in which the pisolites occur suggest the maghemite could have been formed by dehydration of lepidocrocite.

Maghemite is a common but not abundant oxidation product of both nontitaniferous and titaniferous magnetite in iron ores and iron-formations in many parts of Canada. Its identification has been based chiefly on its optical and physical characteristics. Generally, careful and detailed examination of well-polished specimens has shown that maghemite rarely occurs as discrete, homogenous grains amenable to separation for conventional analyses. It does form as a fine, usually irregular, thread-like product in and around magnetite grains under oxidizing conditions, and with exceptionally favourable circumstances it may completely replace entire magnetite crystals. Associated development of martite and goethite indicate maghemite may form under conditions favourable for the formation of goethite from pyrite or iron oxides, yet may survive in an environment where magnetite is oxidized directly to martite. Maghemite is metastable and may alter to hematite, or may be hydrated to goethite.

There is apparently a relationship between maghemite development and polarmagnetism of samples, although not all lodestones examined were found to contain maghemite.

As noted by van Rensburg (1966), iron ore beneficiation by magnetic concentration and possibly exploration by geomagnetic methods may be influenced by the presence of maghemite.

ACKNOWLEDGMENTS

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