AEROMAGNETICS, GEOLOGY AND ORE ENVIRONMENTS, I. MAGNETITE IN IGNEOUS, SEDIMENTARY AND METAMORPHIC ROCKS: AN OVERVIEW

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ABSTRACT

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Aeromagnetic (AM) surveys continue to play a prominent role in mineral exploration. The function of AM surveys is to map the distribution of magnetic minerals in the bedrock. Rock magnetic properties originate from the opaque minerals, of which the most abundant is magnetite. Interpretation is the drawing of inferences about the geology and ore potential of a given region from AM survey data; but it is hampered by a lack of clearly stated principles relating magnetic minerals to geology and to ore environments.

This article, the first of a series, is a culling of materials from the geological literature which relate to the production and annihilation of magnetite in various geological environments. It begins with a description of the Fe-Ti oxide minerals (the primary opaque oxide minerals in all rocks) and the factors which determine their induced and remanent magnetizations. The role of deuteric oxidation is of particular importance: rocks which have had different cooling histories will also have different magnetic properties, even if they have similar chemical compositions. The magnetic properties of rocks are determined by the partitioning of iron between the oxides of iron and titanium on the one hand, and (Fe, Mg) silicates on the other. The partitioning is controlled primarily by oxygen fugacity and temperature, and only secondarily by bulk chemistry. Biotite plays a special role in determining the amount of magnetite that can form during magmatic emplacement and also during subsequent metamorphism.

Primary basaltic magmas differentiate along two different trends, depending upon whether oxygen levels are maintained externally, or whether they are allowed to drop. Magmas which follow the first trend produce primary Fe—Ti oxides and silica-rich end members. These give the calc-alkaline series, which are relatively deficient in magnetite. The second differentiation trend leads to primary Fe-silicates and FeO-rich end members which are silica-deficient. Rocks which follow this trend are relatively magnetic. The two trends correspond with quite different tectonic environments. The highest magnetic susceptibility values in either series should be found in rocks of intermediate composition approximating that of dacite or diorite, unless there has been alteration.

During progressive regional metamorphism secondary magnetite can be produced at all stages, but mostly it develops under rather low-grade conditions by the conversion of hematite, or under high-grade conditions from the breakdown of hydrous (Fe, Mg) silicates such as biotite and hornblende into simpler orthosilicates. The magnetite-producing

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capacity of a rock during metamorphism is determined by attributes which are largely inherited from the premetamorphic state, of which the most important are total iron content, oxidation state, and degree of silica saturation. Other influencing factors include magnesium, aluminum and carbon content. Magnetite is destroyed during granitization and by low-temperature alteration.

In interpreting AM survey data, close attention should be paid to all of the local factors that might have an influence upon magnetite, including mineralogy, chemical composition and metamorphic grade. Magnetite in metamorphic terrains often reflects the premetamorphic lithostratigraphy; hence magnetic interpretation maps should not be constrained to resemble maps of the existing geology.

INTRODUCTION

Aeromagnetic (AM) surveying continues to be the most widely used geophysical method in the search for metallic minerals, a rank which it has held since the earliest surveys began shortly after World War II. According to a widely held opinion, a primary function of AM surveys in exploring for minerals is to subdivide large areas at a very early stage of exploration into smaller regions that are comparatively favourable and into those that are less favourable for finding ores, so that the more costly follow-up work may be concentrated in those areas which are perceived as having the highest economic potential. In other words, the aim is to increase exploration costeffectiveness.

But how is this done? The literature on aeromagnetics is distressingly meagre on this important topic. This unsatisfactory situation has existed for a very long time, and has been commented upon by other writers (e.g. Zeitz and Bhattacharyya, 1975; Emerson, 1978). A recent article by McIntyre (1980) is one of the very few that offers practical guidance. The primary purpose of this and a following article is to present in an organized form what is presently known about the relationships of magnetic minerals (chiefly magnetite) to geology and to ore environments. The aim is to provide a reference for geophysicists who are involved in mineral exploration, and to suggest some ideas on interpretation methodology.

This article deals with factors controlling the occurrence of magnetic minerals (mainly magnetite) in igneous, sedimentary and metamorphic rocks — that is, with the relationship of magnetite to the geological environment. A second article will deal with observational relationships between magnetite and the depositional and present-day environments of base metal, gold and uranium ores — i.e., with magnetite as a pathfinder. Future articles are planned which will illustrate some of the principles discussed in these two papers in relation to a few of the best-known gold and base metal mining camps in Canada and Australia.

STATEMENT OF THE PROBLEM

Magnetometer surveys map the distribution of magnetic minerals in the earth's crust. That is all that they do. The major magnetic minerals are magnetite, titanmagnetite, titanhematite, maghemite, pyrrhotite and native iron or Fe—Ni—Co alloys. These minerals give rise to magnetic anomalies, either because of their abnormally large magnetic susceptibilities or because they have high remanent magnetizations. Of the magnetic minerals that occur in nature, magnetite is the most abundant. On a global basis, the others can probably be ignored. Thus AM surveys, in practical terms, map the magnetite in the rocks below the aircraft. Interpretation, in a broad sense, is the drawing of inferences about the geology and the ore potential of a region from the distribution of magnetite.

Magnetite is a minor accessory mineral which is present in most rocks only in very small amounts — rarely more than one per cent by volume of the whole rock. The presence of magnetite, or the lack of it, reveals little about what minerals make up the other 99% of the rock. Thus magnetic properties will not by themselves identify rock type, at least, not in a conventional classification system that is based principally upon silicate and carbonate mineralogy. Moreover, changes in magnetite concentration levels seldom correlate with lithological divisions which are defined by the conventional silicate carbonate nomenclature. Accordingly, it must be said at the outset that attempts to infer lithological boundaries solely on the basis of AM survey data usually fail. There are, nonetheless, geological parameters which can be inferred from magnetics, and that is the central theme of this article. Before we discuss them, some background on the mineralogy of magnetic minerals is necessary.

MAGNETIC MINERALOGY

Magnetite and other magnetic minerals

All of the common magnetic minerals except pyrrhotite are within the Fe-Ti-O system. Perhaps the most convenient overview of the mineralogy of this system is provided by the ternary diagram shown in Fig. 1. The double lines indicate the two-component solution series that occur in nature, and the solid portions of these lines show the regions in which complete solubility exists at room temperature. The open sections indicate solubility gaps, and the temperatures at which these gaps close are noted. To give an example, the solid solution series between magnetite and ulvöspinel is continuous at temperatures above 600° C. With falling temperature, however, a miscibility gap opens up between the two end members, and by the time room temperature is reached, the gap has widened to the position that is shown. Solid solutions within this gap which have crystallized at higher temperatures will tend to exsolve spontaneously into usp-rich and mt-rich solid solution intergrowths. The process tends to accelerate as the temperature continues to fall and as the miscibility gap continues to widen. As ulvöspinel exsolves from solid solution, it has a tendency to oxidize toward ilmenite and magnetite (Buddington and Lindsley, 1964) according to the reaction:

The reaction will move toward the right as long as dissociated water $(H_2 + \frac{1}{2}O_2)$ is present in the mineral assemblage. Therefore, as deuteric cooling reactions proceed the opaque oxide minerals tend to develop a lamellar intergrowth structure consisting of titaniferous magnetite and ferrian ilmenite. It should be noted that the addition of oxygen to the system brings about an increase in the total amount of magnetite.

Note that two processes are at work during the deuteric cooling phase, both of which tend to make the rock more magnetic. The first is the spontaneous separation of magnetite—ulvöspinel solid solutions into end-member enriched components. The second process is the oxidation of ulvöspinel toward ilmenite. Both of these reactions take place slowly and simultaneously, at a rate which depends to a large extent upon the availability of oxygen, and for practical purposes they can be thought of as a single process.

The speed of cooling is important (Haggerty, 1976a). If cooling has been rapid and most of the volatiles have been allowed to escape, the iron and titanium oxides will stay in solid solution where they can remain for a very long time in metastable equilibrium. Thus basaltic lavas, for example, which are relatively rich in iron—titanium oxides, tend to have low magnetic susceptibilities. Mafic intrusions, on the other hand, containing about the same quantities of opaque oxide minerals as basaltic lavas but which have cooled



Fig. 1. Review of mineralogical and magnetic data pertaining to the Fe-Ti-O system.

306

more slowly, generally contain more magnetite and have stronger magnetic properties. Reheating and recooling during regional metamorphism tends to promote the exsolution of magnetite, especially if an external supply of oxygen is available. Regional metamorphism, moreover, often involves mechanical deformation (folding) as well as heating, and this tends to cause the opaque oxide minerals to recrystallize into coarser textures. Coarsely crystalline magnetite has a higher magnetic susceptibility (and a lower magnetic remanence) than finely crystalline magnetite, due to the increased ease of magnetic domain boundary movement. Thus regional metamorphism tends to increase the magnetic susceptibilities of rocks in two ways, namely, through reheating and through mechanical deformation. There is also a third reason why magnetic properties tend to be strengthened by metamorphism, and that has to do with the production of secondary magnetite, a process that we shall be discussing later at some length. All three enhancement processes gather strength toward the higher levels of regional metamorphism, and are strongest within the upper amphibolite and lower granulite facies. When these levels are reached, increases in magnetic susceptibilities by as much as tenfold are not uncommon.

The compositions of the opaque oxides found in igneous rocks, both acidic and basic, tend to cluster about the magnetite—ilmenite join (Fig. 1), whereas the opaque oxides found in metamorphic rocks cover a much wider field, which lies mostly to the right of this line. Among igneous rocks, those of acidic composition contain oxides having a higher proportion of magnetite to ilmenite than basic rocks, although the total quantity of iron titanium oxides in acid igneous rocks is usually much less than in basic rocks. Typical concentrations of primary opaque oxides in acidic suites are about 1% by volume, while in basic suites they are usually about 5% by volume.

Remanent vs induced magnetization

Thus far we have spoken of the magnetization, the magnetic susceptibility, and the magnetic properties of an oxide mineral assemblage as being somehow synonymous with its magnetite content. This is true in a general sense, but it requires some qualification.

To a very good approximation the *induced magnetization* is directly proportional to magnetite content. One rule of thumb that is often used for relating the volume magnetic susceptibility of a rock to its magnetite content is an approximate version of an empirical relationship determined by Balsley and Buddington (1958), viz.:

 $K = 2.6 \cdot 10^{-3} \text{ V e.m.u.} (33 \cdot 10^{-3} \text{ V SI})$

where V is the volume percentage of magnetite in the rock. The other oxides of iron and titanium have such small susceptibilities that their contribution to the induced magnetization can be ignored. Thus contour lines of equal magnetic susceptibility, shown schematically in Fig. 1, form a series of concentric curves about Fe_3O_4 . Magnetic susceptibility is effectively zero for ulvöspinel:magnetite, ilmenite:magnetite and ilmenite:maghemite/hematite ratios higher than about 3:1 (Akimoto et al., 1957).

The situation is quite different for *natural remanent magnetization* (NRM). Pure magnetite rarely develops a remanent magnetization unless it is very fine-grained; but magnetite which is contaminated with even small amounts of ulvöspinel or ilmenite can acquire a significant magnetic remanence. Not only members of the magnetite—ulvöspinel and magnetite—ilmenite solid solution series, but also members of the hematite—ilmenite series — oxides which have virtually zero susceptibility — can acquire remanent magnetizations under appropriate conditions. Thus there is quite a broad region of Fig. 1 within which oxide minerals can be remanently magnetized; and indeed it would appear from the work of Balsley and Buddington that relatively strong remanent magnetizations can occur in oxide minerals of all compositions.

The most important carriers of NRM in most rocks, however, seem to be the titanhematites, i.e., members of the hematite—ilmenite solid solution series whose compositions lie between about hem₄₀ ilm₆₀ and hem₈₅ ilm₁₅ (Hargraves and Banerjee, 1973). The strongest NRM's are found in oxides in which the proportion of hematite to ilmenite is approximately 1:1. Usually these consist of ferrian ilmenites with titanhematite microintergrowths (Balsley and Buddington, 1958). The presence of oxide minerals having this composition implies quite a high degree of oxidation. According to Fig. 1, the probability of finding carriers of NRM within the oxide minerals is highest among anorthositic suites and the higher-grade metamorphic rocks.

One of the oddities of NRM is its propensity to take on a direction that is antiparallel to that of the inducing field. The phenomenon is called "selfreversal", and it now seems to be recognized that it will occur if (i) exsolved phases of the hematite—ilmenite solid solution series are present, and (ii) the proportion of ferrian ilmenite to titanhematite is greater than about 2:1. Titanhematite is still the carrier of NRM, but for reasons that have never been fully explained the direction is normal if the solid solution is predominantly hematitic, but is likely to be inverted if the composition is predominantly ilmenitic. This is a complex phenomenon involving many variables, of which we have mentioned only what appear to be the most important ones. For a more thorough treatment of NRM and of the self-reversal phenomenon, we refer the reader to the more specialized works on rock magnetism (e.g. Nicholls, 1955; Stacey and Banerjee, 1974).

As Fig. 1 suggests, magnetite—ilmenite solid solutions normally coexist with hematite—ilmenite solid solutions. Consequently, most magnetic rocks have a magnetic susceptibility which gives them an induced magnetic moment, and they also have a remanent magnetization which usually consists of two or more components. The dominant NRM is usually carried by members of the hematite—ilmenite solid solution series. If the composition is ilmenitic, the dominant NRM may be inverted. The resultant vector may be in almost any direction, but it has a tendency to lie in directions that are either roughly parallel or roughly antiparallel (to within about 30°) to the direction of the induced magnetic moment (Balsley and Buddington, 1958). Selfinverted NRM appears to be one of the most widespread causes of anomalous magnetizations, at least among older rocks, and it is evidently related to the rock's primary oxidation state and to its metamorphic history. It is favoured by (i) a high initial oxidation state inherited from the premetamorphic rock, or (ii) a metamorphic history that has brought about a significant increase in oxidation, and (iii) primary opaque oxides that are relatively rich in titanium. Anomalous magnetizations are thought to be caused by events which have acted during the period of cooling in which the temperature has remained above the Curie point (for titanhematite, this temperature is about 600°C). The most likely cause would appear to be deuteric oxidation, accompanied by self-reversal. Among igneous rocks, quite a large proportion of anomalous magnetizations can be accounted for more easily by oxidation processes than by hypothetical reversals of the geomagnetic field. The most prevalent carriers of anomalous NRM are basic rocks which have become oxidized during or after emplacement.

In our discussion of magnetic minerals we have thus far said nothing about pyrrhotite, the only magnetic mineral of widespread occurrence which does not belong to the Fe—Ti—O system. Pyrrhotite, although a fairly common mineral, is restricted in its occurrence largely to sulfide facies iron formations and to iron-rich sulfide deposits. On a global basis it is so rare compared with magnetite, that except in some special situations its contribution to aeromagnetic anomaly maps can be safely ignored.

The Fe–Ti–O geothermometer and oxygen geobarometer

What determines the amount of primary magnetite and ilmenite in rocks? The three most important physical parameters of a melt which determine the composition and the amount of opaque oxide minerals which can form are its temperature, oxygen availability and bulk chemistry. Of these, the last is of much less importance than the first two. Variations in Na and K appear to have some effect upon the ratio of magnetite to ilmenite, but it is relatively minor (Carmichael and Nichols, 1967). The curves in Fig. 2 show the relationships between temperature and oxygen availability (expressed as "oxygen fugacity", which is given in units of pressure and designated with the symbol fO₂) which lead to the crystallization of solid solutions of magnetite and ulvöspinel and of hematite and ilmenite having various compositions. They are the result of measurements made by Buddington and Lindsley (1964), and they are known as the "Fe-Ti-O geothermometer and oxygen geobarometer", because they yield unique values for the temperatures of crystallization and oxygen fugacities of mineral assemblages containing coequilibrated magnetite-ulvöspinel and hematite-ilmenite pairs. The measurements were made at a pressure of approximately 1 kbar; but the effect



Fig. 2. The Buddington-Lindsley curves for the magnetite-ulvöspinel and hematiteilmenite solid solution series. The FMQ curve is from Wones and Eugster (1965).

upon these curves of changing the external pressure is so minor, even up to pressures of several kilobars, that to a first approximation the depth at which the minerals have formed is unimportant. For more accurate determinations, a small correction may be applied to the fO_2 values for pressures exceeding 1 kbar. Of course, the Buddington-Lindsley curves apply only to solid solution pairs that are in equilibrium — a condition which may not have been reached in many cases (particularly if rapid cooling has taken place) — and in that sense they are ideal. However, even for those assemblages which are not in equilibrium, the curves indicate the compositions toward which the Fe-Ti oxides must tend.

Adding SiO₂ to the system restricts the stability field of the magnetite ulvöspinel solid solution series by establishing a minimum fO_2 level at each value of T, below which Fe^{2+} will enter the non-magnetic iron silicate fayalite in preference to magnetite. The presence of SiO₂ therefore buffers the system with respect to oxygen, according to the reaction:

$$3 \text{FeSiO}_3 + \frac{1}{2}\text{O}_2 \approx \text{Fe}_3\text{O}_4 + 3\text{SiO}_2$$

fayalite magnetite quartz

The fO_2 vs T relationship that governs this reaction is known as the "fayalite-magnetite-quartz (FMQ) buffer". It is shown, for a system that is fully saturated with respect to silica, in Fig. 2. In rocks that are undersaturated in silica the FMQ buffer will fall below the position that is shown, since Fe^{2+} must now compete with other cations for the available silica. When this occurs the magnetite—ulvöspinel field will increase in size, and more magnetite will be able to form relative to Fe-silicates. Moreover, in silica-undersaturated rocks the primary opaque oxides are almost always titanium-poor. This is because assemblages that are low in silica tend to form sphene (CaTiSiO₅) or perovskite (CaTiO₃) in preference to ilmenite or rutile at lower temperatures, while at higher temperatures the Ti is more likely to be taken up by the pyroxenes and other silicates than by the oxide minerals (Haggerty, 1976b). Thus rocks that are unusually low in silica tend to contain more magnetite than siliceous rocks having the same amount of iron (syenites, for example, are almost invariably more magnetic than granites).

An upper limit to the oxygen fugacity at which magnetite can exist as a stable compound is given by the fO_2 vs T relationship that governs the oxidation of magnetite to hematite, i.e.:

 $2Fe_3O_4 + \frac{1}{2}O_2 \Rightarrow 3Fe_2O_3$ magnetite hematite

This curve is called the "hematite—magnetite (HM) buffer", and it specifies for each temperature the maximum oxygen fugacity at which magnetite is stable against oxidation. Mineral assemblages such as sedimentary iron formations which contain both magnetite and hematite are buffered with respect to oxygen by these two oxides, and during temperature changes the oxygen fugacity will follow the HM buffer. This is evidenced by the fact that magnetite—hematite boundaries in these rocks are preserved with almost perfect precision throughout all levels of regional metamorphism (Klein, 1973). Similarly, in rocks such as pyroxenites which contain both magnetite and fayalite, the oxygen fugacity will follow the FMQ buffer during heating or cooling, and unless oxidation occurs there is minimal exchange of iron between oxides and silicates.

According to Fig. 2, the order in which minerals in the Fe-Ti-SiO₂-O system will form with increasing oxidation, beginning from the lowest levels, is the following: (1) Fe-silicates; (2) titanmagnetites (mt:usp ratio increasing); (3) titanhematites (hem:ilm ratio increasing); (4) hematite.

At high temperatures (T > 600° C) oxidation is caused primarily by the dissociation of H₂O, with loss of H₂ and retention of O₂. The rate at which it occurs depends in large measure upon the amount of hydrogen that is allowed to escape (Haggerty, 1976a). Thus oxidation tends to be maximum for subaerially extruded basalts, intermediate for hypabyssal and plutonic rocks, and minimum for submarine basalts. However, oxidation can be highly variable within a single body; and different Fe—Ti oxide assemblages may exist within different parts of the same unit. This probably accounts for the "birds-eye" anomaly patterns that are so common among subaerially extruded basaltic flows, for example. If allowed to proceed far enough, high-temperature oxidation causes magnetite—ilmenite solid solution intergrowths

to transform toward hematite—ilmenite pseudomorphs. Thus in highly oxidized igneous rocks such as flood basalts NRM is very common, and in many cases it is as likely to be anomalous as normal. In submarine basalts, on the other hand, NRM is uncommon, and magnetic anomalies with inverted polarity are quite unusual.

MAGNETITE IN IGNEOUS ROCKS

Primary magnetite

Having looked at the mineralogy of the iron titanium oxides, let us now consider how primary magnetite forms, and what are the conditions that tend to augment or diminish it after crystallization has taken place. Osborn (1962) has shown that primary basaltic magmas differentiate along either of two trends, leading to two quite different series of subalkaline igneous rocks. The two reaction series are indicated in Fig. 3. The first (Fig. 3a) leads toward residual liquids which are high in silica and low in iron. This is the sequence that is followed by basaltic magmas in which oxygen availability is maintained during fractional crystallization by external sources – usually by an abundant supply of water. The rock assemblages formed by these magmas are typically of the kind that are characteristic of orogenic belts. Iron is prevented from accumulating in the residual liquids by the separation of Fe-Ti oxides as a primary phase. As crystallization proceeds and the liquid becomes progressively more enriched in silica, the oxidation level rises. These liquids form the calc—alkaline series of igneous rocks. The cooling path for this series is indicated by the "calc-alkaline trend" in Fig. 2. Notice that most of the Ti crystallizes out early in the sequence; so that the ultrabasic and basic rocks, which have the higher crystallization temperatures, contain oxides having lower Fe: Ti ratios (therefore weaker magnetic properties) than the intermediate and acidic rocks.



Fig. 3. Two magmatic reaction series (Osborne, 1962).

The second reaction series, shown in Fig. 3, leads toward residual liquids that are rich in ferrous iron and low in silica. This is the trend that is followed by basaltic magmas when no external supply of oxygen is available. As crystallization proceeds the residual liquid attains a progressively lower state of oxidation, so that Ti tends to remain in solution. The end members of this series are Fe-rich gabbroic rocks. The assemblage is typical of mafic intrusions, such as layered gabbroic complexes. The cooling path for this series is indicated in Fig. 2 by the "gabbroic trend". Notice that fO_2 levels fall more rapidly along this trend than along the FMQ buffer; thus iron silicates rather than titanmagnetites crystallize out as a primary phase. However, as the residual liquid becomes progressively more undersaturated in silica other cations compete with Fe^{2+} to form silicates, leaving an excess of FeO in the fluid. This permits titanmagnetite to form at a relatively late stage during the crystallization sequence. One might expect these oxides to have fairly low Fe: Ti ratios and the rocks to be essentially nonmagnetic, but this is not always the case. Some of the well-known mafic complexes such as Skaergaard and Bushveld are in fact strongly magnetic in places. The reason, we think, is that titanium preferentially enters the silicate phase of the gabbros, which are in the lowest oxidation state, leaving the oxides relatively magnetite-rich. Also, the slower cooling of these rocks compared with, say, lavas permits a more complete exsolution to take place between magnetite and ilmenite, and a stronger remanent magnetization to develop.

Which of the two series, (a) or (b), the differentiation path will follow, will depend almost entirely upon the supply of oxygen. Systems that are "closed" with respect to oxygen, i.e., those that maintain their original chemical composition, will experience a continuous decline in oxygen pressure as crystallization proceeds, and they will follow a reaction path that is similar to that of series (b). The mineral assemblages that will develop are those that are characteristic of non-orogenic regions, where the primary magma has moved to the surface through fissures in a competent crust. Systems that are "open" with respect to oxygen, i.e. those which have access to an abundant water supply, will maintain a more nearly constant level of oxygen pressure during crystallization and will follow a reaction path that is similar to that of series (a). The types of minerals that will develop are those that are commonly found in orogenic belts. The two reaction series produce rocks having distinctly different magnetic properties.

Haggerty (1976b) has compiled an impressive quantity of data from various sources on the (fO_2,T) conditions found in igneous rocks, which are shown synoptically in Fig. 4. We can summarize by saying that, on average, extrusive rocks of acidic and intermediate composition are the most highly oxidized of all the groupings and therefore will contain oxides having the highest Fe:Ti ratios. Basic extrusive rocks are in a distinctly more reduced state, and form oxides having low Fe:Ti ratios which therefore have weak susceptibilities. The acid—intermediate intrusive group is a little more complex. Granites are in a relatively oxidized state, similar to that of acid extrusive rocks, and therefore might be expected to contain strongly magnetic iron oxides. Syenites and monzonites (rocks which are low in SiO₂) have oxidation levels that are similar to those of basic extrusive rocks; while shonkinites show oxidation levels below that of the FMQ buffer. Samples from layered





Fig. 4. Summary of data on igneous rocks (Haggerty, 1976b).

intrusive suites for the most part lie close to the FMQ buffer, but the larger complexes (Stillwater, Bushveld, Skaergaard) indicate differentiation paths which fall below this curve. Magmatic ore deposits of apatitic association are comparatively oxidized, while those of anorthositic and gabbroic association lie on both sides of the FMQ buffer. These data provide solid support for Osborn's two reaction series, and for the trend lines shown in Fig. 2.

Fig. 5 shows a plot of total iron (expressed as percent by weight FeO + Fe_2O_3) versus total silica (percent by weight SiO₂) for (a) volcanic rocks and



Fig. 5. Trends in total iron, Fe:Ti ratio, and magnetite in igneous rocks. Data from Nockolds (1954) and from Buddington and Lindsley (1964).

(b) layered intrusive rocks. The data on volcanic rocks are from Nockolds (1954) and from Turner and Verhoogen (1960); the layered intrusion field is drawn from data on the Bushveld and Stillwater complexes (Hess, 1960) and on the Skaergaard complex (Buddington and Lindsley, 1964). Superimposed upon the compositional data are two other pairs of curves which are only schematic, and not the result of actual measurements. One pair shows trends in the iron:titanium ratio as deduced from the Buddington-Lindsley curves. The other pair shows general trends in bulk magnetic susceptibility by using the empirical relationship obtained from Balsley and Buddington's (1958) data. The curves indicate that among volcanic rocks of series (a), bulk magnetic susceptibility should attain a maximum within the dacite compositional range, and that fresh, unaltered basalt and andesite should be distinctly less magnetic. Among unaltered intrusive rocks, the peak of magnetic susceptibility should occur within the quartz diorite compositional range. These observations actually do conform in a general way with the writer's experience, and they are not difficult to explain. There appears to be a well-established trend toward higher oxidation levels, therefore higher Fe:Ti ratios, with increasing SiO_2 and lower freezing temperatures among both extrusive and intrusive igneous rocks. Against this trend must be balanced the fact that Fe—Ti oxides begin to crystallize at temperatures above 1100° C, beginning with ilmenite and ulvöspinel, and that they are fully crystallized at temperatures of about 700°C, ending with magnetite. Most of the iron and virtually all of the titanium enters the differentiates of basic and ultrabasic composition, which have the higher crystallization temperatures. Here they form iron-titanium oxides that are relatively rich in titanium and therefore weakly magnetic. By the time the melt has attained the freezing temperatures of the acidic end members, very little iron and virtually no titanium remain; but what little iron is left forms almost pure magnetite. The trade-off between increasing Fe: Ti ratios and a steadily diminishing supply of iron results in maximum magnetic susceptibilities occurring within the felsic-intermediate compositional range.

The distinction between the two magmatic series of igneous rocks is of great importance in mineral exploration, since quite different types of ores are associated with the two different groups.

Oxides vs silicates, and the role of biotite

A major defect in the simple scheme that we have used thus far is that it ignores the influence of cations other than Fe and Ti in determining the division between oxide and silicate phases, and it therefore imposes upon the system a very simple mineralogy which consists entirely of the oxides and silicates of iron-titanium. The real mineralogical world is vastly more complicated, chiefly owing to the abundant presence of Mg, Ca, K and Al in virtually all rocks. These additional cations give rise to a mineral chemistry of enormous richness and variety which involves much more complex interrelationships than any that we have dealt with so far. Common examples are found in the complex Fe-Mg-Ca-Al silicates which exist under the general names of pyroxenes, amphiboles and micas. Since all of these silicates to some degree compete with the oxides for the available iron, their influence upon the amount of magnetite that can form within a given mineral assemblage, and therefore upon its magnetic properties, cannot be ignored.

Among the rock-forming ferromagnesian silicates, only biotite has been studied in sufficient detail to enable us to discuss its relationship with the primary opaque oxide minerals. The conclusions probably also apply in a general way to amphiboles and pyroxenes.

Let us begin with the simplest of the biotites, namely iron biotite or annite, which can be obtained by adding Al and K to the Fe—Ti—Si—O system. Annite is a relatively low-temperature mineral. It begins to break down at about 500° C. At high oxygen pressures it breaks down into K-feldspar and magnetite (Wones and Eugster, 1965), i.e.:

while at lower oxygen pressures, it decomposes into K-feldspar and Feolivine:

$$\begin{array}{rcl} \mathrm{KFe_{3}AlSi_{3}O_{10}}\left(\mathrm{OH}\right)_{2} \ + \ \frac{3}{2} \ \mathrm{SiO}_{2} \ \ \Rightarrow \ \ \mathrm{KAlSi_{3}O_{8}} \ \ + \ \frac{3}{2} \ \mathrm{Fe_{2}SiO_{4}} \ \ + \ \mathrm{H_{2}O} \\ & & & & \\ \mathrm{Fe-biotite} & & & & \\ \mathrm{quartz} & & & & \\ \mathrm{K-feldspar} & & & & \\ \mathrm{Fe-olivine} \end{array}$$

The water vapour that is produced in this reaction is slightly oxidizing, so that in time it will bring the oxygen fugacity back to the level at which magnetite begins to form once again. The two reactions thus proceed simultaneously, the relative rates being such that the oxygen fugacity remains close to the FMQ buffer. This means that more Fe^{2+} enters into the silicates than into magnetite; although the proportion of Fe^{2+} forming magnetite will begin to rise if there is depletion in SiO₂.

The stability field of annite (Fe_{100}) is shown superimposed on the Buddington—Lindsley curves in Fig. 6. Notice the degree to which it limits the formation of magnetite at low temperatures and at low oxygen pressures.

If there is an excess of Al in the system, i.e., if there is insufficient K to form enough biotite to take up all of the available aluminum, annite becomes unstable at higher oxygen pressures against transformation into muscovite. One such reaction is the following:

$$\begin{array}{cccc} \mathrm{KFe_{3}AlSi_{3}O_{10}} & \mathrm{(OH)_{2}+Al_{2}SiO_{5}} + \frac{1}{2}O_{2} \\ & & \\ \mathrm{Fe-biotite} & \text{sillimanite} & \mathrm{muscovite} & \mathrm{magnetite} & \mathrm{quartz} \end{array}$$

Another similar reaction involves chlorite in place of sillimanite.

An excess of aluminum (or deficiency of potassium) thus enlarges the stability field of magnetite at low temperatures and oxygen pressures. The oxygen fugacity-temperature relation corresponding to this reaction is shown in Fig. 6. The data are from Wones and Eugster (1965).



Fig. 6. Temperature vs oxygen fugacity conditions for biotite (Wones and Eugster, 1965). The data on granites are from Haggerty (1976b).

The effect of adding Mg to the system is to enlarge the stability field of biotite as shown in Fig. 6. The various curves have been drawn from data of Wones and Eugster (1965), and they indicate the stability limits for biotites having various Fe:Mg ratios. At high oxygen pressures the biotite fields are limited by decomposition into K-feldspar and (Fe, Mg) oxides; at lower oxygen pressures, by breakdown into K-feldspar and pyroxene, i.e.:

$$\begin{array}{rl} K(Fe,Mg)_{3}AlSi_{3}O_{10}(OH)_{2} + 3SiO_{2} & \rightleftharpoons KAlSi_{3}O_{8} + 3(Fe,Mg)SiO_{3} + H_{2}O_{10}O_{1$$

Fig. 6 explains a number of known facts. For example:

(a) In systems that are internally buffered by their mineral assemblages biotites become more iron-rich with lower temperatures of crystallization. Thus biotites occurring in acidic rocks tend to be more iron-rich than those occurring in basic rocks.

(b) Biotites and other silicates will attract Fe^{2+} away from the oxide phases during crystallization, so that rocks that are rich in biotite/hornblende tend to be depleted in magnetite. The effect becomes more pronounced with decreasing crystallization temperatures, so that granites, for example, commonly contain Fe-rich biotite and very little magnetite.

(c) Biotites become progressively more Mg-rich with increasing levels of oxidation at all crystallization temperatures, indicating that the higher the oxidation state of the assemblage, the more Fe^{2+} will be available to form magnetite.

Thus characterizing accessory minerals such as biotite or hornblende play an important role in determining the amount of primary magnetite that is able to form during crystallization. It is therefore necessary to consider the influence of these minerals in any relationship involving igneous rock types and magnetic properties. We will return to this problem later.

Secondary magnetite

Theoretically, mafic and especially ultramafic rocks should, on account of their low oxidation states, be nonmagnetic or only weakly magnetic. In practice, these types of rocks frequently produce magnetic anomalies that compare in intensity with those caused by magnetite—quartzite iron formations. The magnetite in these cases is almost always secondary, that is, it has developed as a result of alteration processes that have occurred since primary deposition.

Of the alteration processes that lead to the creation of magnetite the most important is serpentinization, which in varying degrees affects most mafic and almost all ultramafic rocks. Basically, serpentinization involves the transformation of olivine and orthopyroxene (enstatite) in peridotites, dunites or harzburgites into hydrous (Fe, Mg) silicates and magnetite (Moody, 1976). It is a retrometamorphic process, in the sense that the direction in which it proceeds is toward lower temperatures and lower oxidation states. A possible



Fig. 7. Oxygen fugacity and temperature conditions during serpentinization (Page, 1967).

path for serpentinization in (fO_2,T) space has been given by Page (1967), and is shown in Fig. 7. This curve illustrates an intriguing point about the serpentinization process that has been remarked upon by Haggerty (1979), namely, that it leads to such low oxidation states that native iron or iron—nickel alloy (awaruite) should be able to form; and indeed these substances may be important contributors, as Haggerty has suggested, to the magnetic properties of serpentinized ultramafic rocks.

MAGNETITE IN SEDIMENTARY ROCKS

Weathering and the sedimentary environment

It is unusual to find magnetite in unmetamorphosed sedimentary rocks except in very, very minor amounts. The reason is simple: magnetite is unstable in the low-temperature, highly oxidizing environment of chemical weathering and sedimentation. Sediments may contain a great deal of iron, but it is commonly in the form of hydrous ferric oxides, hematite, and siderite. To a first approximation, therefore, unmetamorphosed sediments may be considered non-magnetic. Beach sands, river placers and other sedimentary formations in which detrital magnetite is sometimes found may be capable of producing magnetic anomalies, but in general they are very weak when measured from the air. The effect of chemical weathering and sedimentation on iron can be summed up as follows.

Stage 1 (Chemical weathering.) Attack by groundwater containing CO_2 causes the ferrous iron minerals eventually to break down, Fe^{2+} being slightly soluble in water containing CO_2 . The Fe^{2+} which goes into solution is readily oxidized to Fe^{3+} , which is much less soluble. This leads to the precipitation of hydrated ferric oxides such as goethite (Berner, 1980), which are usually colloidal but in any case extremely fine-grained.

Stage 2 (Leaching.) Soils formed from breakdown products may, under persistent rain attack, become leached of their more soluble components, forming laterite deposits. Rich in hematite, these deposits sometimes contain small amounts of maghemite. Laterites can produce spotty but quite detectable aeromagnetic anomalies. These are usually caused by minor concentrations of maghemite, rarely by magnetite.

Stage 3 (Transportation.) During transportation by rivers and by groundwater, colloidal ferric hydroxyls become preferentially attached to particles of clay or silt (Carroll, 1958), and sometimes to particles of organic matter, but rarely to sand grains. Being fine-grained, the clay particles with their iron hydroxide coatings deposit in quiet, relatively deep-water environments. Thus iron that is derived from chemical weathering is preferentially concentrated in argillaceous sediments, which almost invariably contain more iron than arenaceous deposits (James, 1966).

Stage 4 (Compaction and early diagenesis.) During compaction, the ferric hydroxides form hematite. Magnetite has such a limited field of stability in



Fig. 8. Stability fields for minerals in the Fe-S-O system, in terms of Eh and pH (Garrels and Christ, 1965).

the presence of natural waters (Fig. 8) that it could never form on the floor of today's oceans. However, below the sea water/sedimentary interface conditions of sufficiently low Eh and high pH might conceivably exist (where alkaline brine solutions are in contact with a reducing (anaerobic) environment, for example) in which magnetite might form by the reduction of hematite or by the oxidation of pyrite. The conditions that are needed to form magnetite occur rarely in sedimentary environments, however. There is much debate about whether the ocean environment was less oxidizing and perhaps contained less sulfur during earlier geological epochs than it does at present: if so, the stability field for magnetite would have been larger. However, a careful study of sedimentary iron formations of all ages indicates that magnetite does not, and never has, formed in significant quantities by diagenesis (Laberge, 1964). The iron minerals that are able to form in the diagenetic environment, and which are primary constituents of virtually all sedimentary iron formations, are (i) hematite (formed in aerobic environments), (ii) pyrite (formed in organic, bacteria-rich environments), (iii) siderite (formed in organic, fresh-water environments) and (iv) greenalite. Magnetite is almost always a secondary mineral. It forms chiefly in the biotite-chlorite zone of the greenschist facies of regional metamorphism (Laberge, 1964; French, 1973), usually by the oxidation of greenalite:

or of siderite:

 $3Fe_2CO_3 + \frac{1}{2}O_2 \Rightarrow 2Fe_3O_4 + CO_2$ siderite magnetite

In unmetamorphosed iron-rich sediments which are the precursors of sedimentary iron formations, magnetite is only occasionally present as a primary mineral, and only in very minor amounts.

Titanium, unlike iron, is completely insoluble in groundwater. Thus the titanium oxides remain with the solid fraction, usually as rutile (TiO_2) , which tends to concentrate in arenaceous sediments, especially in beach sands. The close chemical relationship that exists between iron and titanium in igneous rocks is broken by chemical weathering and sedimentation; and not until levels of regional metamorphism are reached at which partial melting occurs do the two elements re-unite to form the opaque oxide minerals again.

MAGNETITE IN METAMORPHIC ROCKS

Primary controls

Magnetite is produced by the breakdown of (Fe, Mg) silicates at all levels of regional metamorphism. The two most important determinants of how much secondary magnetite can form during metamorphism are total iron content and oxidation state. The first fixes an upper limit on the potential production, while the second controls the partitioning of iron between the oxide and silicate phases.

Iron-poor rocks can never form significant quantities of magnetite, no matter what their oxidation state. Among sedimentary and metasedimentary rocks, this self-evident fact imposes a clear distinction between carbonates and sandstones and their metamorphic derivatives on the one hand, and argillaceous sediments (shales) and their metamorphic derivatives on the other. This is because shales generally contain more iron than sandstones or carbonate rocks due to the tendency of iron to become attached to clay particles during sedimentation. The difference in magnetic properties grows larger with rising metamorphic grade. For example, graywackes are usually more magnetic than quartzites or dolomites; chlorite schists normally contain more magnetite than quartz schists or calc schists. This division persists up to the highest metamorphic levels.

The controlling influence of oxidation on the partitioning of iron between oxides and silicates in metamorphic rocks is clearly demonstrated in a study by Chinner (1960) of the major element chemistry of a sequence of pelitic metasediments in the Scottish Grampian Highlands which have been regionally metamorphosed within the sillimanite zone. Chinner considered the partitioning of total iron between the silicate and oxide minerals as a function of overall oxidation ratio. His results (Fig. 9) show quite clearly that there is a definite peak in the percentage of total iron that is in the form of magnetite, and it is centered at an O-ratio (defined as $Fe^{3+}/Fe^{2+} + Fe^{3+}$) of approximately 0.5. Magnetite takes up a significant fraction of the total iron if the O-ratio lies between about 0.4 and 0.6. At lower O-ratios, the iron is concentrated preferentially in the silicate phases; at higher ratios, it forms hematite + ilmenite. These observations are in accord with the Buddington—Lindsley curves of Fig. 2.



Fig. 9. Chinner's (1960) data on metamorphic rocks near Angus, Scotland (from Mc-Intyre, 1980).

Chinner's observations were made upon rocks which were metamorphosed under medium or high grade conditions. An important point to consider is whether oxidation ratios show a tendency to rise or fall with progressive metamorphism, since this will affect the magnetite-producing potential of all metamorphic rocks. No evidence has been put forward that oxidation state is related in any obvious way to metamorphic grade (Eugster, 1959). On the contrary, studies of banded iron formations by Klein (1973) have shown that magnetite—hematite boundaries are maintained with complete precision throughout all levels of regional metamorphism. This suggests that systems tend to be buffered during metamorphism by the mineral assemblages which they contain. To the extent that internal buffering prevails, overall oxidation state will be preserved during metamorphism, and will reflect the premetamorphic chemical condition of the rock.

Other factors also play a role in the formation of magnetite during metamorphism, but they are of less importance than total iron content and oxidation state. Essentially, these additional influences relate to the effects which cations other than Fe and Mg may have upon the oxidation state of a mineral assemblage. The only two that it is worthwhile to discuss in this regard are C and Al.

Carbon is a reducing agent, and its presence lowers the oxygen fugacity of a rock. This creates a further restriction upon the size of the stability field

of magnetite by interposing a siderite buffer between the HM and the FMQ buffers at low pressures and temperatures. If the magnetite field is already restricted by the presence of silica and titanium, the presence of carbon may eliminate it altogether. Thus one often encounters a complete absence of magnetite in graphitic metasediments and in rocks which have undergone carbonate alteration.

The effect of excess *aluminum* is to favour the production of muscovite over biotite within the biotite—muscovite zone of regional metamorphism. This results in the development of magnetite over sillimanite as a secondary mineral. The reaction, according to Wones and Eugster (1965), is:

$$\begin{array}{rll} \mathrm{KFe_3AlSi_3O_{10}}\left(\mathrm{OH}\right)_2 + \mathrm{Al_2SiO_5} + \frac{1}{2}\mathrm{O_2} \\ \Rightarrow \mathrm{KAl_3Si_3O_{10}}\left(\mathrm{OH}\right)_2 + \mathrm{Fe_3O_4} + \mathrm{SiO_2} \\ & \text{iron biotite} \\ & \text{sillimanite} \\ & \text{muscovite} \\ \end{array}$$

The addition of Al favours the right-hand assemblage, as does the addition of O. Increasing the temperature favours the left-hand assemblage. Thus during early metamorphism, aluminous metasediments tend to form magnetite more readily than non-aluminous sediments.

Production of magnetite during metamorphism

There are many reactions which lead to the production of secondary magnetite during regional metamorphism. We list some of the more important ones below.

(1) Reactions in the lower greenschist facies (chlorite—biotite zone: $T \sim 250^{\circ}-350^{\circ}C$). Probably the most important one from our point of view is the transformation of chlorite + hematite to chloritoid + magnetite + quartz, i.e.:

 $\begin{array}{rl} \mathrm{Fe_7Al_4Si_4O_{15}(OH)_{12}+5Fe_2O_3 \end{array} \approx 2\mathrm{FeAl_2SiO_5(OH)_2+5Fe_3O_4+2SiO_2+4H_2O}\\ \mathrm{chlorite} & + & \mathrm{hematite} & \mathrm{chloritoid+magnetite+quartz} \end{array}$

Notice that this reaction involves dehydration, with accompanying compaction. Although magnetite replaces hematite as the iron oxide mineral, this does not come about through reduction of Fe^{3+} to Fe^{2+} . Rather, FeO is taken from the silicate and enters the iron oxide phase. The O-ratio of the assemblage does not change.

(2) Reactions in the upper greenschist facies (biotite-muscovite zone: $T \sim 350^{\circ}-450^{\circ}C$). The following reaction:

chlorite ± biotite + hematite \rightleftharpoons muscovite ± K-feldspar + magnetite + SiO₂ + H_2O

together with the transformation of chlorite to chloritoid is one of the principal mechanisms by which magnetite replaces hematite as the major iron oxide mineral in metasedimentary rocks. Both reactions involve dehydration, compaction, and the production of magnetite—quartzite assemblages. The FeO needed to form magnetite is withdrawn from the silicates. The transformation of the iron oxides from a predominantly hematitic to a predominantly magnetitic composition is more or less completed at this stage of regional metamorphism.

(3) Reactions in the epidote amphibolite facies (almandine—staurolite—kyanite zone: $T \sim 450^{\circ}-550^{\circ}C$). In the epidote amphibolite facies of regional metamorphism, chloritoid breaks down into (Fe, Al) silicates ± magnetite as follows (Ganguly and Newton, 1968). At relatively low oxygen fugacities:

chloritoid + $O_2 \Rightarrow$ almandine + staurolite + magnetite + H_2O

The reaction quickly becomes self-limiting, however, because the consumption of oxygen will lower the oxygen fugacity to the point where the following reaction takes over:

chloritoid + SiO₂ \Rightarrow almandine + staurolite + H₂O

At increasing temperatures and oxygen fugacities the first reaction changes to the following one:

chloritoid + $O_2 \Rightarrow$ staurolite + magnetite + SiO_2 + H_2O

and at still higher temperatures and oxygen pressures:

chloritoid + $O_2 \Rightarrow$ kyanite + magnetite + H_2O

so that the general reaction involving the breakdown of chloritoid can be written as:

chloritoid \pm SiO₂ \pm O₂ \Rightarrow staurolite \pm almandine \pm kyanite \pm magnetite + H₂O

In all of these reactions, rising temperature and oxygen pressure favour the right-hand assemblages. The equilibrium temperature for the staurolitemagnetite-quartz reaction at a total pressure of 5 kbar is approximately 525°C, according to experiment.

(4) Reactions in the amphibolite facies (sillimanite zone: $T \sim 550^{\circ} - 650^{\circ}C$). In the sillimanite zone, the biotites begin to break down. The break-down sequence begins with iron biotite, i.e.:

 $\begin{array}{rl} KFe_{3}AlSi_{3}O_{10}(OH)_{2} \ + \frac{1}{2}O_{2} \ \rightleftharpoons \ KAlSi_{3}O_{8} \ + \ Fe_{3}O_{4} \ + \ H_{2}O_{10}O_{$

Notice that this reaction involves the oxidation of Fe^{2+} to Fe^{3+} to form magnetite. As the system is buffered, the oxygen fugacity will drop. As the oxygen fugacity drops to the point where silicates begin to form, the following reaction takes over:

$$\begin{array}{ll} \mathrm{KFe_{3}AlSi_{3}O_{10}(OH)_{2}} \rightleftharpoons \frac{3}{2} \mathrm{SiO_{2}} \rightleftharpoons \mathrm{KAlSi_{3}O_{8}} + \frac{3}{2} \mathrm{Fe_{2}SiO_{4}} + \mathrm{H_{2}O} \\ \mathrm{iron\ biotite} & \mathrm{quartz} & \mathrm{K-feldspar} & \mathrm{Fe-olivine} \end{array}$$

The two reactions proceed simultaneously in such a manner that the oxygen fugacity stays close to the FMQ buffer. This means that more Fe^{2+} will enter the silicate phase than the oxide phase. In general, the amount of magnetite

324

that forms as a result of these breakdown processes is relatively minor at first, but increases as the reaction proceeds.

If magnesium is added to the system, there is a tendency to form pyroxene rather than olivine, i.e.:

 $\begin{array}{lll} K(Fe,Mg)_3 \ AlSi_3O_{10}(OH)_2 \ + \ 3SiO_2 \ \approx \ KAlSi_3O_8 \ + \ 3(Fe,Mg)SiO_3 \ + \ H_2O \\ & \ biotite & \ K-feldspar & \ pyroxene \end{array}$

Thus the general reaction involving the breakdown of biotite during amphibolite facies metamorphism is:

biotite \pm SiO₂ \pm O₂ \Rightarrow K-feldspar + (Fe,Mg) silicates \pm magnetite + H₂O

where (Fe,Mg)silicates include pyroxene, olivine and amphibole.

(5) Reactions in the granulite facies (cordierite zone: $T \sim 650^{\circ} - 750^{\circ}C$). Granulite facies metamorphism is characterized by the final breakdown of the micas and the appearance of hypersthene, i.e.:

biotite \pm muscovite + SiO₂ \Rightarrow hypersthene + K-feldspar + cordierite \pm magnetite + H₂O

There is also a tendency for the iron pyroxenes to break down into magnetite + quartz:

 $3 \operatorname{Fe_2SiO_4} + \operatorname{O_2} \neq 2 \operatorname{Fe_3O_4} + 3 \operatorname{SiO_2}$

The general reaction involving magnetite production during granulite facies metamorphism is therefore:

hydrous (Fe,Mg) Al-silicates \pm SiO₂ \pm O₂ \rightleftharpoons K-feldspar + (Fe,Mg) silicates \pm magnetite + H₂O

Summarizing these reactions, increasing temperatures favour the breakdown of hydrous (Fe,Mg) silicates into progressively less hydrous and chemically simpler compounds, beginning with complex substances like chloritoid and ending up finally with simple silicates like hypersthene. Secondary magnetite is produced from these reactions and silica is consumed at all stages of progressive metamorphism; but significant production of magnetite takes place either under relatively low-grade conditions — usually in rocks that are hematitic — or under sufficiently high grade conditions that there is a significant breakdown of biotite and amphibole and a loss of silica. Thus there is a general tendency for iron-bearing rocks to become more magnetic with increasing metamorphic grade.

With the attainment of granulite facies temperatures, two things happen that have a further impact upon rock magnetic properties, namely, (1) partial melting begins to take place, and (2) the magnetite—ulvöspinel solid solution miscibility gap closes. With anatexis, the silica-rich, low-melting-point minerals start to segregate, leaving the high-melting point, low-silica plus the opaque oxide minerals in the restite portion. As differential melting proceeds the restites attain a progressively lower oxidation state; and since they are now free to do so, iron and titanium oxides will begin to recombine to form magnetite—ilmenite solid solutions. Thus we should expect a loss of magnetization to occur during migmatization and granitization. This may be offset to some extent by the effect of silica undersaturation if the loss of silica (and other volatiles) has been great; but in general, extreme metamorphism seems to be accompanied by a marked reduction in magnetic strength.

It is interesting to see to what extent these laboratory-based inferences are corroborated in the field. Fig. 10 shows general trend-lines for (i) magnetite content, (ii) percentage by weight of iron+magnesium+manganese+titanium oxides and (iii) induced magnetization as functions of the percentage by weight of silica, among metamorphic rocks of all compositions in the Ukrainian Shield (Krutikhovskaya et al., 1979). This is the only comprehensive study of rock magnetic properties throughout a major geological province that I know of. According to the authors, it includes several hundreds of thousands of measurements. Notice that the amount of iron in the form of oxides (as apposed to silicates) increases steadily with metamorphic grade; but notice also that as the highest levels are reached, the magnetite content increases less rapidly than the total amount of oxides. These observations are consistent with the notion that magnetite is derived to a significant degree for the progressive breakdown of (Fe,Mg) silicates, and that the process is internally buffered by the oxide and silicate mineral assemblages. The formation of secondary magnetite appears to accelerate somewhat within the upper am-



Fig. 10. Trends in magnetite, primary oxides and magnetization of rocks from the Ukrainian Shield (Krutikhovskaya et al., 1979).

phibolite and granulite facies of regional metamorphism, due perhaps to increasing silica undersaturation.

It is also interesting to note that induced magnetization increases more rapidly than magnetite content within the upper amphibolite and granulite metamorphic facies. This implies that magnetic susceptibility rises with magnetite content at a more rapid rate than a simple first-power law among strongly metamorphosed rocks. This can probably be attributed to the development of coarser crystalline textures and the attainment of crystal sizes that permit easier domain wall movement.

The ratio of remanent to induced magnetization (the Q-ratio) of the Ukrainian Shield rocks tends to remain at about unity. It is distinctly higher than unity among certain high-grade rocks, such as cherty iron formations and pyroxenites. There are some questions concerning the identity of the carriers of the remanent magnetization in these rocks: In the pyroxenites, the carrier would appear to be fine-grained magnetite occurring within the pyroxene matrix (Evans and McElhinney, 1969); in the iron formations, it is likely to be titanhematite. It is interesting to note that the rocks having the highest Q-values are mostly within the amphibolite facies of regional metamorphism, which agrees with my own observations in other Precambrian shield areas. The great majority of the remanent magnetizations are "normal", that is, they are more or less in the direction of the geomagnetic vector. Only a small proportion of the samples that were measured had abnormal NRM's and these were confined to limited areas*¹. None of the samples had Q values that were much below unity.

Fig. 11, also from Krutikhovskaya's paper, shows the general trend of magnetic susceptibility plotted against degree of granitization. With the transformation of crystalline meta-igneous and metasedimentary rocks



Fig. 11. Changes in magnetic susceptibility with degree of granitization among Ukrainian Shield rocks (Krutikhovskaya et al., 1979).

^{*&}lt;sup>1</sup>There appears to be a possible relationship between abnormal NRM's and the occurrence of sulfide minerals, which we shall discuss in a subsequent paper.

(orthogneiss, paragneiss) into migmatites and finally into granites, magnetic susceptibility declines sharply. No explanation for this was offered; but I believe that it may be related to the closing of the miscibility gap between magnetite and ulvöspinel. It seems highly unlikely that the oxides of iron and titanium which are high temperature minerals, would decompose into other substances. The general level of the magnetic susceptibility curve is higher for basic rocks of igneous origin than for metasediments, but the trends are similar for both series.

CONCLUSION

Aeromagnetics and geological mapping

It is abundantly clear that magnetite is far from being an inert mineral; it reacts with its environment in a variety of ways. The magnetic properties of a rock are determined not only by its original chemistry, but also by nearly everything that has happened to it since it was emplaced. In the hierarchy of influencing factors, major mineralogy seems to be of relatively little importance.

Consequently, magnetite is not, by itself, a reliable lithological tracer. The problem is to ascertain what kinds of geological information can be obtained trustworthily from aeromagnetic surveys, and what rules there are for educing this information.

Basically, the problem reduces to one of nomenclature. It has been said earlier, and we re-iterate, that it is practically impossible to determine silicate/carbonate mineralogy from magnetic surveys; consequently, conventional lithological nomenclature is of little use in naming rock units that are defined solely by concentration levels and distribution patterns of magnetite. What is needed is a classification system that is more directly based upon opaque oxide mineralogy, and upon the partitioning of iron between oxide and silicate minerals. In order to be useful for interpretating magnetic survey data, such a system must recognize the factors which are the most influential in determining bulk magnetic properties. These include the following.

(1) Total iron content. Iron-rich rocks, whatever their condition, have a higher magnetite-producing potential than iron-poor rocks. Rocks containing unusually large amounts of iron generally characterize areas in which an abnormally high degree of crust—mantle interaction has occurred during the period of formation.

(2) Oxidation state. If the oxidation ratio is very low, most of the iron will enter the silicates. If it is too high, the iron will form hematite + ilmenite. Among metamorphic rocks, the oxidation ratio is largely an inheritance from the premetamorphic state. It remains essentially unaltered or increases only slightly during metamorphism.

(3) Initial crystallization environment. Igneous rocks which have formed in an environment that is "closed" with respect to oxygen (usually anhydrous) tend to be more iron-rich than those which have formed in an "open" (usually orogenic) environment. Although the iron is mostly fixed in nonmagnetic silicates (amphibole, pyroxene, biotite), the rocks have a relatively high magnetite-producing potential during subsequent metamorphism.

(4) Degree of metamorphism. One of the main causes of the increase in magnetic properties that is often seen to occur in rocks which have been metamorphosed under higher-grade conditions is the progressive breakdown of hydrous, iron-rich (Fe,Mg) silicates such as biotite and amphibole toward magnesium-rich orthosilicates such as pyroxene. Magnetic properties become further strengthened by repeated cycles of regional metamorphism.

(5) Degree of silica saturation. Rocks that are deficient in silica usually contain more magnetite and less ilmenite than silica-saturated rocks having the same amount of iron.

(6) Grain size of original sediment (in metasedimentary rocks). Pelitic metasediments which have been derived from fine-grained sedimentary rocks almost invariably contain more iron (and more magnetite) than psammites.

(7) Major element chemistry. Among metasedimentary rocks, a higher aluminum content favours the formation of muscovite+magnetite over biotite. Among igneous rocks, a low magnesium content allows greater amounts of primary magnetite to form. A deficiency in *titanium* leads to higher magnetic susceptibilities. A loss of titanium from the primary opaque oxides to the silicates is most likely to be associated with the formation of sphene in silica-undersaturated rocks.

In addition to these intrinsic rock properties, there are certain exogenous conditions which, if they are imposed upon the rock, will usually lead to an increase or decrease in magnetic properties. Conditions which tend to increase the magnetization of rocks, either by increasing their magnetic susceptibility or by creating new magnetite, include: (1) mechanical deformation; (2) repeated metamorphism; (3) high-temperature hydrous alteration (serpentinization); while conditions that tend to destroy magnetite include: (1) low-temperature alteration processes (carbonatization, chloritization, sericitization); (2) extreme oxidation, including chemical weathering and leaching; (3) granitization or metasomatism.

In addition to the controls on magnetic susceptibility, conditions which favour strong remanent magnetizations should also be recognized. These include: (1) sufficiently high levels of oxidation that hematite—ilmenite microintergrowths are able to form; (2) relative enrichment in titanium; (3) small crystal size; (4) sulfide mineralization.

A nomenclature which recognizes all or most of these factors would be ideally suited to magnetic interpretation. At some point, however, the new system must be related to a more conventional geological scheme in order to apply existing knowledge of ore genesis to the problem of appraising economic potential. These relationships will have to be established for each survey by means of a ground-truth study program. It is important, for example, to have an approximate idea of the distribution of characterizing accessory minerals and metamorphic grades. Volcanic features such as pillow structures can also be important. Samples from key formations should be taken for laboratory analysis, which will include major element chemistry, opaque mineralogy, and the measurement of $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratios and magnetic properties, including remanence. A mapping and sampling program along these lines can be carried out efficiently by keeping to limited objectives and narrowly-defined goals, and large areas can be covered in a short time.

Toward a magnetic classification: The granitoid series

Ishihara (1977, 1981) has shown that granitoid rocks in Japan can be divided on the basis of their opaque mineralogy into two distinct species, which he has termed "magnetite series" and "ilmenite series" granitoids. The magnetite series granitoids by definition contain more than 0.1 vol.% of primary opaque oxide minerals, of which magnetite constitutes approximately 90%. The ilmenite series granitoids contain less than 0.1% of primary opaque oxides, which consist almost entirely of ilmenite. They contain practically no magnetite. The magnetite series granitoids have magnetic properties and produce magnetic anomalies, whereas the ilmenite series granitoids are virtually non-magnetic. Geographically, the two series follow distinct belts or zones which have clearly defined borders, suggesting that they have different magnetic origins.

Mineralogically, the two granitoid series differ in the following ways. In the magnetite series, biotite and hornblende are relatively magnesium-rich. In the ilmenite series, biotite is generally iron-rich besides being more plentiful, while hornblende is usually absent. Silicates become progressively more magnesium-rich with increasing silica content in magnetite-series host rocks, whereas in those of the ilmenite series they become progressively more ironrich. This suggests that magmas which produce magnetite series granitoids differentiate along trend (a) of Fig. 3, while ilmenite series magma differentiate along trend (b). Sphene, epidote and other minerals belonging to this group are commonly present in granitoid rocks of the magnetite series, but are seldom found in ilmenite series rocks; garnet, on the other hand, is much more prevalent in rocks of the ilmenite series. Graphite is also a fairly common accessory mineral in ilmenite series rocks, whereas it is totally lacking in magnetite series granitoids. In all other respects, the overall chemical compositions are similar (the ilmenite series granites are generally more salic, but this has not been noted as a primary distinguishing characteristic). It is probably reasonable to conclude from Fig. 6 that the magnetite series granitoids have evolved at higher temperatures and under higher oxygen fugacity conditions than the ilmenite series granitoids, and it is therefore likely that they have originated from a greater depth within the mantle. It is also important to note that the magnetite series rocks have the higher oxidation ratios. Roughly speaking, the O-ratios of magnetite series granitoids fall within the range 0.3–0.5, versus values smaller than 0.2 for ilmenite series granitoids. This accounts for why the latter contain so little opaque oxide minerals. Finally, it should be noted that sulfur isotopic ratios correlate closely with the primary opaque oxides: without a single exception, δ^{34} S is positive for magnetite series granitoids, and is predominantly negative for ilmenite series granitoids among the samples that were measured.

The classification of granitoid rocks into magnetite series and ilmenite series is somewhat analogous to the subdivision of the Australian granites into I (for igneous)-type and S (for sedimentary)-type, based upon their characterizing mineral assemblages (Chappell and White, 1974). The criteria are not quite the same, however and so there is not a simple and straightforward correspondence between the two classification systems (Takahashi et al., 1980). Ishihara's scheme is more directly related to opaque oxide mineralogy and to magnetite, and is the more useful system for geophysicists. Furthermore, the division of granitoid rocks into magnetite series and ilmenite series has direct implications for metallogeny, and may provide a potentially useful new regional exploration concept. We shall discuss this aspect of the new classification system in a sequel paper.

CONCLUSION

Magnetometer surveys tell us very little about the silicate or carbonate mineralogy of the rocks beneath us, but they can tell us much about their origin and their oxidation state if they are supported by adequate groundtruth and laboratory studies. Magnetite concentration patterns can thus help to lift aside the metamorphic veil and to identify ancestral or premetamorphic lithologies; but to do this requires a geological nomenclature and classification system that is based primarily upon the opaque oxide minerals rather than upon silicates or carbonates. Such a system is not yet in place; but studies are being carried out which appear to be converging toward a solution to this practical and important problem.

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REFERENCES

- Ade-Hall, J.M., 1964. A correlation between remanent magnetism and petrological and chemical properties of Tertiary basalt lavas from Mull, Scotland. Geophys. J. R. Astron. Soc., 8: 403-423.
- Ade-Hall, J.M., Palmer, H.C. and Hubbard, T.P., 1971. The magnetic and opaque petrological response of basalts to regional hydrothermal alteration. Geophys. J. R. Astron. Soc., 24: 137-174.
- Ade-Hall, J.M., Wilson, R.L. and Smith, P.J., 1965. The petrology, Curie points and natural magnetizations of basic lavas. Geophys. J. R. Astron. Soc., 9: 323-336.
- Akimoto, S., Katsura, T. and Yoshida, M., 1957. Magnetic properties of TiFe₂O₄-Fe₃O₄ system and their change with oxidation. J. Geomagn. Geoelectr., 9: 165-178.
- Balsley, J.R. and Buddington, A.F., 1958. Iron-titanium oxide minerals, rocks, and aeromagnetic anomalies of the Adirondack area, New York. Econ. Geol., 53: 777-805.
- Berner, R., 1980. Iron. In: K. Wedepohl (Editor), Handbook of Geochemistry. Springer-Verlag, New York, N.Y., Ch. 26.
- Buddington, A.F. and Lindsley, D.H., 1964. Iron-titanium oxide minerals and synthetic equivalents. J. Petrol., 5: 310-357.
- Carmichael, C.M. and Nicholls, J., 1967. Iron-titanium oxides and oxygen fugacities in volcanic rocks. J. Geophys. Res., 72: 4665-4688.
- Carroll, D., 1958. The role of clay minerals in the transportation of iron. Geochim. Cosmochim. Acta, 14: 1–23.
- Chappell, B.W. and White, A.J.R., 1974. Two contrasting granitic types. Pacific Geol., 8: 173-174.
- Chinner, G.A., 1960. Pelitic gneisses with varying ferrous/ferric ratios from Glen Clora, Angus, Scotland. J. Petrol., 1: 178-217.
- Emerson, D.W., 1978. Comments on applied magnetics in mineral exploration. Bull. Aust. Soc. Explor. Geophys., 10: 3-6.
- Eugster, H.P., 1959. Reduction and oxidation in metamorphism. In: P.H. Abelson (Editor), Researches in Geochemistry. Wiley, New York, N.Y., vol. 1, pp. 397-426.
- Evans, M.E. and McElhinney, M.B., 1969. An investigation of the origin of stable remanence in magnetite-bearing igneous rocks. J. Geomagn. Geoelectr., 21: 757-773.
- French, B.M., 1973. Mineral assemblages in diagenetic and low grade metamorphic iron formations. Econ. Geol., 68: 1063-1074.
- Ganguly, J. and Newton, R.C., 1968. Thermal stability of chloritoid at high pressure and relatively high oxygen fugacity. J. Petrol., 9: 444-466.
- Garrels, R.M. and Christ, C.L., 1965. Solutions, Minerals and Equilibria. Harper and Row, New York, N.Y., 450 pp.
- Haggerty, S.E., 1976a. Oxidation of opaque mineral oxides in basalts. In: D. Rumble III (Editor), Oxide Minerals. Miner. Soc. Am. Short Course Notes, Hg 1-Hg 100.
- Haggerty, S.E., 1976b. Opaque mineral oxides in terrestrial igneous rocks. In: D. Rumble III (Editor), Oxide Minerals. Miner. Soc. Am. Short Course Notes, Hg 101-Hg 300.
- Haggerty, S.E., 1979. The aeromagnetic mineralogy of igneous rocks. Can. J. Earth Sci., 16: 1281-1293.
- Hargraves, R.B. and Banerjee, S.K., 1973. Theory and nature of magnetism in rocks. Ann. Rev. Earth Planet. Sci., 1: 269-296.
- Hargraves, R.B. and Peterson, N., 1971. Notes on the correlation between petrology and magnetic properties of basaltic rocks. Z. Geophys., 37: 367-382.
- Ishihara, S., 1977. The magnetite-series and ilmenite-series granitic rocks. Mining Geol., 27: 293-305.
- Ishihara, S., 1981. The granitoid series and mineralization. In: B.J. Skinner (Editor), Econ. Geol. 75th Anniv. Vol., pp. 458-484.
- James, H.L., 1966. Chemistry of iron-rich sedimentary rocks. U.S. Geol. Surv. Prof. Pap. 440W, 61 pp.

- Klein, C., 1973. Changes in mineral assemblages with metamorphism in some banded Precambrian iron formations. Econ. Geol., 68: 1075–1088.
- Krutikhovskaya, Z.A., Silina, I.M., Bondareva, N.M. and Podolyanko, S.M., 1979. Relation of magnetic properties of the rocks of the Ukrainian Shield to their composition and metamorphism. Can. J. Earth Sci., 16: 984-991.
- Laberge, G.L., 1964. Development of magnetite in iron formations of the Lake Superior region. Econ. Geol., 59: 1313-1342.
- Lindsley, D.H., Andreasen, C.E. and Balsley, J.R., 1966. Magnetic properties of rocks and minerals. Geol. Soc. Am., Mem., 97.
- McIntyre, J.I., 1980. Geological significance of magnetic patterns related to magnetite in sediments and metasediments a review. Bull. Aust. Soc. Explor. Geophys., 11: 19-33.
- Moody, J.B., 1976. Serpentinization: A review. Lithos, 9: 125-138.
- Nicholls, G.D., 1955. The mineralogy of rock magnetism. Advan. Phys., 4: 113-190.
- Nockolds, S.R., 1954. Average chemical compositions of some igneous rocks. Geol. Soc. Am. Bull., 65: 1007–1032.
- Osborne, E.F., 1962. Reaction series for subalkaline igneous rocks based on different oxygen pressure conditions. Am. Miner., 57: 211-226.
- Page, N.J., 1967. Serpentinization at Burro Mountain, California. Contrib. Mineral. Petrol., 14: 321-342.
- Stacey, F.D. and Banerjee, S.K., 1974. The Physical Principles of Rock Magnetism. Developments in Solid Earth Geophysics, vol. 5, Elsevier, Amsterdam, 195 pp.
- Takahashi, M., Aramaki, S. and Ishihara, S., 1980. Magnetite series and ilmenite series versus I-type and S-type granitoids. Min. Geol., Spec. Iss., 8: 13–28.
- Vernon, R.H., 1976. Metamorphic Processes. Allen and Unwin, Ltd., London.
- White, A.J.R. and Chappell, B.W., 1977. Ultrametamorphism and granitoid genesis. Tectonophysics, 43: 7-22.
- Wones, D.R. and Eugster, H.P., 1965. Stability of biotite: theory and application. Am. Mineral., 50: 1228–1272.
- Zeitz, I. and Bhattacharyya, B.K., 1975. Magnetic anomalies over the continents and their analyses. Rev. Geophys. Space Phys., 13 (3): 176-179.