SVERIGES GEOLOGISKA UNDERSÖKNING

SERIE C NR 625 AVHANDLINGAR OCH UPPSATSER ÅRSBOK 61 NR 10

RUDYARD FRIETSCH

THE RELATIONSHIP BETWEEN MAGNETITE AND HEMATITE IN THE IRON ORES OF THE KIRUNA TYPE AND SOME OTHER IRON ORE TYPES



STOCKHOLM 1967

SVERIGES GEOLOGISKA UNDERSÖKNING

SERIE C NR 625

ÅRSBOK 61 NR 10

RUDYARD FRIETSCH THE RELATIONSHIP BETWEEN MAGNETITE AND HEMATITE

IN THE IRON ORES OF THE KIRUNA TYPE AND SOME OTHER IRON ORE TYPES

Manuscript received May 8th, 1967

Editor: Per H. Lundegårdh

Stockholm 1967

Kungl. Boktryckeriet P. A. Norstedt & Söner

CONTENTS

Abstract
Introduction
The relationship between magnetite and hematite in iron ores of the Kiruna type
Northern Sweden
Central Sweden
Chile
Mexico
United States
The formation of hematite in iron ores of the Kiruna type
Examples of the occurrence of hematite in connection with metasomatic processes 2
The relationship between magnetite and hematite in the non-apatitic iron ores of Central
Sweden
Conclusions
Acknowledgements
References 2

ABSTRACT

In the magmatic iron ores of the Kiruna type the primary iron oxide is mostly magnetite. Hematite is rather common and except when due to superficial weathering is a later metasomatic alteration of the magnetite. The alteration in the wall-rock (and to a less extent in the ore) has given rise to new minerals, e. g. quartz, muscovite, chlorite, calcite, clay minerals and small amounts of tourmaline, fluorite, barite, allanite and zircon. It is a later phase of the main oreforming process. The temperature at which the alteration took place is, on account of the mineral paragenesis in the altered wall-rock, believed to have been moderate to low. The main factor in the alteration of magnetite to hematite is the high oxygen fugacity in the metasomatic process. The Kiruna type also includes some hydrothermal, metasomatic hematite ores which represent a late, low-temperature stage in the magmatic differentiation that gave rise to the main mass of the ores of this type. In these the formation of the ore and the metasomatic alteration are contemporaneous. Due to the low temperature and the high content of volatiles, i. e. the high oxygen fugacity, hematite and not magnetite was formed.

Some examples of the association of hematite with metasomatically formed sillimanite, muscovite, barite and tourmaline in other, non-sedimentary iron ores, are given. Further the relationship between magnetite and hematite in the sedimentary quartz-banded iron ores of Central Sweden is dealt with. The formation of magnetite after hematite is here connected with regional metamorphism but is due not only to an increase of temperature but also to the reducing conditions existing during the metamorphism.

The common occurrence of hematite in the iron ores of the Kiruna type is facilitated by the absence of reducing agents such as sulphides, graphite and ferrous silicates. Thus the oxidation of magnetite is not inhibited as in other types of iron ore where the conditions are reducing. When prospecting for iron ores of this type metasomatic alterations of the kind described above have to be sought, since they are connected with the formation of hematite which might be the only iron oxide present. Such an ore is best indicated by gravimetric measurements.

INTRODUCTION

The iron oxides magnetite and hematite are interesting because of their ubiquitous occurrence and economic importance. The relationship between them is a complex problem which is not yet fully understood. Both occur as primary constituents in igneous and sedimentary rocks and are formed under varying geological conditions. The important factors determining whether magnetite or hematite will be formed in magmatic and metamorphic rocks are oxygen fugacity and temperature and in sedimentary rocks the oxidation potential and the hydrogen-ion concentration. The role of pressure is, in both cases, not known.

The main scope of this paper is to elucidate the relationship between magnetite and hematite in the magmatic iron ores of the Kiruna type. In many deposits of this kind hematite is encountered, and where the relationship between magnetite and hematite can be established, magnetite is the primary mineral from which hematite has been formed by oxidation. The conversion of magnetite to hematite is often, except in those cases where it is due to superficial weathering, connected with a special paragenesis in the wall-rock and to some extent in the hematite, indicating that the conversion was a metasomatic one. The role of water or water vapour, which possibly arises from the same source as the ore, is most likely of the greatest importance.

Ideal magnetite contains 72.4 per cent iron and 27.6 per cent oxygen and ideal hematite 69.94 per cent iron and 30.06 per cent oxygen. The formation of hematite from magnetite takes place according to the formula $2 \text{ Fe}_3 \text{O}_4 + \frac{1}{2} \text{ O}_2 = 3 \text{ Fe}_2 \text{O}_3$, that is an increase of the oxygen content and the degree of oxidation. The opposite reaction means a decrease of these two factors. The increase in volume during the conversion magnetite to hematite is small — about 2.5 per cent.

Knowledge of the stability of magnetite and hematite in non-sedimentary processes is imperfect but these minerals are clearly formed at varying temperatures and pressures. Magnetite is however sometimes considered as the high temperature form. Besides temperature the other main factor for this pair of minerals is the oxygen fugacity existing during their formation. The stability of magnetite-hematite is thus controlled by the presence of oxidizing or reducing agents. The oxidizing agent must in many cases be water or water vapour. It is a well known fact that water is of decisive importance for the degree of oxidation (expressed by the ratio ferric-ferrous iron) in magmatic rock differentiation. Gold-schmidt (1943, 1954) pointed out that the degree of oxidation increases during a fractional crystallization, being lower in the older, more basic members than in the younger, more acid members. In his opinion the increase is connected with the successive increase of volatiles in the residual magma and in most cases it is water or water vapour that was responsible for the change. In effusive rocks where atmospheric oxygen has also taken an active part, the degree of oxidation is higher

than in magmatic rocks. The role of water in the evolution of a basic magma has been dealt with by Bowen (1947) when discussing the Skaergaard intrusion. As shown by Wager & Deer (1939) the fractional differentiation of this magma resulted in a progressive enrichment in iron so that the last phase is a ferrogabbro extremely rich in iron. Bowen supposed that this is due to a dry differentiation consequent upon the thin and porous character of the roof of the magma chamber. Kennedy (1955) and Osborn (1959) have pointed out the important role water plays in the trend of the differentiation of a basic magma. The course of the differentiation is determined by the ratio of the iron oxides which depends on the partial pressure of oxygen which is in turn a function of the available water. If the oxygen pressure is high the iron in the magma is oxidized and separated at an early stage of the differentiation. There will then be an enrichment of silica and alkalies in the residual solutions. If, on the contrary, the oxygen pressure is low the iron will remain in the magma without any appreciable change in the silica content during the differentiation.

Laboratory work concerning the influence of oxidizing processes on the system magnetite-hematite is rather scanty. There are however several investigations on the oxidation of magnetite by heating the mineral in air (Gruner 1926, Grieg et al. 1935, Gheith 1952, Schmidt & Vermas 1955, Lepp 1957, Basta 1959 and Gokhale 1961), but these have little to do with natural conditions. Most of these investigations concern the stability conditions between magnetite — γ -Fe₂O₃ (maghemite) — α -Fe₂O₃ (hematite) at rather high temperatures. The main purpose was in many cases to investigate if γ -Fe₂O₃ exists as an intermediate phase between magnetite and hematite. One interesting conclusion is that the rate of oxidation of magnetite to hematite depends not only on temperature and oxygen pressure but also on the grain size. Thus smaller grains with a greater surface energy are more rapidly oxidized than coarser grains (Gruner 1926, Schmidt & Vermas 1955 and Lepp 1957).

Water at relatively low temperatures can oxidize magnetite to hematite as has been shown by Gruner (1930) from laboratory work. The oxidation by means of water or water vapour is found to occur at a temperature of about 260° C and probably also occurs below this temperature.

The ability of water to oxidize magnetite to hematite depends on the relative value of the partial oxygen pressure of coexisting water and the system magnetite-hematite. The partial oxygen pressures of the system magnetite-hematite at different temperatures are given by Muan (1958), Holland (1959), Mueller (1961) and Verhoogen (1962). A comparison with the values of the partial oxygen pressures given by Eugster (1959) and Verhoogen for pure water at a total pressure of 1 atmosphere at different temperatures, shows that the oxygen pressure in equilibrium with water is higher than the oxygen pressure of the system magnetite-hematite up to a temperature of about 1100° C. Above this temperature the conditions are inverted. From this Verhoogen (ibid.,

p. 173) concluded that "thus water at 1 atmosphere would oxidize magnetite at room temperature, but not at 1200° C". The same author further pointed out that hematite is the stable phase in presence of air or water at ordinary temperatures and that magnetite persists in rocks only because the rate of oxidation is very low. "But this rate increases rapidly with increasing temperature, and the possibility exists that some or all of the oxides that precipitate from a magnatic melt at high temperature might undergo partial or complete oxidation during cooling in the presence of magnatic vapors" (loc. cit.). The last statement is supported by the investigations of Baker (1955, p. 1529) who studied the reaction $2 \text{ Fe}_3\text{O}_4 + \frac{1}{2} \text{ O}_2 = \text{ Fe}_2\text{O}_3$ at various temperatures and pressures: "in cooling from a magnetite-hematite-water equilibrium there is a continual production of 'excess' O_2 so that magnetite is continually oxidized to hematite, hence some martite is a retrograde mineral".

The equilibrium magnetite-hematite in aqueous solution is, however, also controlled by the partial pressure of hydrogen that has been formed from the dissociation of water in the reaction 2 Fe₃O₄+H₂O= 3 Fe₂O₃+H₂. The partial pressure of oxygen in equilibrium with magnetite-hematite is, according to values taken from the above mentioned papers of Eugster and others, about 10⁻²³ atmospheres at 400° C and about 10⁻⁹ atmospheres at 900° C. The equilibrated partial pressure of hydrogen at a water pressure of 1 atmosphere is about 10⁻⁵ atmospheres at 400° C and about 10^{-3.5} atmospheres at 900° C. The oxygen pressure is thus lower than the hydrogen pressure both of which are small compared to the water pressure. The conversion of magnetite to hematite according to the formula above can only proceed when the hydrogen in the reaction is released. Eugster (1959) pointed out that hydrogen should be one of the most mobile constituents during metamorphism and that "the diffusion of hydrogen in one direction has the same net effect on redox reactions as the diffusion of oxygen in the opposite direction. Diffusion rates of hydrogen are much greater than those of either water or oxygen" (ibid., p. 411). The oxidation of magnetite in the presence of water must therefore occur in a more or less open system where hydrogen is more easily released than oxygen or water.

The influence of reducing agents in natural conditions on the system magnetite-hematite is poorly known. The presence of sulphides together with iron oxides results in a high sulphur fugacity and a corresponding low oxygen fugacity as shown by Kullerud (1959) and Barnes & Kullerud (1961) and thus in some cases prevents the formation of hematite. The reducing influence of graphite has been demonstrated by Chinner (1960) in regionally metamorphosed pelitic gneisses in Scotland. The graphite-bearing schists have a low and constant degree of oxidation, which is partly reflected by the relative amount of hematite to magnetite, compared to the graphite-free schists which have a higher and varying degree of oxidation. Further the influence of varying contents of ferrous silicates in a mineral assemblage with magnetite-hematite must be taken into consideration.

If such silicates are present during oxidizing conditions they are changed to form iron-poor or iron-free silicates, the iron released forming ferrous-ferric or ferric oxides. From laboratory work it is known that by an increase of the partial pressure of oxygen fayalite is changed to form magnetite and quartz (Eugster 1959) and biotite (annite) to form magnetite and sanidine or hematite and sanidine depending on the temperature (ibid.). In regional metamorphic processes with an increase of the oxygen biotite and almandine are changed to form muscovite, iron oxides and quartz (Chinner 1960) or sillimanite, microcline and hematite (Buddington 1966). Mueller (1961) showed, in connection with oxidation processes in metamorphic or magmatic rocks where ferromagnesian minerals are present, that those which coexist with hematite are poor in ferrous iron and those coexisting with magnetite are frequently rich in this ion. In these minerals the ratios MgO/(MgO+FeO) and Fe₂O₃/FeO increase with increasing partial pressure of oxygen. In all the examples given concerning the alteration of silicates with ferrous iron, oxygen is consumed and partly bound up in iron oxides. This means that the oxygen available to convert magnetite to hematite in mineral assemblages is controlled by the amount of ferrous silicates and that they act as reducing agents in this connection.

The relationship between magnetite and hematite in magmatic and metamorphic processes is, however, controlled not only by temperature and the presence or absence of oxidizing or reducing agents, but also by the degree of acidity. Mason (1943) pointed out that the oxidation of ferrous to ferric iron takes place much more readily in alkaline than in neutral or acid solutions. "Alkaline solutions therefore, even without the presence of atmospheric oxygen, probably have an oxidizing effect on magnetite, whereas acid or neutral solutions do not have this effect" (ibid., p. 128). The same opinion is expressed by Korshinskij (1965) who, when discussing metasomatic processes, considered the acidity-basicity in the solutions to be important for the oxidation. The higher the acidity of the solution the lower is the activity of oxygen, while an increase in the basicity means an increase in the activity of oxygen. He furnishes examples from post-magmatic processes where a basic stage is followed by an acid and later again by a basic stage. In some skarn deposits the increase of the acidity caused the primary hematite to be altered to magnetite, i.e. a partial reduction of the iron oxide, and this in turn was followed of a replacement of the iron oxides by iron sulphides. By a following increase of the alkalinity in the solutions and a consequent higher oxygen activity the sulphides were again replaced by hematite.

Summarizing the above, it seems that the relationship between magnetite and hematite in magnatic and metamorphic processes is controlled by the temperature and the chemical environment, oxidizing or reducing agents being of the greatest importance. It can be concluded that one of the main chemical factors is water or water vapour. If present it can, in many cases, oxidize magnetite to hematite. This can, however, only occur at temperatures below

1100° C and in the absence of reducing materials such as sulphides, graphite and ferrous silicates which prevent a high partial oxygen pressure. In a magmatic environment at moderate temperatures with a high content of volatiles hematite should be expected to be a more common mineral than magnetite. This opinion has already been stated by Goldschmidt (1954, p. 661): "Ferric iron ores seem to be connected with late stages of magmatic development, often associated with pneumatolytic or hydrothermal processes". This applies fairly well to the magmatic iron ores of the Kiruna type. In these it is often found that the primary iron oxide formed at higher temperatures is magnetite, and by a later process this mineral is oxidized to hematite. In some cases this is naturally due to superficial weathering, but in others it seems that the oxidation is confined to a certain chemical environment, namely that arising from metasomatic action at moderate or low temperatures.

THE RELATIONSHIP BETWEEN MAGNETITE AND HEMATITE IN IRON ORES OF THE KIRUNA TYPE

The iron ores of the Kiruna type are made up of magnetite and to a lesser degree by hematite. They are mostly relatively rich in apatite, but some deposits or parts of deposits are rather poor in this mineral. Besides apatite the most common non-metallic minerals are actinolite and diopside. According to Geijer (1931 B, 1935) these ores have been formed by magmatic differentiation in which volatiles (mainly water) played a decisive role. While the main part of the magma crystallized as intermediate or more rarely acid or basic extrusive rocks, the ore remained in solution and separated as a late phase with low viscosity. The ore behaved like an intrusive rock and is closely connected in time with the volcanics in which it occurs. Somewhat different from the Kiruna type proper is a variety represented by the highly phosphoric hematite-magnetite ores Haukivaara, Henrymalmen, Nokutusvaara, Rektorn and Pattovare, all in the Kiruna region in Northern Sweden. They are also intrusive in character but have apparently been formed at a lower temperature and with a higher content of volatiles than the main part of the ores of the Kiruna type. A third variety forming the final stage in the ore-forming process is made up of some hydrothermal, metasomatic hematite ores formed at still lower temperatures and by a still greater amount of volatiles.

In the following pages the relationship between magnetite and hematite in the ores of the Kiruna type is dealt with and the conversion of magnetite to hematite in connection with metasomatic processes exemplified.

Northern Sweden. As pointed out by the author (Frietsch 1966, p. 274) some deposits of the Kiruna type in Northern Sweden show a spatial relationship between the occurrence of hematite in the ore and a metasomatic alteration of

the feldspar-rich wall-rock. The alteration is characterized by the formation of sericite and quartz and more rarely by calcite and chlorite. Occasionally sillimanite and kaolinite are encountered. In the altered rocks small amounts of tourmaline, barite, allanite, fluorite and zircon occur. The minerals mentioned occur to some extent in the hematite but not in every case. Chemical analyses show that the alteration of the wall-rock means an increase of Fe3+, K and H2O and a decrease of Na, Ca, Mg and Fe2+. Si and Al show smaller changes both negative and positive. The total amount of iron has not been subject to any appreciable change. The altered rocks have a high K/(Na+K)-quotient (0.72-0.91), a high $Fe^{3+}/(Na+K)$ $(Fe^{2+}+Fe^{3+})$ -quotient (0.85-0.93) and a low $Mg/(Mg+Fe^{2+}+Fe^{3+}+Mn)$ quotient (0.11—0.22) compared to the unaltered rocks. In some deposits it is possible to demonstrate that hematite is formed from magnetite and it is therefore probable that the alteration of the wall-rock and conversion of magnetite to hematite belong to the same metasomatic process. The alteration is considered to be due to oxidizing solutions. Examples of this alteration are found in the deposits Ainasjärvi, Gruvberget, Leveäniemi, Malmberget (Gällivare), Kuosatjvare, Tjaskajåkk and in the ores in the Lower Hauki series near Kiruna comprising Haukivaara, Henrymalmen, Nokutusvaara, Rektorn and the Hauki hematite ores. Little is known about the age of the alteration but in all deposits except Malmberget the alteration is older than the intrusive rocks that occur in the vicinity of the ores and there is no connection between the alteration and the igneous activity. In Malmberget however the formation of sillimanite, muscovite etc. is related to the intrusion of pegmatites connected with the late Archean Lina granite. In the others deposits it is reasonable to suppose that the alteration has occurred in connection with the formation of the ores as a late phase. This is obvious in the ores of the Lower Hauki series where the alteration of the wallrock (and the formation of the Hauki hematite ores) by Geijer (1931A, 1935) is considered as a late, hydrothermal phase in the activity that gave rise to the nearby porphyritic rocks and iron ores at Kiirunavaara and Luossavaara.

In the deposits mentioned above magnetite is the primary iron oxide from which hematite is secondarily formed. In the Hauki hematite ores and in Ainasjärvi, the last mentioned considered by the author (Frietsch 1966) to be metasomatic, it seems probable that hematite is of primary origin. In both cases the formation of the ore and the alteration of the wall-rock occurred simultaneously. In Ainasjärvi, however, magnetite occurs outside the area of sericitization.

It is now possible to furnish additional data concerning the spatial relationship between the occurrence of hematite in the ore and a metasomatic alteration of the wall-rock in some other deposits of the Kiruna type in Northern Sweden.

The Ekströmsberg iron ore deposit situated 30 kilometers WSW of Kiruna is made up of several parallel ore bodies steeply or vertically dipping. The main ore body consists of magnetite and to the southwest there is a somewhat smaller body of hematite. In between occur several smaller bodies of both magnetite and

hematite. The host rock is a quartz-bearing porphyry with minor intercalations of syenite-porphyry.

In earlier investigations, one of the most important being that of Geijer (1912), and in more recent investigations carried out in the beginning of 1950 by the Geological Survey of Sweden, the relationship between magnetite and hematite in the deposit could not be fully established. Geijer, however, considered both iron oxides to be primary. In 1964 the Geological Survey started new drilling operations and geological mapping which show that hematite must be of secondary origin. In a broad zone between the main magnetite ore body and the main hematite ore body, ore showing all transitions from magnetite to hematite is found. Indeed, mapping of the ore in this area is rendered difficult as the magnetite contains hematite and vice versa. Microscopic investigations show that in this transition zone the term "martite" is adequate. The magnetite has been oxidized mostly along the octahedral planes. In the hematite small remnants of magnetite are sometimes encountered and there seems no doubt about the secondary origin of the hematite. Zones of martite are also found locally in the main magnetite ore body and to a small extent in the main hematite ore body. It is therefore probable that the latter was originally made up of magnetite.

The factors which caused the alteration of magnetite to hematite in Ekströmsberg are not quite established. Superficial weathering can be ruled out as the alteration affects the ore to a depth of at least 250 meters. Furthermore, the largest part of the ore, the main magnetite ore body, is only locally altered to hematite. It is therefore more reasonable to relate the conversion of the iron oxides to an alteration of the enclosing quartz-bearing porphyry. This rock is very often strongly schistose, especially in the area between the main magnetite ore body and the main hematite ore body, and is locally metasomatically altered. Thus zones up to several meters wide are found which consist almost entirely of sericite and quartz. Moreover traces of this alteration are found adjacent to these zones. A microscopic investigation reveals that the porphyry and the hematite ore contain a number of secondary minerals, often in the form of small veins. Quartz and sericite are most common and sometimes chlorite also. As accessory minerals are found calcite, zircon, allanite, tourmaline and fluorite. In some places the hematite ore contains several volume per cent of allanite, which thus occurs in fairly high amounts in the ore.

This secondary association with quartz, sericite and chlorite and accessory amounts of calcite, zircon, allanite, tourmaline and fluorite, is quite similar to that described from other metasomatically altered iron ores of the Kiruna type in Northern Sweden. Furthermore, the quartz-bearing porphyry shows the same chemical characteristics as the altered wall-rock in the other deposits with a secondary formation of hematite from magnetite. As has already been stated the altered rocks have high K/(Na+K)- and $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ -quotients and a low $Mg/(Mg+Fe^{2+}+Fe^{3+}+Mn)$ -quotient compared to the unaltered rocks. A chem-

ical analysis of the quartz-bearing porphyry from Ekströmsberg, taken from the vicinity of the main hematite ore body, is given by Geijer (1931A, p. 182). It shows the same characteristic features as the other altered rocks: the K/(Na+K)-quotient is 0.74, the $Fe^{3+}/(Fe^{2+}+Fe^{3-})$ -quotient is 0.79 and the $Mg/(Mg+Fe^{2+}+Fe^{3+}+Mn)$ -quotient is 0.09.

In Ekströmsberg it is yet not possible to find any close spatial connection between the alteration of the wall-rock and the ore. There is, however, evidence, as is the case for many other apatitic iron ores in Northern Sweden, that a spatial relationship exists between the alteration of the wall-rock and the conversion of magnetite to hematite. Nothing is known about the age of the alteration in Ekströmsberg but it possibly represents a late phase in the ore-forming process. Geijer (1912, p. 748) considered the alteration of the wall-rock to be a "late- or post-volcanic thermal action" and of the same nature, though much less intense than the alteration of the Lower Hauki series near Kiruna, which is also due to a late-magmatic phase of the process that gave rise to the main iron ores in Kiruna.

Skuokiinjokk, previously described by Svenonius (1900) and Geijer (1931A), furnishes a further example of the occurrence of hematite together with metasomatically altered rocks. The ore, which is situated about 8 kilometers SE of Ekströmsberg, is some meters wide and is made up of fine-grained, somewhat banded siliceous hematite containing up to one decimeter wide intercalations of a brown-red hematite-rich quartzite. The mineralogical composition of the ore is simple consisting of hematite and quartz. Accessory minerals include chlorite and allanite, the last mentioned occasionally in relatively large amounts. The immediate wall-rock is not known but about 50 meters SW of the ore there occurs a bleached, schistose and altered quartz-bearing porphyry. The microscope reveals that the rock contains a lot of small veins with sericite and quartz together with a brown, as yet unidentified clay mineral. Zircon is found in accessory amounts. Further to the southwest the porphyry is crushed, silicified and locally sericitized. Some hundred meters to the northeast of the ore the porphyry is partly fresh, partly crushed and altered. The whole association with siliceous hematite in silicified and sericitized porphyries is rather similar to the Lower Hauki series near Kiruna.

At Pidjastjåkko about 400 meters ENE of the summit of the hill and about 4 kilometers SE of Ekströmsberg several small lenses of a fine-grained hematite are encountered. These vertical ore bodies strike NE-SW and are about 2 decimeters wide. The length of the ore-bearing area is about 50 meters. The contact between the ore and the wall-rock is normally sharp but may be diffuse when the ore replaces the wall-rock. This is made up of a quartz-bearing porphyry which is somewhat schistose adjacent to the ore and shows a varying degree of alteration, mostly weak, with the formation of sericite, quartz and fluorite. The content of the last mentioned mineral is sometimes rather high. In accessory amounts

tourmaline, allanite and zircon are found. All the minerals mentioned, except tourmaline and zircon, also occur in the ore. The alteration of the wall-rock and the formation of the ore belong to the same metasomatic process. This deposit is in general character similar to the Hauki hematite ores and to the ore at Skuokim-jokk.

The Pattovare (Pattok) iron ore deposit situated about 40 kilometers SW of Kiruna has a length of about one kilometer and strikes NW-SE. In the southeastern end the ore is a magnetite rich in apatite (about 3 per cent phosphorus). The northwestern continuation is as yet only known as a gravimetric anomaly. Drilling operations on this part of the deposit started recently and to date only one hole has been drilled; however some preliminary data can already be given. The ore is a dense hematite, rich in apatite, with small amounts of biotite, chlorite and limonite. Locally the ore is porous and rich in small cavities. The hematite contains accessory amounts of magnetite which occurs as irregular remnants in the centre of the grains. Occasionally a martite texture is observed. Towards the northeastern border the magnetite however dominates. There seems little doubt about the secondary origin of the hematite. The wall-rock to the SW is an altered syenite-porphyry rich in phenocrysts of microcline and sometimes also plagioclase. These are more or less sericitized. The matrix is built up of small laths of an untwinned potash feldspar together with small amounts of quartz, sericite, hematite and accessory amounts of tourmaline. The rock is rich in small cavities and veins filled with quartz, sericite, chlorite, hematite, apatite, tourmaline, fluorite, sphene and limonite. The wall-rock to the NE is a grey porphyry of intermediate composition which is tectonized and chloritized.

The above indicates that in the iron ore deposits of the Kiruna type in Northern Sweden where the relationship between magnetite and hematite can be established magnetite is the primary mineral and hematite has been formed from it by oxidation. This conversion seems, in many cases, to follow a metasomatic alteration of the wall-rock. In the hydrothermal, metasomatic deposits comprising the Hauki hematite ores, Ainasjärvi, Skuokimjokk and Pidjastjåkko, where the formation of ore and the alteration of wall-rock are contemporaneous, hematite is most likely of primary origin.

The conversion of magnetite to hematite in connection with a metasomatic alterations of the wall-rock is not restricted to the apatitic iron ores of Northern Sweden. A study of the current literature concerning the iron ores of the Kiruna type in other parts of the world shows it to be rather common. Examples are given below. It should be mentioned that the magnatic origin of some of the deposits is debatable and the author follows the opinion of Geijer (1931B) in this respect.

Central Sweden. The apatite iron ores in Central Sweden are somewhat different from the other ores of the Kiruna type as regards the relationship

between magnetite and hematite. According to Magnusson (1938) the ore in Grängesberg is mainly magnetite, hematite occurring in subordinate amounts. Often the hematite ores are more or less intermingled with magnetite. This is especially the case when the hematite is intruded by pegmatites (of late Archean age), in connection with which hematite was altered to magnetite. Furthermore, there occurs occasionally according to H. Johansson (1910) a type of magnetite which is rich in rhombohedra of hematite. Even if magnetite tends to form from hematite Magnusson considers the distribution of these minerals primary. Indications that some hematite formed from magnetite is, however, given by Looström (1939) who mentions that at Lönnfallet (in the southern part of the deposit of Grängesberg) very small amounts of secondary hematite occur in the magnetite. It is possible that the hematite in the ore type described by Johansson is also secondary.

The other smaller deposits of the Kiruna type in Central Sweden consist of magnetite and hematite and the distribution of these minerals is, in many cases, rather similar to that described above. Geijer & Magnusson (1944) considered the main distribution in these deposits as in Grängesberg to be a primary one.

If the interpretation given by Geijer and Magnusson that magnetite and hematite in the apatite ores of Central Sweden are formed simultaneously is correct, it means that there must have been variations in the oxygen fugacity during the formation of ore even if temperature and pressure were similar for both minerals.

Chile. The Chilean iron ore deposits Algorrobo and Tofo are in the opinion of Geijer (1931B), magmatic segregations of the Kiruna-type and contain magnetite and hematite. The hematite is of secondary origin (martite) and in the Algorrobo deposit is considered by Geijer to be a result of superficial weathering. This is also the view of Wüst (quoted from Brüggen 1934) for this deposit and for Tofo. Wüst considers the formation of martite to be due to superficial weathering in a dry climate. In both deposits it has been observed that at quite shallow depths the content of magnetite increases significantly. There are, however, some indications in the ore of Algorrobo that the alteration of the magnetite might be due to metasomatic alterations. Geijer (1931B, p. 24) describes it as follows "Quite locally, the Algorrobo ore shows another character, being made up of small specular hematite plates that enclose rounded lumps of a fairly coarsegrained tourmaline rock". Also the wall-rock is according to Geijer, sometimes strongly altered in connection with the intrusion of the ore with the formation of actinolite, biotite, chlorite and scapolite. Another type of alteration has resulted in the formation of tourmaline, quartz and hematite and quite exceptionally, bodies of martitized magnetite occur in this association. In places the rock has been completely silicified. Further, Brüggen describes an alteration of the country

rock in connection with the intrusion of the ore: by this alteration chlorite and in some cases kaolinite, were formed.

Even if the formation of hematite from magnetite in Algorrobo is mostly, according to the above mentioned authors, a result of superficial weathering, one cannot rule out the possibility that the conversion of the iron oxides is partly connected with metasomatic activity during the intrusion of the ore.

Mexico. At Cerro Mercado in Mexico the ore consists of martite (Foshag 1928, Geijer 1931B) and only small amounts of magnetite occur locally (Rangel 1902, Farrington 1904). In connection with the ore intrusion the wall-rock was altered, partly to diopside skarn. A latite was altered to a hydrous aluminium silicate (montmorillonite). In other parts where the wall-rock is a rhyolite extensive silicification has occurred locally. According to Foshag the following paragenetical steps can be observed: brecciation of the country rock — introduction of magnetite — introduction of apatite and diopside — brecciation of the ore — formation of goethite — formation of sepiolite, colourless apatite, dahllite, quartz, calcite and barite — formation of chalcedony — formation of opal — formation of limonite. Regarding the relationship between magnetite and hematite Foshag stated (p. 16): "Concerning one of the most important steps of the sequence — the conversion of magnetite to hematite — we have as yet no data. It is the writers' opinion that this took place after the brecciation of the ore and during the hydrothermal stage that resulted in the formation of the sepiolite, quartz, calcite and barite".

At Cerro Mercado the change of magnetite to hematite is, according to Foshag, connected with hydrothermal activity which, with the formation of such minerals as quartz, calcite and barite, resembles to a certain degree the alterations described from the apatitic iron ores in Northern Sweden. It should be further mentioned that fluorite is also described from the ore (Farrington quoting Chrustschoff 1879) and topaz (Farrington) which indicates metasomatic activity. In the wall-rock the formation of montmorillonite in the host latite rock and the silicification of the rhyolite point to such a process. It is interesting to note that the analysis of the rhyolite given by Farrington (p. 229) has a high K/(Na+K)-quotient (0.78) and a high $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ -quotient (0.89) and a low $Mg/(Mg+Fe^{2+}+Fe^{3+}+Mn)$ -quotient (0.25), a feature which, as has been pointed out before, is characteristic for the altered wall-rock in the apatite iron ores in Northern Sweden. It is not known whether this is a primary or secondary feature.

United States. The iron ore deposits of southeastern Missouri, which are characteristic representatives of the ore of the Kiruna type, also furnish examples that hematite in the ore is later than magnetite and that there are metasomatic alterations in the wall-rock. A comprehensive study of the geology of these deposits has recently been given by Kisvarsanyi (1966).

According to Geijer (1931B) the ore in the deposit at Iron Mountain is a comparatively coarse hematite which in part is martitic. Kisvarsanyi showed, on the basis of older studies of the paragenetical relationships, that several phases of mineralization can be recognized and in the following order: salite, apatite, actinolite, garnet — hematite, magnetite — hematite — garnet — calcite, dolomite, pyrite, tourmaline, fluorite, barite. Kisvarsanyi mentioned that hematite frequently replaces magnetite. The last mineral phase with calcite etc. is clearly of metasomatic origin and it is possible that this conversion is related to this phase.

The ore-body of Pilot Knob is, according to Geijer (1931B, p. 15) "the Missourian counterpart of the Hauki hematite ores near Kiruna. It is a bedded deposit, composed of two hematite layers separated by a bed of sericite schist". In the deposit occur both a dense, finely bedded hematite and a breccia, in which the fragments are quartz-porphyry and the matrix hematite. In the bedded ore occur, according to Singewald & Milton (1929), besides hematite also quartz, greater or smaller amounts of muscovite and some tourmaline. Crane (1912) and Geijer also mentioned feldspar and barite. In the breccia the porphyry-fragments are to a great extent altered to quartz and sericite. In the matrix of this ore type martite and tourmaline are found.

The Pea Ridge deposit contains according to Kisvarsanyi, mainly magnetite. In the upper levels of the deposit specularite is however always present in small amounts. To the paragenesis belong quartz, apatite, pyrite, chalcopyrite, fluorite and calcite, and in local cavities quartz, calcite, chalcopyrite and barite. Hematite replaces magnetite along microstructures, and also occurs as martite. In the host rock sericite, chlorite and vermiculite are common alteration minerals.

In the Bourbon deposit the main iron oxide is, according to Kisvarsanyi magnetite. Hematite occurs in the margins of the deposit. The gangue is made up of apatite, actinolite, quartz and fluorite. In the wall-rock there is an intense silicification and a local argillitic alteration.

The Shepherd Mountain deposit is, according to Kisvarsanyi, made up of magnetite and hematite, the last mentioned mineral being an oxidation product of magnetite, indicated by the presence of martite and maghemite. The gangue consists of pyrite, quartz, apatite and clay minerals.

The Cedar Hill deposit is, according to Crane (1912), in its physical characteristics and manner of occurrence like the Pilot Knob deposit. The iron oxide is solely hematite. The bed rock is, according to Singewald & Milton (1929), pyroclastic and ranges from tuff to agglomerate in structure. The principal minerals of the rock are quartz, orthoclase and muscovite. With the hematite are associated quartz, mica, chlorite and orthoclase, and according to Crane, also amphibole and apatite. The quartz is considered to be secondary by Crane. The same author mentions barite cementing joints. According to Kisvarsanyi this is the main gangue mineral observed.

In all the above mentioned iron ore deposits of southwestern Missouri, except

Pilot Knob and Cedar Hill, it is more or less obvious that hematite is replacing magnetite. In many cases there is an intensive alteration of the wall-rock resulting in the formation of muscovite, quartz and argillitic minerals. In the ore quartz, carbonates, muscovite, chlorite, clay minerals, sulphides, tourmaline, fluorite and barite are encountered. The secondary mineral association in the wall-rock and the ore is most likely of hydrothermal origin.

THE FORMATION OF HEMATITE IN IRON ORES OF THE KIRUNA TYPE

In all iron ore deposits of the Kiruna type where magnetite and hematite occur together and the relationship between these minerals can be established, magnetite is the primary mineral from which hematite has been formed by oxidation. The reverse case that magnetite is formed from hematite is not known. In most of the examples given there is also an alteration of the wall-rock indicating a metasomatic activity. The main new formed minerals are quartz, muscovite, chlorite, calcite and clay minerals and in small amounts occur tourmaline, fluorite, barite, allanite and zircon. To some extent the secondary minerals are also found in the hematite.

It has already been mentioned that in the apatite iron ores of Northern Sweden there is probably a relationship between the conversion of magnetite to hematite and the metasomatic alteration of the wall-rock. As in the deposits of the Kiruna type outside Northern Sweden the same relationship is encountered, it is reasonable even for these ores to believe that the alteration of magnetite to hematite, except in those cases where it is due to a superficial weathering, is related to the metasomatic activity that altered the wall-rock. In many deposits there seems to be a close connection with the main formation of the ore and the metasomatism and it can therefore be assumed that this metasomatism is a late- or post-magmatic process in the ore formation. The ores of the Kiruna type are, according to Geijer, formed by magmatic differentiation in which volatiles (mainly water) played a great role. It is therefore likely that the water in the ore-forming process was responsible for the magnetite-hematite alteration and the alteration in the ground rock. During the crystallization of the ore the amount of water increased so that it was higher in the late- or post-magmatic stage than in the main ore-forming stage. This might be best exemplified by the Lower Hauki series near Kiruna, where the formation of the Hauki hematite ores and the alteration of the wall-rock according to Geijer is due to a late hydrothermal activity belonging to the same process that gave rise to the main ore-bodies at Kiruna.

The fact that in the ores of the Kiruna type, except in the hydrothermal, metasomatic variety, the primary iron oxide is magnetite formed at rather high temperatures and that it is later converted to hematite with a decrease of temperature and an increase in the content of volatiles, is in accordance with what has

been said above (p. 6) regarding the stability of magnetite-hematite in the presence of water or water vapour. At elevated temperatures the stable phase is magnetite and at lower temperatures hematite. It is therefore logical to find that during a late- or post-magmatic activity when the temperature is lower and the content of volatiles higher than during the main ore-forming phase of the apatite iron ores, hematite occurs together with magnetite and that hematite has been formed from magnetite. The occurrence of hematite is thus not only due to lower temperatures but also due to the higher content of volatiles, i.e. a higher oxygen fugacity.

It is possible that in the hydrothermal, metasomatic deposits which are somewhat different from the main mass of the ores of the Kiruna type, the primary iron oxide is hematite and not magnetite. This variety includes the Hauki hematite ores, Ainasjärvi, Skuokimjokk and Pidjastjåkko all in Northern Sweden, the quartz-tourmaline-bearing ores in Algorrobo in Chile and Pilot Knob and Cedar Hill in Missouri. In all these deposits, which form the final stage in the magmatic differentiation that gave rise to the iron ores of the Kiruna type, the formation of the ore and the alteration of the wall-rock seem to belong to the same metasomatic process. The physical conditions have, in this case, promoted the formation of hematite. Magnetite, except at Ainasjärvi, is thus not formed. The only deposits of the "normal" variety of the ores of the Kiruna type formed at a higher temperature, with a lower content of volatiles and where hematite seems to be of primary origin are that at Grängesberg and the other apatitic iron ores in Central Sweden. These deposits thus form an odd exception in this connection.

The reason for the alteration of magnetite to hematite by metasomatic processes in some deposits of the Kiruna type and not in others, cannot yet be explained. It is possible that the chemical conditions prevailing during the formation of the ore were not quite similar in all deposits in spite of the fact that deposits of the Kiruna type have the same origin. It is more likely, however, that there were some differences in the physical features in the wall-rock and the ore. The grain size and the porosity might have been of some importance. Probably most important are the tectonic differences. Thus a high frequency of fissures will permit more extensive alteration. Support for this theory is given by the author (Frietsch 1966) for Gruvberget, Leveäniemi and Ainasjärvi in Northern Sweden. In these deposits zones of tectonization occur and have apparently facilitated the penetration of solutions responsible for the alteration of magnetite to hematite. This might also be the case in some other deposits in Northern Sweden and there are indications of a relationship between fault lines and the alteration.

Considering the physical conditions under which the late- or post-magmatic activity took place in the ores of the Kiruna type it can be stated that the pressure must, on account of the common occurrence of the ores as shallow intrusions (Geijer 1931B), have been rather moderate. The paragenesis in the altered wall-rock indicates that the late- or post-magmatic activity took place at moderate or

low temperatures. Thus muscovite, which is a fairly common mineral in the altered rocks is, according to Hemley & Jones (1964), formed at a temperature between about 200° and 500° C. The occurrence of chlorite and clay minerals indicates a still lower temperature. The formation at Malmberget of sillimanite, might, as the author pointed out (Frietsch 1966), indicate a higher temperature of formation. Sillimanite in this deposit is associated with subordinate amounts of sericite and accessory amounts of corundum and andalusite. In all the other deposits of the Kiruna type the alumino-silicates in the altered wall-rock are hydroxyl-bearing, which is natural according to the metasomatic environment in which the alteration occurred. At Malmberget the alumino-silicates of the wallrock are only to a minor degree hydroxyl-bearing indicating the existence of different conditions during their formation. Sillimanite is mostly formed in the higher grades of metamorphism but a metasomatic mode of formation is also known (Huang 1957, Härme 1958, Korikovskiy 1963, Buddington et al. 1963, Pitcher 1965 and Buddington 1966). Pitcher (p. 336) pointed out the pneumatolytic role of sillimanite and "that late stage and partly independent growth has been favoured in a number of modern studies", and that "there is a close association in time and space between the growth of sillimanite and the formation of migmatites". According to Geijer (1930) the formation of sillimanite at Malmberget is a result of the action of high-temperature solutions that are connected with the intrusion of pegmatites which, in turn, belong to the late Archean Lina granite. It is therefore reasonable to suppose that the mineral assemblage that was formed in the wall-rock at moderate temperatures during the late- or post-magmatic activity following the main ore-forming stage has been changed to the present composition by the action of the pegmatites. This would explain the presence of the hydroxylfree alumino-silicates. Khitarov et al. (1963) and Bell (1963) who investigated the stability of the Al₂SiO₅-polymorphs showed that sillimanite can only form at high pressures (more than about 4 000 atmospheres) and rather high temperatures (more than about 400° C). The high pressure of formation indicates that the sillimanite at Malmberget cannot possibly have been formed by the magmatic activity when rather moderate pressure prevailed. Sillimanite in accessory amounts is also known in the sericite-altered wall-rock at Leveäniemi. It is therefore probable, according to what has been said above, that the formation of sillimanite is a later process than the sericitization in this deposit also. Near the altered wall-rock occur Lina granite and associated pegmatites which can be responsible for this conversion.

The common occurrence of hematite in the ores of the Kiruna type is due to the fact that these do not contain reducing agents such as sulphides, graphite or ferrous silicates. The presence of these would have lowered the oxygen fugacity in the solutions connected with the metasomatic activity and consequently prevented the formation of hematite from magnetite.

The occurrence of barite in connection with hematite in the iron ores of the

Kiruna type is a characteristic feature. As pointed out by the author (Frietsch 1966) it is remarkable that metasomatic alteration of the wall-rock of the iron ores of the Kiruna type in Northern Sweden did not give rise to sulphide minerals despite the addition of sulphur shown by the presence of barite. That sulphates and not sulphides have been formed depends on the fact that the partial pressure of oxygen in the solutions causing alteration was too high. The deposits of the Kiruna type in southeastern Missouri offer in this case however an exception. In these deposits both barite and sulphides in the form of pyrite and chalcopyrite are common. Here the sulphur fugacity must still have been high enough to allow the formation of sulphides, but not sufficiently high to prevent the formation of hematite.

EXAMPLES OF THE OCCURRENCE OF HEMATITE IN CONNECTION WITH METASOMATIC PROCESSES

It should be pointed out that the occurrence of hematite in connection with metasomatic processes is not restricted to the iron ores of the Kiruna type. Sedimentary iron ores in which magnetite and hematite occur as primary minerals or are formed from other iron minerals by metamorphism, are omitted from the discussion, as the formation of magnetite and hematite in these ores is controlled by others factors among which the depositional environment is most important. In the following pages the occurrence of hematite and associated metasomatic alterations in the wall-rock is described.

The magnetite deposits of New York and New Jersey in the Adirondack area in the United States offer an interesting example of the formation of hematite in connection with an intense formation of sillimanite in the host rock. These ores are, according to Buddington (1966), magnetite (minor hematite) deposits in gneiss, associated with magnetite skarn. Sillimanite is one of the major contemporaneous gangue minerals associated with magnetite (hematite) deposits as replacement in quartz-microcline gneiss. All the ore minerals and genetically related gangue minerals have definitely replacement relationships to their host rock. The ores are considered by Buddington to be of magmatic origin and related to igneous granites. The relationship between hematite and sillimanite-rich rocks is clearly established in the Benson mine. Here the description of Buddington (p. 489) is quoted: "The ore includes two varieties, one in which the ore mineral is predominantly magnetite (accessory hematite) occurs in a garnetiferous biotitic thin-layered variety of the gneiss; the feldspar in the gneiss includes both K feldspar and some plagioclase. A second variety in which the ore mineral is predominantly crystalline hematite occurs exclusively in sillimanitic quartz-microcline gneiss, which has only little plagioclase". The hematite, which is titaniferous is considered to be formed simultaneously with magnetite. The sillimanitic quartzmicrocline gneiss that is the host rock of the hematite facies has been interpreted

by Buddington (p. 490) "as the product of metasomatism of an original biotite (av. 18%)-rich quartz-plagioclase paragneiss". Further he said that "the hematite ores formed at such T and Po₂ that biotite and almandine were altered to yield sillimanite, microcline, and hematite".

The same alteration as in the Benson mine has also been described from the main igneous complex of the Adirondack area (Buddington et al. 1963). Here the metasomatism of biotite-quartz-plagioclase gneisses to sillimanitic quartz-microcline gneisses is accompanied by a decrease in mafic silicates and an increase in the degree of oxidation so that the first formed magnetite is altered to hematite. Here the phases with a high degree of oxidation are connected with the formation of sillimanite, muscovite and chlorite.

As previously described in this paper the occurrence of barite in connection with hematite in the iron ores of the Kiruna type is a characteristic feature which indicates that the sulphur involved in the metasomatic alteration process due to the high oxygen pressure has been precipitated as sulphate and not as sulphide. A further example of the association hematite-barite is furnished by the iron ore at Taporova near Kolari in Northern Finland. The orc is rather lean and is made up of hematite and to a smaller extent of magnetite occurring finely divided in a schistose quartzite of uncertain origin. Hematite and magnetite form separate grains. The magnetite is sometimes somewhat corroded and rich in small inclusions of quartz. The quartzite shows under the microscope a recrystallized, almost parallel texture. The main mineral is quartz occurring as irregular grains. In minor amounts muscovite, microcline and sometimes sillimanite and biotite are found. Barite is a common mineral and occurs in fairly high amounts, Schmidt (1960) reported between 3 and 10 per cent of this mineral. In accessory amounts tourmaline and zircon are found. Schmidt and Mikkola (1960) considered the ore to be of sedimentary origin but it is possible that the present mineral composition is due to the metasomatic action of granitic and pegmatitic dikes which are rather common in the quartzite. Leaving out of consideration the origin of the ore it is however interesting to note that hematite in this deposit is associated with quartz, muscovite, sillimanite, barite and tourmaline, a mineral assemblage similar to that encountered in the metasomatically altered wall-rock of the iron ores of the Kiruna type.

THE RELATIONSHIP BETWEEN MAGNETITE AND HEMATITE IN THE NON-APATITIC IRON ORES OF CENTRAL SWEDEN

As has been pointed out in the introductory part of this paper the relationship between magnetite and hematite in magmatic and metamorphic processes depends on the temperature and the chemical environment, the oxidizing-reducing conditions being decisive. This statement applies fairly well to the iron oxides in the deposits of the Kiruna type. The relationship between magnetite and

hematite in these ores is mainly controlled by the temperature and by the oxygen fugacity in the solutions connected with the magmatic activity that gave rise to the ore. In regional metamorphic processes it is often supposed that only temperature (and pressure) determine whether magnetite or hematite is formed. Magnetite is sometimes believed to be the high-temperature mineral. In such processes, however, not only the temperature but also the chemical environment is of importance for the system magnetite-hematite. This is exemplified by the regional metamorphism that affected the non-apatitic iron ores of Central Sweden. In the quartz-banded ores magnetite has commonly been formed from hematite. In the two other types, the skarn ores and the limestone ores, only magnetite is known. In the non-apatitic iron ores of Central Sweden there is no formation of hematite from magnetite except that magnetite in the skarn ores and limestone ores has been locally altered by superficial weathering to martite (Geijer & Magnusson 1926, 1944). Geijer and Magnusson (1952) considered the quartzbanded ores to be original sediments subjected to a metamorphism which is "connected with the main folding of the ore-bearing leptite series and the intrusion of the first great group of Archean granites" (op. cit., p. 481). The metamorphism has in many cases caused internal adjustments within the ores, e.g. recrystallization of the hematite, some of which changed to magnetite, a mineral generally indicating a higher degree of metamorphism. During the same intrusive epoch of the granites the ores and their country rock were subjected to a metasomatic addition of magnesium in great amounts. By this process an addition of iron also occurred with the formation of magnetite as a pyrometasomatic product. Also connected with this metasomatism is the formation of sulphide ores containing pyrite, pyrrhotite, chalcopyrite, sphalerite and galena.

The origin of the skarn ores and the limestone ores is much debated. According to Geijer and Magnusson these might be partly mobilized ores of sedimentary origin which have been affected by the regional metamorphism, partly true pyrometasomatic deposits. A clear division into ores of primary, sedimentary origin and those of pyrometasomatic origin is not always possible.

It is not the purpose here to deal with the intricate problem of the origin of the skarn ores and the limestone ores in Central Sweden. Attention is, however, drawn to the important fact that during regional metamorphism and metasomatism iron oxides in the quartz-banded ores have been altered to magnetite and that in the pyrometasomatic deposits the primary iron oxide is magnetite. That means that during this regional process the iron ores not only recrystallized but also that the conditions under which this occurred must have been reducing ones. Merely an increase of temperature and tectonic influence could not have been sufficient for magnetite to replace hematite in the quartz-banded ores. Reducing conditions must also have existed. The assumption of a reducing environment during the regional metamorphism is supported by the following features. The metasomatic activity is followed by the forma-

tion of sulphides which does not allow a high degree of oxidation. The country rock — the feldspar-quartz-containing leptites — has been strongly altered in connection with the metasomatic activity and minerals such as andalusite, cordierite, anthophyllite, gedrite, cummingtonite, almandine and more rarely staurolite have been formed (Geijer & Magnusson 1944). It is remarkable that in all these ironbearing silicates (excluding andalusite) the iron occurs in the ferrous state. This is true for the silicates in the ores. This skarn, formed by earlier internal reactions and in which ferric iron occurs in andradite and epidote, has been affected by the metasomatism to form the magnesia-rich silicates anthophyllite and talc, of which the first also contains ferrous iron. Silicates with ferric iron are thus totally absent in connection with the magnesia-metasomatism. The low degree of oxidation during the magnesia-metasomatism is also shown by chemical analyses of the leptites which have been affected by this activity. A study of analyses given by Geijer (1923) from the area of Riddarhyttan and by Magnusson (1925) from the area of Persberg shows that the $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ -quotient in these rocks is usually lower than 0.1, while the unaltered leptites usually have a value greater than 0.3 and which mostly goes up to 0.4-0.5. Only an anthophyllite-cordieritequartzite from Riddarhyttan (Geijer 1923, p. 24, analysis no. 7) shows a value of 0.3. A low quotient — lower than 0.1 — is also encountered in the corresponding magnesia-rich alteration rocks in the Orijärvi area in Finland (Eskola 1914).

The folding of the ore-bearing leptites, the intrusion of the first group of Archean granites and the magnesia-metasomatism are closely connected in time. The alteration of hematite to magnetite in the quartz-banded ores has occurred in connection with tectonism and the increase of temperature during the folding and the intrusion of the granites. Further the formation of the pyrometasomatic iron ores and sulphide ores belong to the same process. As has been shown above the conditions for both the alteration of hematite to magnetite and the magnesia-metasomatism must have been reducing ones. It is not the purpose here to state that the alteration of hematite to magnetite is a result of the magnesia-metasomatism, only to point out that reducing conditions prevailed during both alterations. The formation of sulphides means that the oxygen pressure cannot have been high. Further it must be pointed out that where the magnesia-metasomatism has been most active magnetite and not hematite is encountered.

The somewhat anomalous relationship between magnetite and hematite in the apatite iron ores in Central Sweden (see p. 13) with a simultaneous formation of both minerals, compared to the consistently later formation of hematite in other deposits of the Kiruna type, cannot be connected with the reducing process of the magnesia-metasomatism. In the Blötberget deposit, to the north of Grängesberg, there are some indications of this metasomatic process, but no change in the relationship between magnetite and hematite is known in this connection.

CONCLUSIONS

In the apatitic iron ores of the Kiruna type which have been formed by a magmatic differentiation the iron oxide is mostly magnetite but in many deposits hematite is also encountered. In all cases where the relationship between the two minerals can be established magnetite is the primary mineral from which hematite has been formed by oxidation. The conversion from hematite to magnetite is not known in this type of iron ore. In some cases the alteration of magnetite to hematite is due to superficial weathering but in most cases the alteration is considered to be of metasomatic origin. In many deposits there is a spatial relationship between the occurrence of hematite in the ore and a metasomatic alteration of the wall-rock. This alteration is characterized by the formation of quartz, muscovite, chlorite, sillimanite, calcite and clay minerals and small amounts of tourmaline, fluorite, barite, allanite and zircon. To some extent these minerals are also found in the hematite. In the ores of Northern Sweden the altered wall-rock compared to the unaltered rock shows high K/(Na+K)- and Fe³⁺/ $(Fe^{2+}+Fe^{3+})$ -quotients and a low $Mg/(Mg+Fe^{2+}+Fe^{3+}+Mn)$ -quotient. The alteration means an increase in Fe³⁺, K and H₂O and a decrease in Na, Ca, Mg and Fe2+. Si and Al and the total amount of iron is not much altered. In many deposits of the Kiruna type it is reasonable to assume that the alteration of the ore and of the wall-rock is due to a late- or post-magmatic activity in the same process that gave rise to the ore. In the formation of the ores of the Kiruna type, volatiles, mainly water, are believed to have played a decisive role. The late- or post-magmatic activity in which the amount of volatiles is greater than in the main ore-forming phase, has thus altered the ore and the wall-rock in the above described way. The magnetite formed at elevated temperatures is changed to hematite by the decrease in temperature and the higher amount of volatiles indicating high oxygen fugacity. This is in accordance with what is known from laboratory work about the stability of magnetite and hematite in the presence of water or water vapour: at elevated temperatures (above 1100° C) magnetite is the stable phase and at lower temperatures hematite is the stable phase. The temperature during which the alteration took place is, on account of the mineral paragenesis in the altered wall-rock, considered to have occurred at moderate or low temperatures. The common presence of muscovite indicates a temperature between about 200° and 500° C and the occurrence of chlorite and clay minerals still lower temperatures. The formation of sillimanite indicates higher temperatures and pressures. It is probable that in deposits where this mineral is encountered (Malmberget and Leveäniemi, both in Northern Sweden) the mineral assemblage formed by the metasomatic activity at moderate or low temperatures has been later changed to form sillimanite by the action of granites and pegmatites that intrude these deposits.

The ores of the Kiruna type include some hematite deposits of hydrothermal,

metasomatic origin representing a later stage in the magmatic differentiation that gave rise to the main mass of the deposits. Here the formation of the ore and metasomatic alteration of the type described above are contemporaneous. The hematite is probably of primary origin. The presence of hematite in these deposits as the primary iron oxide and not magnetite as in the more magmatic, "normal" deposits of the Kiruna type, depends on the fact the formation of ore here occurred at lower temperatures and with a greater amount of volatiles, i.e. by a higher oxygen fugacity, than in the main mass of the ores.

The common occurrence of hematite in the ores of the Kiruna type also depends on the absence of reducing agents such as sulphides, graphite and ferrous silicates, which, if present, would prevent the high oxygen fugacity necessary for the oxidation of magnetite. The presence of barite in the altered wall-rock and partly in the hematite indicates that sulphur has been introduced during the metasomatism but that the high partial oxygen pressure prevented the formation of sulphides. In the present paper some other examples are given of the occurrence of hematite in connection with metasomatic processes where the conditions have been non-reducing. In these cases, as in some of the magnetite-hematite ores of the Adirondack area in the United States, the same phenomena as in the ores of the Kiruna type are met with: hematite occurs together with rocks rich in sillimanite and muscovite. In the iron ore at Taporova in Northern Finland barite and tourmaline also belong to the association.

In regional metamorphic processes the relationship between magnetite and hematite is in many cases believed to be controlled by temperature (and pressure) and magnetite is sometimes considered as the high temperature form. In such processes however the oxidizing-reducing conditions are also of importance. This is exemplified by the regional metamorphism that affected the non-apatitic iron ores of Central Sweden, namely the quartz-banded ores, skarn ores and limestone ores, and their country rock. The metamorphism is connected with the main folding of the ore-bearing leptite series and the intrusion of granites. By this process the hematite in the quartz-banded ores, which are considered as sedimentary, has recrystallized and partly been converted to magnetite. During the epoch of folding and granite intrusions there occurred a large scale metasomatic activity by which great amounts of magnesium and smaller amounts of sulphides and iron were added. The iron formed magnetite which partly makes up the skarn ores and limestone ores. It is remarkable that in all the ores considered the only iron oxide that has been formed during the regional metamorphism is magnetite. Hematite is totally absent. It therefore seems probable that conditions during the regional metamorphism were of a reducing nature. That the oxygen fugacity has been low is indicated by the formation of sulphides. This is further supported by alterations of silicates that took place in the leptites and ores in connection with the metasomatic activity. The metasomatism in the leptites resulted in the formation of andalusite, cordierite, anthophyllite, gedrite, cummingtonite, almandine

and more rarely staurolite. In all these minerals (excluding and alusite) the iron is in the ferrous state. This is true for the newly formed skarn minerals in the ores which are rich in magnesium and ferrous iron. Silicates with ferric iron have not been formed in connection with the magnesia-metasomatism. The low degree of oxidation during this process is also shown by the fact that the $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ -quotients in the altered leptites are low, usually less than 0.1, compared with the quotients of 0.3—0.5 in the unaltered leptites. From what has been said it can be concluded that the conversion of hematite to magnetite in the quartz-banded iron ores of Central Sweden was caused by increase in temperature and pressure associated with regional metamorphism and by the existence of reducing conditions.

An important consequence arising out of the relationship between magnetite and hematite discussed above, is that, when prospecting for iron ore in a wall-rock where reducing agents such as sulphides, graphite and ferrous silicates are absent, careful search must be made for the presence of metasomatic alteration in the wall-rock. This alteration is oxidizing and magnetite is thereby converted to hematite. If the conversion is complete the resultant ore does not show up magnetically but can be detected by gravimetric surveying. The discovery during the recent years of the hematite ores at Haukivaara and Pattovare in the Kiruna region in Northern Sweden, both iron ores of the Kiruna type, by gravimetric measurements, support this statement. Geological investigations and magnetic measurements formerly made at these localities failed to detect the presence of the hematite ore.

ACKNOWLEDGEMENTS

The writer is indebted to Dr. O. Brotzen and Dr. P. Padget who have read the manuscript and made many helpful suggestions. Dr. P. Padget has kindly corrected the English of the manuscript.

REFERENCES

- BAKER, D. R., 1955: Stability of magnetite and hematite in a hydrothermal environment from thermodynamic calculations (abstract), Bull, Geel, Soc. Am. 66, p. 1528—1529.
- BARNES, H. L. & KULLERUD, G., 1961: Equilibria in sulfur-containing aqueous solutions, in the system Fe-S-O, and their correlation during ore deposition. Econ. Geol. 56, p. 648-688.
- Basta, E. Z., 1959: Some mineralogical relationships in the system Fe₂O₃-Fe₃O₄ and the composition of titanomaghemite. Econ. Geol. 54, p. 698-719.
- Bell, P. M., 1963: Aluminum silicate system: Experimental determination of the triple point. Science 139, p. 1055-1056.
- Bowen, N. L., 1947: Magmas. Bull. Geol. Soc. Am. 58, p. 263—279.
- BRÜGGEN, J., 1934: Grundzüge der Geologie und Lagerstättenkunde Chiles, Mat. Naturwiss, Klasse Heidelberger Akad. der Wissenschaften, Tübingen.
- BUDDINGTON, A. F., 1966: The Precambrian magnetite deposits of New York and New Jersey.
- Econ. Geol. 61, p. 485—510.
 BUDDINGTON, A. F. & FAHEY, J. & VLISIDIS, A., 1963: Degree of oxidation of Adirondack iron oxide and iron-titanium oxide minerals in relation to petrogeny. Jour. petrology 4, p. 138-169
- CHINNER, G. A., 1960: Pelitic gneisses with varying ferrous/ferric ratios from Glen Clova, Angus, Scotland. Jour. Petrology 1, p. 178-217.
- Crane, G. W., 1912: The iron ores of Missouri, Missouri Bureau of Geology and Mines, 10, 2.
- Chrustschoff, 1879: Einiges über den Cerro del Mercado. Würzburg.
- ESKOLA, P., 1914: On the petrology of the Orijärvi region in southwestern Finland. Bull. Comm. géol. Finlande 40.
- EUGSTER, H. P., 1959: Reduction and oxidation in metamorphism. In: Abelson, P. H. (ed.) Researches in geochemistry, p. 397-426. John Wiley, New York.
- FARRINGTON, O. C., 1904: Observations on the geology and geography of western Mexico including an account of the Cerro Mercado, Field Columbian Museum 2, p. 210—228.
- Foshag, W. F., 1928: Mineralogy and geology of Cerro Mercado, Durango, Mexico. Proc. US National Museum 74, p. 1—27.
- Frietsch, R., 1966: Berggrund och malmer i Svappavaarafältet, norra Sverige. English summary. Sveriges Geol. Unders. C 604.
- GEIJER, P., 1912: Studies on the geology of the iron ores of Lappland. Geol. Fören. Förh. 34, p. 727 - 789.
- 1923: Riddarhytte malmfält. Geologisk beskrivning. Kungl. Kommerskollegium, beskrivningar över mineralfyndigheter 1.
- 1930: Gällivare malmfält. Geologisk beskrivning. English summary. Sveriges Geol. Unders. Ca 22.
- 1931 A: Berggrunden inom malmtrakten Kiruna Gällivare Pajala. English summary. Sveriges Geol. Unders. C 366.
- 1931 B: The iron ores of the Kiruna type. Geographical distribution, geological characters, and origin. Sveriges Geol. Unders. C 367.
- 1935: Die nordschwedischen Eisenerze und verwandte Lagerstätten als Beispiele eruptiver Spaltungsprozesse. Geol. Rundschau 26, p. 351—366.
- GEIJER, P. & MAGNUSSON, N. H., 1926: Mullmalmer i svenska järngruvor. English summary. Sveriges Geol. Unders. C 338.
- 1944: De mellansvenska järnmalmernas geologi. Sveriges Geol. Unders. Ca 35.
- 1952: The iron ores of Sweden. In: Symposium sur les gisements de fer du monde, p. 477— 499. XIX Congrès Géologique International, Alger.
- GHEITH, M. A., 1952: Differential thermal analysis of certain iron oxides and oxide hydrates. Am. Jour. Sci. 250, p. 677-695.
- GOKHALE, K. V. G. K., 1961: Studies on the oxidation of magnetite. Econ. Geol. 56, p. 963—
- Goldschmidt, V. M., 1943: Oksydasjon og reduksjon i geokjemien. Geol. Fören. Förh. 65, p. 84--85.
- 1954: Geochemistry. Oxford Univ. Press, London.
- GREIG, J. W. & POSNJAK, E. & MERWIN, H. E. & SOSMAN, R. B. 1935: Equilibrium relationships of Fe₃O₄, Fe₂O₃, and oxygen. Am. Jour. Sci. 30, p. 239—316.

Gruner, J. W., 1926: Magnetite-martite-hematite. Econ. Geol. 21, p. 375—393.

 1930: Hydrothermal oxidation and leaching experiments; their bearing on the origin of Lake Superior hematite-limonite ores. Econ. Geol. 25, p. 697—719.

Hemley, J. J. & Jones, W. R., 1964: Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. Econ. Geol. 59, p. 538—569.

HOLLAND, H. D., 1959: Some applications of thermochemical data to problems of ore deposits. I. Stability relations among the oxides, sulfides, sulfates and carbonates of ore and gangue metals. Econ. Geol. 54, p. 184—233.

Huang, W. T., 1957: Origin of sillimanite rocks by alumina metasomatism, Wichita Mountains, Oklahoma (abstract). Bull Geol. Soc. Am. 68, p. 1748.

Härme, M., 1958: Examples of the granitization of plutonic rocks. Bull. Comm. géol. Finlande 180, p. 45—64.

JOHANSSON, H., 1910: Die eisenerzführende Formation in der Gegend von Grängesberg. Geol. Fören. Förh. 32, p. 239—410.

Kennedy, G. C., 1955: Some aspects of the role of water in rock melts. Geol. Soc. Am., Spec. paper 62, p. 489—503.

KHITAROV, N. I. & PUGIN, V. A. & PIN CHAO & SLUTSKII, A. B., 1963: Relations between andalusite, kyanite and sillimanite at moderate temperatures and pressures. Geochemistry, p. 235—244.

Kisvarsanyi, G., 1966: Geochemical and petrological study of the Precambrian iron metallogenic province of southeast Missouri. Dissertation. Univ. Missouri at Rolla.

Korikovskiy, S. P., 1963: Quartz-sillimanite facies of acid leaching in granite-gneiss complexes. Doklady Acad. Science, U. S. S. R., 152, p. 141—143.

Korshinskij, D. S., 1965: Abriss der metasomatischen Prozesse. Akademie-Verlag, Berlin.

Kullerud, G., 1959: Sulfide systems as geological thermometers. In: Abelson, P. H. (ed.). Researches in geochemistry, p. 301—355. John Wiley, New York.

LEPP, H., 1957: Stages in the oxidation of magnetite. Amer. Min. 42, p. 679-681.

LOOSTRÖM, R., 1939: Lönnfallet, southernmost part of the Expert field at Grängesberg. Sveriges Geol. Unders. C 428.

Magnusson, N. H., 1925: Persbergs malmtrakt och berggrunden i de centrala delarna av Filipstads bergslag. Kungl. Kommerskollegium, beskrivningar över mineralfyndigheter 2.

— 1938: Neue Untersuchungen innerhalb des Grängesbergfeldes. Sveriges Geol. Unders. C 418. Mason, B., 1943: Mineralogical aspects of the system FeO-Fe₂O₃-MnO-Mn₂O₃. Geol. Fören. Förh. 65, p. 97—180.

Mikkola, T., 1960: Kolarin rautamalmeista. Geologi 8, p. 89-90. Helsinki.

Muan, A., 1958: Phase equilibria at high temperatures in oxide systems involving changes in oxidation states. Am. Jour. Sci. 256, p. 171—207.

MUELLER, R. F., 1961: Oxidation in high temperature petrogenesis. Am. Jour. Sci. 259, p. 460—480

Osborn, E. F., Role of oxygen pressure in the crystallization and differentiation of basaltic magma. Am. Jour. Sci. 257, p. 609—647.

PITCHER, W. S., 1965: The aluminium silicate polymorphs. In: Pitcher, W. S. & Flinn, G. W. (ed.) Controls of metamorphism, p. 327—341. Oliver & Boyd, Edinburgh—London.

RANGEL, F., 1902: Los criaderos de fierro del Cerro de Mercado en Durango. Bol. Inst. Geol. Mexico 16.

Schmidt, K., 1960: Neue Eisenerze bei Kolari (Lappland). Zeitschr. f. angew. Geologie 6, p. 11-13.

Schmidt, E. R. & Vermas, F. H. S., 1955: Differential thermal analysis and cell dimensions of some natural magnetites. Amer. Min. 40, p. 422—431.

SINGEWALD, J. T., Jr., & Milton, Ch., 1929: Origin of iron ores of Iron Mountain and Pilot Knob, Missouri. Amer. Institute of Mining and Metallurgical Engineers, technical publ. 197, New York.

Svenonius, F., 1900: In: Underdånig berättelse om en undersökning af mindre kända malmfyndigheter inom Jukkasjärvi malmtrakt och dess omgifningar. Sveriges Geol. Unders. C 183. Verhoogen, J., 1962: Oxidation of iron-titanium oxides in igneous rocks. Jour. Geol. 70, p. 168—181.

WAGER, L. R, & DEER, W. A., 1939: The petrology of the Skaergaard intrusion, Kangerdlugssuaq, East Greenland. Medd. om Grönland 105, no. 4.