11. The Formation of Iron Ores in View of the Oxidation State of the Upper Lithosphere

By

Sture Landergren

ABSTRACT.—The distribution of iron and oxygen in the upper lithosphere is discussed. It seems unlikely that the enrichment of iron to ore concentrations is possible solely by means of magmatic differentiation processes during the development of rock magmas.

The oxidation of ferrous compounds to the degree of oxidation of magnetite or hematite by means of volatiles (H_2O, CO_2) present in rock magmas at high temperature ($> 700°C$) is inconsistent with thermochemical considerations.

It is concluded that the primary link in a chain of processes leading to the formation of magmatic iron ores is the enrichment of iron and oxygen under surface conditions in the presence of water and, directly or indirectly, in communication with atmospheric oxygen.

Introduction

The origin of iron ores has long been the subject of research, and one might think that all discussion of basic genetic problems would be essentially exhausted. However, investigations in recent years have shed new light on the development of the upper lithosphere. As examples may be mentioned studies on oxidation and reduction in metamorphic processes (EUGSTER 1959), stability relations in the iron oxide–water system (GARRELS 1960), the distribution of minor elements in iron ores (LANDERGREN 1948), and many others. As a consequence, conception of the prerequisites for the formation of iron ores has changed considerably. There still exists a divergence between the views of field geologists and that of geochemists on the formation of magmatic iron ores, but this divergence may be more apparent than real.

This paper presents some viewpoints on the formation of magmatic iron ores with special reference to the oxidation state of the upper lithosphere.

The Enrichment of Iron in Connection with Orogenetic Cycles

It is evident that the processes leading to the formation of ores are associated with orogenetic periods in the Earth's history. In consequence of this periodicity in the geochemical development of the upper lithosphere part of the material composing the Earth's crust can move between two opposite states of equilibrium: the magmatic phase (in the broad sense) with the homogeneous silicate magma as extreme result, and the phase prevailing at the surface, where

the weathering material is mechanically and chemically separated into resistates, hydrolyzates, oxidates, precipitates, and evaporates. In the different phases of an orogenetic cycle these actions of different geological processes affect the material in various ways. For example, a sediment containing an association of elements in equilibrium with surface conditions, and subsequently entering into a magmatic environment will try to adapt its composition to the new equilibrium state, since chemical composition is, among other factors, a function of temperature and pressure. This change of environment can give rise to hydrothermal and pneumatolytic activity with removal of volatile elements and compounds unstable in the magmatic environment. This kind of activity may be considered in connection with the formation of epigenetic sulphide ores.

The conception of the periodicity in the development of the upper lithosphere is one of the foundation stones of modern geochemistry, and was early adopted by V. I. VERNADSKY, A. E. FERSMAN, and V. M. GOLDSCHMIDT. Their ideas have been paraphrased by S. I. TOMKEIEFF (1960): ... "The product of these transformations, apparently stable minerals and rocks, are only temporary phases of this cyclic process. To understand them properly one must understand the nature and direction of changes and the energy sources behind these changes."

Consequently, when dealing with genetic problems it is necessary to consider the formation of ores as links in a chain of possible reactions taking place at the surface of the Earth's crust and within the upper lithosphere. One primary link may represent the basic enrichment process, another may be the formation of the mineral assemblage. The last perceptible link is formed by the geological processes that have given rise to actual feature of the ore body as observed by the geologist. Clearly, the border lines between the different steps in the development of an ore may be diffuse, and the subdivision suggested is tentative. In addition, a secondary enrichment can occur due to magmatic activity, for example when siderite is converted into magnetite.

The Enrichment of Iron and Oxygen in the Upper Lithosphere

In the geological literature dealing with the problem of iron ore formation too little attention has been paid to the concentration of oxygen in connection with the formation of magnetite and hematite, the two predominant ore minerals. This is surprising in view of the fact that during the last few decades many useful investigations into this topic have been presented by petrologists, mineralogists, geochemists, and others. A selection of this literature is found in papers by B. MASON (1943), H. L. JAMES (1955), H. P. EUGSTER (1959), and R. M. GARRELS (1960).

It is well known that the enrichment of iron occurs by means of both sedimentary and magmatic processes. It is also well recognized that there exist large bodies of iron ores classified as magmatic, sedimentary, and metamorphic.

Table I. The content of SiO_2, Fe (tot.), FeO, Fe_2O_3, degree of oxidation and maximum content of magnetite in the layered series of the Skærgaard Intrusion, eastern Greenland (after L. R. WAGER and R. L. MITCHELL 1951).

	SiO_2	Fe (tot)	FeO	Fe_2O_3	Degree of oxidation[a]	Maximum content of magnetite
Average composition of original magma	47.9	7.6	8.7	1.2	11.1	1.7
Gabbro-picrite	41.3	10.1	10.5	2.7	18.7	3.9
Olivine gabbro	46.2	6.9	8.2	0.8	8.0	1.1
Olivine gabbro	47.0	7.6	9.1	0.7	6.4	1.0
Hypersthene-olivine gabbro	46.4	9.2	10.4	1.1	8.4	2.2
Middle gabbro	48.2	9.2	9.5	2.5	19.0	3.6
Middle gabbro	45.7	13.9	14.9	3.4	17.1	4.9
Hortonolite ferrogabbro	44.8	15.6	16.7	3.8	17.1	5.4
Ferro-hortonolite ferrogabbro	44.6	19.0	22.7	2.1	7.7	3.0
Fayalite ferrogabbro	41.1	23.5	26.6	4.1	12.2	5.9
Fayalite ferrogabbro	48.3	20.6	22.9	4.1	13.9	5.9
Fayalite ferrogabbro	45.2	22.5	23.8	5.8	18.0	8.4
Basic hedenbergite granophyre	52.1	12.6	11.2	5.6	31.0	8.1
Magnetite					66.7	
Hematite					100	

[a] Calculated as: $\dfrac{100\ Fe^{3+}}{Fe^{2+} + Fe^{3+}}$.

The question may be asked, however, whether all those ores which from a field-geological point of view are called magmatic really have been formed by means of purely magmatic processes in the interior of the Earth or iron and oxygen have been enriched in the uppermost part of the Earth's crust by sedimentary processes, and this material has secondarily been involved in a later magmatic evolution of the region.

Iron is number four in the abundance series of elements. The average content in the upper lithosphere is 5 per cent by weight. In a magmatic ore iron is enriched by a factor of about ten. Such an enrichment of one of the major constituents in the upper lithosphere solely by some kind of magmatic differentiation process is unlikely. In the course of crystallization of a rock magma, the bivalent magnesium ion enters the structure of silicate minerals somewhat earlier than the bivalent iron ion in crystallizing magnesium-iron silicates due to the higher melting point of the magnesium-rich members of these mineral series. Consequently, iron becomes relatively enriched towards a later stage of development of a rock magma. This feature is normal and easily understood from a crystal-chemical point of view. That enrichment of iron, although not reaching ore concentrations, can be appreciable is demonstrated by two examples.

Table II. The Garabal Hill–Glen Fyne complex, western Scotland (after S. R. NOCKOLDS and R. L. MITCHELL 1948).

	SiO_2	Fe (tot)	FeO	Fe_2O_3	Degree of oxidation[a]	Maximum content of magnetite
Dunite, serpentinized	39.6	13.7	15.1	2.9	14.6	4.1
Augite peridotite	45.8	8.4	9.5	1.5	12.7	2.2
Pyroxenite	46.7	11.2	10.5	4.3	26.9	6.2
Hypersthene gabbro	46.2	7.8	8.3	2.0	18.1	2.9
Fine-grained gabbro	46.4	7.7	8.1	1.9	17.5	2.8
Main gabbro	48.8	7.1	7.1	2.2	21.4	3.1
Mica-pyroxen diorite	51.2	6.8	7.5	1.4	14.3	2.0
Coarse appinitic diorite	48.6	6.8	6.7	2.2	22.5	3.1
Medium appinitic diorite	46.2	7.9	7.5	2.9	25.6	4.2
Medium appinitic diorite	47.5	6.8	6.3	2.8	28.3	4.0
Pyroxene mica diorite	53.9	6.0	6.8	1.0	11.6	1.4
Xenolithic diorite	55.9	4.9	5.1	1.3	19.1	1.9
Fine quartz diorite	58.2	4.5	4.1	1.8	29.0	2.7
Medium granodiorite	60.4	3.7	3.6	1.3	24.6	1.9
Medium granodiorite	64.0	3.6	3.7	1.0	20.1	1.5
Medium granodiorite	66.6	3.0	2.1	1.9	45.0	2.8
Porphyritic granodiorite	67.4	2.1	1.9	0.9	28.9	1.2
Aplite (cutting granodiorite)	77.3	0.5	0.5	0.2	25.1	0.3
Porphyritic granodiorite contaminated with sediment material	62.5	3.5	3.6	1.0	19.4	1.4

[a] Calculation: see Table I.

The first example is the development of the so-called layered rock series of the Skærgaard intrusion in eastern Greenland. In Table I some data from this rock series are given. They are taken from the investigation by L. R. WAGER and R. L. MITCHELL (1951). A second example is taken from the study of the Garabal Hill–Glen Fyne complex in western Scotland by S. R. NOCKOLDS and R. L. MITCHELL (1948). These analyses are presented in Table II. The las⁺ two columns of the two tables show the degree of oxidation, calculated as the percentage content of trivalent iron of the total iron content, and the maximum possible content of magnetite corresponding to the degree of oxidation. As seen from the tables, the concentration of iron can become considerable. In the fayalite ferrogabbro, for example (Table I, analyses Nos. 10–12) the iron content is about 20 per cent by weight. On account of the oxidation state of the environment the maximum magnetite content is, however, not higher than 8 per cent by weight. In Table II (analysis No. 3) an iron content of 10 per cent by weight gives a maximum magnetite concentration of only 6 per cent.

These examples may represent special cases, but a discussion of the pre-

Table III. Average concentration of Si, Mg, Fe, and O in the principal igneous rocks.

	SiO_2	MgO	Fe (tot)	FeO	Fe_2O_3	Degree of oxidation[a]	Maximum content of magnetite
Granite	71.0	0.9	2.6	1.8	1.7	45.7	2.2
Diorite	58.1	3.7	5.4	4.5	2.8	36.2	3.9
Gabbro	48.9	7.0	8.0	7.2	3.4	29.7	4.8
Rhyolite (liparite)	72.3	0.5	2.0	1.2	1.5	52.4	1.5
Andesite	59.1	2.7	4.9	3.3	3.3	47.1	4.1
Basalt	47.8	7.7	8.5	7.0	4.3	35.4	6.0
Magnetite						66.7	
Hematite						100	

[a] Calculation: see Table I.

requisites for the formation of iron ore minerals and especially their enrichment ought to be based upon the normal development of the rock-forming processes in the upper lithosphere, particularly since magmatic ore forming hypotheses are based on the differentiation of rock magmas. Tables III–V serve to give the magnitudes of the quantities of interest.

Table III gives the averages of SiO_2, MgO, iron and iron oxides, the degree of oxidation, and the maximum concentration of magnetite that can be formed at the corresponding oxidation state. From this table can be seen that the degree of oxidation increases with increasing acidity of the rocks (cf. LANDERGREN 1948, p. 49). It is a well-known feature, however, that MgO, iron and iron oxides, and the magnetite content decrease with increasing concentration of SiO_2. Tables IV and V are statistical complements to Table III.

Table IV shows the percentage frequency distribution of total Fe in the different size classes (0–21 per cent). Thus, the concentration of iron can certainly become relatively high in the basic igneous rocks, but the formation of magnetite is limited by the low degree of oxidation in these rocks. This is demonstrated in Table V, where the frequency distribution of maximum possible magnetite concentration in the principal igneous rocks is reviewed.

It is of basic interest to discuss at this point the prerequisites for the formation of iron oxide minerals by purely magmatic processes in such concentration and on such a scale that ore formation results. In older theories oxide ores have been exclusively accounted for by magmatic differentiation, either by means of some kind of crystal-sorting process (GOLDSCHMIDT 1954), or by the splitting-up of a silicate magma into a rock fraction and a magnetite or apatite-magnetite fraction due to liquid immiscibility phenomena (GEIJER 1935; FISCHER 1950). In either case, however, the concentration of oxygen must be considered.

The distribution of oxygen has been discussed from different points of view

Table IV. Percentage frequency distribution of Fe in the principal igneous rocks.

Size class ...	0–1	1–3	3–5	5–7	7–9	9–11	11–13	13–15	15–17	17–19	19–21
Granite	6.7	56.7	27.6	8.2	0.7	0	0	0	0	0	0
Diorite	0.3	15.4	34.3	28.0	11.6	8.5	1.6	0.3	0	0	0
Gabbro	0	1.3	12.6	26.5	28.7	20.2	6.3	1.3	1.3	0.4	1.3
Norite	1.4	8.1	10.8	29.7	16.2	18.9	9.5	1.4	0	0	4.0
Rhyolite (liparite)	59.6	32.5	5.4	1.8	0	0	0	0	0	0	0.6
Leptite	21.3	59.0	12.3	3.3	0	0.8	0.8	2.5	0	0	0
Andesite	2.0	10.2	43.2	34.8	7.5	1.3	0.9	0	0	0	0
Basalt	0.2	0	3.4	20.4	39.6	27.8	6.5	1.9	0	0	0

(BARTH 1948, GOLDSCHMIDT 1954, and LANDERGREN 1948). According to BARTH, oxygen takes part in an important inorganic cycle: highly oxidized sediments and surface rocks are carried to great depths by orogenetic movements. Oxygen slowly returns to the surface, partly in rock minerals and partly combined in H_2O and CO_2, and free oxygen seems to regenerate by dissociation of oxides at high temperature and pressure. Then the new rocks at the surface are oxidized and again reduced at depth. BARTH's concept is consistent with that of the present writer who has called iron the respiratory organ of the upper lithopshere.

It is interesting to note GOLDSCHMIDT's explanation of the low degree of oxidation in basic rocks, or in terms of classical petrology, in the early stage of magmatic development. He suggested that the silicate magma in physicochemical equilibrium with metallic iron in the interior of the Earth must represent a stage of oxidation characterized essentially by ferrous compounds, and that the ratio Fe^{3+}/Fe^{2+} can be used as a measure of the proximity of a magma to primitive, deep-seated conditions. He further concluded that reactions leading to an increase in the degree of oxidation are necessary for the formation of ore minerals, since the available oxygen is "insufficient for the complete saturation of the metals in their highest stage of valency". This is clearly demonstrated in Tables III–V. However, objections can be raised to the conclusion that the decrease in the degree of oxidation in the basic rocks is essentially due to equilibration of the silicate magma with the metal phase of the interior, since it has to be borne in mind that, in addition to other factors, the degree of oxidation is also a function of temperature. GOLDSCHMIDT emphasizes rightly that there must be a reason for the increase in the oxidation state in iron-rich rock magmas. Both he and GEIJER suggest that the presence of volatiles, especially water, and the reactions caused by them could increase the oxidation stage to such a degree that considerable formation of magnetite could occur.

GOLDSCHMIDT suggested that this reaction can in principle be written:

$$3\,Fe_2SiO_4 + 3\,Mg_2SiO_4 + 2\,H_2O = 2\,Fe_3O_4 + 6\,MgSiO_3 + H_2.$$

Table V. Percentage frequency distribution of magnetite in the principal igneous rocks.

Size class ...	0–1	1–3	3–5	5–7	7–9	9–11	11–13	13–15	15–17	17–19	19–21
Granite	23.5	54.5	16.1	3.6	1.1	0.6	0.3	0.2	0	0.2	0
Diorite	5.3	35.9	34.2	15.4	5.0	3.2	0.3	0.3	0	0	0.3
Gabbro	3.6	32.3	28.7	14.3	10.8	4.5	2.2	2.2	0.5	0	0.9
Rhyolite (liparite)	40.7	51.1	6.6	1.6	0	0	0	0	0	0	0
Andesite	5.9	28.5	36.7	19.4	6.9	1.3	0.6	0.5	0.2	0	0
Basalt	2.3	14.1	28.2	23.6	15.2	9.0	4.6	1.3	0.4	1.1	0.2

It is doubtful, whether or not this type of reaction can effectively lead to the formation of an iron ore. In particular, there is an indication that the reaction may proceed in the wrong direction at increased temperature, say about 700°C, resulting not in oxidation but in reduction. EUGSTER (1959, Table 3, p. 408) has given some new data on the composition of aqueous vapour in equilibrium with pairs of iron oxides at 1 atmosphere. These data are reasonably consistent with those earlier presented by the present author (LANDERGREN 1948, p. 131), and are based on the well-known reaction

$$3\,FeO + H_2O = Fe_3O_4 + H_2,$$

where K_p is estimated from the ratio H_2/H_2O.

The figures in Table VI show that the oxidation of iron and the formation of magnetite at temperatures over about 700°C is unlikely as emphasized before. EUGSTER concludes that the role of water in connection with oxidation processes in Nature will be determined by the magnitude of P_{O_2} of the mineral assemblage and of the H/O ratio of the aqueous phase added to the rocks concerned. An analogous relationship holds for the reaction of carbon dioxide:

$$3\,FeO + CO_2 = Fe_3O_4 + CO.$$

On the basis of thermochemical considerations and the geochemistry of iron and oxygen the following conclusions can be drawn:

1. The oxidation state of the upper lithosphere during the development of rock magmas is insufficient to raise the degree of oxidation of iron to that found in iron ore minerals.

2. Oxidation by means of volatiles (water and carbon dioxide) during the development of rock magmas is improbable.

The recent data presented in this paper support the concept of the formation of magmatic iron ores that has been advanced by the present author in previous papers (LANDERGREN 1943, 1948, 1949, 1958).

Table VI (after EUGSTER 1959).

Temp. °C	Per cent (in the pair magnetite–wüstite)		Ratio H_2/H_2O
	H_2	H_2O	
600	63.6	36.4	1.75
700	40.3	59.7	0.68
800	23.5	76.5	0.31
900	14.3	85.7	0.17

FISCHER (1950) has outlined a magmatic differentiation hypothesis for the formation of apatite iron ores of the Kiruna type, where an essexite magma at a late stage of development is split into an apatite–magnetite and an alkali–syenite fraction. The concept is partly based upon laboratory experiments such as those by OELSEN and MAETZ (1941) which show an area of immiscibility in the system $Fe_xO_y–CaF_2–Ca_3(PO_4)_2–SiO_2$, and partly on the field observations by GEIJER (1935) from which he concludes that the ore is to be regarded as a pneumotectic residual magma. FISCHER rightly regards such a system as possible, but, as he himself emphasizes, only under certain assumptions, viz.:

1. The presence of volatiles, especially fluorine.
2. A melt rich in phosphorus.
3. Excess of alkalies over CaO.
4. The presence of heavy metal oxides in a relatively high degreee of oxidation.

The present author has no intention of criticizing the theoretical validity of FISCHER's concept in this connection, but the question must be asked, whether or not the assumed conditions for magmatic development in the upper lithosphere are actually present.

We see, therefore, that FISCHER's hypothesis has not removed the primary difficulties inherent in the development of a magnetite magma by purely magmatic means. On the other hand, if enrichments in iron, oxygen, phosphorus, fluorine, vanadium etc. as they readily take place under surface conditions, are exposed to magmatic development in an orogeny, the prerequisites for the formation of an apatite iron ore of the Kiruna type exist, and the magmatic processes may follow the differentiation path outlined by FISCHER and others. In the words of EITEL (1952, p. 1403): "From a modern standpoint we are more inclined to assume … the genesis and later metamorphosis of such important types of iron-phosphorus ores by sedimentary processes. The geochemical role of phosphorus, vanadium, fluorine, etc. associated in such ores and of the English oölitic 'ironstones' is that of a typical exogenic cycle which also governs the metallurgy of steel production from such ores."[1]

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[1] It is surprising that one of the recent writers of textbooks in economic geology (H. SCHNEIDERHÖHN 1958, p. 283) has completely misunderstood the geochemical viewpoints applied by the present author (1948, 1949) to the formation of apatite iron ores of the Kiruna type.

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