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The Department of Earth and Planetary Sciences
The Johns Hopkins University
Baltimore, Maryland 21218

"Petrologic and Geophysical Study of the Source of Long Wavelength Crustal Magnetic Anomalies"

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Introduction

This is the final report for NASA grant NCC 5-13 entitled: Petrologic and Geophysical Study of the Source of Long Wavelength Crustal Magnetic Anomalies, beginning 1 May 1979 for one year. The summary of what was originally proposed is given below from the abstract of the original proposal.

Original Abstract

In this report we document our progress on "the petrologic and geophysical study of the source of long wavelength crustal magnetic anomalies"; NASA grant NCC5-13. We also request continuation of funding for a three year period. We have made substantial progress in the study of these anomalies by analysis of both aeromagnetic and satellite data; large remanent magnetizations have been identified as sources of several anomalies. We have made a quantitative investigation of POGO satellite orbital errors and their manifestation as pseudo-anomalies, and have synthesized a large body of literature in the separate disciplines of rock magnetism, iron-titanium oxide geochemistry, continental structure, composition, and evolution, and the petrology of igneous and metamorphic rocks (with an emphasis on their Fe-Ti oxide minerals). This synthesis, we feel, is essential in any attempt of data interpretation and source description.

For the new award period we propose theoretical, experimental, and field study of the formation Fe-Ti oxides, their occurrence in crustal rocks, and their consequent magnetic properties during progressive metamorphism. We plan
to study the petrography and magnetic properties of samples collected in the vicinity of the large Mauritanian anomaly. A diversified study of this breadth has not been attempted, do date. Finally, we propose to determine the effect(s) of oxygen fugacity ($f_{O_2}$) on both crystallization and partial melting (e.g. granulite facies metamorphism) of crustal rocks and their constituent Fe-Ti oxides. As a result, we hope to uncover the process which allows, through normal geologic processes and conditions, Fe-Ti oxides to produce these anomalies.

This report is in two parts: (I) The magnetic mineralogy and magnetic signature of banded iron formations; and (II) Phase equilibria of magnetite in orogenic magmas.

Part I

The Magnetic Mineralogy and Magnetic Signature of Banded Iron Formations

In an analysis of either satellitemagnetic or aeromagnetic data one may interpret anomalies, to first approximation, in terms of ideally shaped highly magnetic sources distributed in the crust. From anomaly intensity and signature it is possible to deduce the approximate source magnetization and geometry. The use of further geologic and geophysical constraints serves to produce a more credible model. Iron formations of Precambrian age are known to extend laterally for hundreds of kilometers, however, their average thickness is no more than one kilometer (usually less than several hundred meters) and their average magnetization is poorly known. Here we consider the magnetic mineralogy of iron formations and their
signature in aeromagnetic data.

The worldwide occurrence of vast banded iron formations (BIF) of sedimentary origin in the Precambrian record remains an enigma. Once it was thought that such deposits were coeval with ages clustered at about 1.9 to 2.5 B.Y. (Goldich, 1973). It has recently been proposed (Cole & Klein, 1981) that BIFs are in fact distributed throughout much of the Precambrian, that they are not coeval. The observation remains that the world's largest BIFs are indeed Proterozoic with similar age dates as proposed by Goldich.

Large reserves of iron ore in BIFs are known on every continent. Of the world's greatest deposits those of Lake Superior, U.S.; the Labrador trough, Canada; Krivoy Rog & Kursk, U.S.S.R.; Minas Gerais, Brazil; and the Hammersley Basin, W. Australia are perhaps best known. These deposits are all approximately contemporaneous in age (James & Sims, 1973; Dorr, 1973). The modern thickness and extent of these deposits are often unrelated to their primary geometry as they've often suffered alteration by tectonic deformation by folding and thrusting, erosion, and granitization (Dorr, 1973). The largest BIF deposits known, such as those of the Hammersley group and Frere formation of W. Australia, the Cauê itabirite of the Quadrilátero Ferrifero, Minas Gerais, Brazil, were laid down as extensive blanket deposits. In Brazil the Cauê itabirite is thought to have once covered 100,000 km\(^2\) with an average thickness of 250 m (Dorr, 1973). The Hammersley group may have once extended over 150,000 km\(^2\) with average thickness of 1000 m (Trendall, 1973). Trendall & Blockley (1970) estimate an iron content in the Hammersley basin
of \(10^{20}\) g. The Labrador trough deposits extend almost continuously for over 800 km (Dimroth et al., 1970) and the Kuruman & Penge BIF of South Africa extend discontinuously for 950 km (Beukes, 1973). The width of the South African and Canadian BIF is an order of magnitude less than their linear extent.

Banded iron formations are distinguished on behalf of the mineralogy, or "facies", of their constituent iron-bearing minerals, according to James (1954):

1) Oxide facies, e.g., magnetite, hematite, or both
2) Sulfide facies, e.g., pyrite
3) Carbonate facies, e.g., siderite, ankerite (\(\text{FeMg(CO}_3\text{)}_2\))
4) Silicate facies, e.g., Greenalite (Fe-chorite), Minnesotaite (Fe-talc), Stilpnomelane (layered K-Fe-phyllo silicate), Fayalite, Grunerite (\(\text{MgFe}_7\text{Si}_6\text{O}_{22}(\text{OH})_2\)) or orthopyroxene.

The facies classification is critical for interpretation of the depositional environment of BIF (e.g., James, 1954; Eugster & Chou, 1973; Kimberley, 1978; Gross, 1973, 1980).

We are more interested in the mineralogy of these formations, principally in the oxide and silicate facies, as it relates to their magnetization, hence, the influence of metamorphism is of great importance as most BIFs have been metamorphosed to some degree. The magnetization of BIFs exposed today at the earth's surface reflects their respective diagenetic and metamorphic history; this is also true for unknown formations deep in the crust. Thus, observations of BIFs of differing metamorphic grade will allow us to interpret their mineralogy in terms of consequent magnetization.
To properly examine this issue we will consider the metamorphic mineralogy of deposits from all geologic ages.

Diagenetic (unmetamorphosed) and Low Grade Banded Iron Formations

In the literature there is no consensus on the primary mineralogy of BIFs; most have been metamorphosed to some degree and I will avoid a detailed discussion of this controversy. In a study of very low grade Archean BIF from W. Australia Gole (1980) reported samples from all facies of James (1954). His relevant overvations include:

1) Absence of hematite in fresh (unweathered) samples
2) Ubiquitous appearance of magnetite, in highly variable amounts but secondary in abundance to Minnesotaite ($\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), siderite and quartz.
3) Magnetite is never observed in reaction textures.

French (1973, p. 1069) claims that "virtually all of the magnetite in the Biwabik iron-formations and other iron-formations in the L. Superior region is relatively coarse grained and secondary (La Berge, 1964; French, 1968; Han, 1972) and forms by replacement of pre-existing silicates and carbonates". The oxidation of siderite to magnetite (Klein, 1973) by the reaction

$$6\text{FeCO}_3 + O_2 \rightarrow 2\text{Fe}_3\text{O}_4 + 6\text{CO}_2$$

is thought to explain the petrographic evidence for such replacement (La Berge, 1964). In a compilation of diagenetic and low-grade metamorphic
replacement textures, (French, 1973) magnetite is seen to be present in secondary assemblages but only on one occasion is it replaced by a carbonate, ankerite. Klein & Fink (1976) in their study of very low-grade assemblages within the Proterozoic Sokoman iron-formation (Howells river area, Labrador trough) found:

1) Magnetite occurs in primary form, recrystallized after a fine grained magnetite or hydromagnetite \( \text{Fe}_3\text{O}_4\cdot n\text{H}_2\text{O} \) precursor. This interpretation origin is contested by Floran & Papike (1978) and French (1973) --see below.

2) Hematite occurs in primary form.

3) Magnetite bearing facies are the most common in the sedimentary column: both silicate and hematite bearing facies also contain magnetite. "Magnetite is pervasive in the silicate, oxide, carbonate facies (Klein & Bricker, 1977)."

4) The sulfide facies is of minimal extent in the column.

In a study of the 2 b.y. old contact metamorphosed Gunflint iron-formation, Minnesota, Floran & Papike (1978) conclude:

1) Magnetite is ubiquitous in all zones formed by reduction of hematite.

2) Where magnetite is involved in prograde metamorphic reactions such as the disappearance of greenalite, \( \text{Fe}_6\text{Si}_4\text{O}_{10}(\text{OH})_8 \), by reactions:

\[
\text{Greenalite} + 1/2\text{O}_2 \rightarrow \text{Minnesotaitie} + \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{O}
\]

\[
\text{Greenalite} + 1/2\text{O}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + 4\text{SiO}_2 + 4\text{H}_2\text{O}
\]

it is always a product and never a reactant.
Alternatively Klein (1978) documents the reaction

\[ \text{Greenalite} + 4\text{SiO}_2 + \text{Minnesotaite} + 2\text{H}_2\text{O} \]

in the regionally metamorphosed Labrador trough.

**High-Grade Mineralogy**

Gole & Klein (1981a) described the high-grade mineralogy of Archean BIFs in W. Australia. The occurrence of coexisting clinopyroxene, orthopyroxene, and fayalite allow estimation of pressure and temperature using 2-pyroxene and olivine-orthopyroxene geothermometers \( T = 670\pm50^\circ\text{C}, P = 3-5\text{kb} \). They found:

1) "Magnetite is not a major constituent...at any of the locations".

Even so they state that magnetite "is abundant in quartz rich assemblages and is a minor constituent of most other...assemblages".

Unfortunately, no modal measurements are presented. In a review of South American iron-formations Dorr (1973) notes that iron rich bands in itabirite contain hematite at lower metamorphic grades and magnetite at higher metamorphic grades. Sulfide facies iron-formations while volumetrically minor contains pyrite throughout low to moderate-grades of metamorphism, however, under high-grade conditions pyrrhotite is instead present (Gunderson & Schwartz, 1962; French, 1968).

The mineralogy of a single iron-formation exhibiting assemblages ranging from essentially unmetamorphosed variants up to transitional amphibolite-granulite facies equivalents has been reviewed by Klein (1978).
Iron-formations of the Labrador trough extend for nearly 700 miles in a north-south direction; in the south unmetamorphosed iron-formation grades into the Grenville front where high-grade assemblages are to be found. The range of P-T conditions varies from 150°C at 1-2 kb in the north to 700-750°C at 10-11 kb in the south; relevant observations, interpretations, and conclusions include (Klein, 1978):

1) "The highest grade iron-formation assemblages contain abundant orthopyroxene, magnetite, carbonates, some almandine and only minor amphiboles. This is a common assemblage in several other iron-formations of high-grade origin".

2) Quartz, hematite, and magnetite are ubiquitous in samples ranging from very low-grade to high-grade, however, samples may contain only hematite or only magnetite. Magnetite and hematite occasionally coexist and their textures imply equilibrium along the Fe₃O₄–Fe₂O₃ buffer.

The behavior of magnetite and hematite in banded iron-formations throughout metamorphism can now be summarized. In the oxide facies both minerals are stable over the entire range of metamorphic pressures and temperatures; locally oxidizing or reducing conditions will determine their relative stability or coexistence. Clearly, if hematite is initially present, the reduction to magnetite will require the presence of one or more of free carbon, CO, or H₂ (Eugster, 1972). In the silicate, oxide, and carbonate facies oxidation or decarbonation of siderite during diagenesis may yield magnetite (Han, 1972; Beukes, 1973; Klein, 1973; French, 1968).
In general magnetite appears to be if not primary then a secondary or replacement product of diagenetic and metamorphic reactions. Additionally the sulfide facies undergoes transition from non-magnetic pyrite bearing assemblages to magnetic pyrrhotitic assemblages in response to high-grade metamorphism. From field studies of many of the world's greatest iron-formations we have evidence indicating the stability of magnetite over hematite in highly metamorphosed locations (Dorr, 1973). Deposits with hematite are thought to result from near-surface or surface oxidation of magnetite (Tolbert, et al., 1973; Dorr, 1973; DeVilliers, 1971). Such near-surface oxidation and ore enrichment processes generally produce hematite and martite (hematite pseudomorph of magnetite and, sometimes, pyrite) at the expense of magnetite. At any metamorphic grade there is a considerable quantity of Fe bound by silicate and carbonate phases; we cannot assume that the majority is contained within the oxides. In spite of this observation the magnetic mineralogy of unaltered to highly metamorphosed iron-formation at the surface or as yet undiscovered at depth can be interpreted as consisting of magnetite, hematite, and on occasion, pyrrhotite. Measurement of relevant magnetic properties would be useful for our general knowledge yet given the blanket or through nature of BIF, however laterally extensive, we may tentatively conclude that only the largest deposits might be crustal sources of regional magnetic anomalies. Also, it seems to be the case that metamorphism does enhance the magnetization of banded iron-formations whatever their type facies, sulfide, carbonate, silicate, or oxide.

A crude estimate of the potential magnetization of the larger banded iron-formation provinces such as the Hammersley basin of W. Australia can
be made using Trendall & Blockley's (1970) estimate of total Fe content
in the Hammersley basin: $\sim 10^{22}$ grams. Typical estimates of source
dimensions of larger regional magnetic anomalies such as that over the
Central African Republic are $\sim 1000$ km by $\sim 100$ km by $\sim 20$ km thick. Modeling
(e.g., Regan & Marsh, 1982) indicates a magnetic susceptibility for such
a source region of $\sim 10^{-2}$ c.g.s. (12.56$\times 10^{-2}$ SI). Such a susceptibility can
be attained with 3% by volume of magnetite, or $\sim 6\times 10^{18}$ cm$^3$, or equivalently,
$\sim 3\times 10^{19}$ g. Multiplying this mass of magnetite by the ratio, molecular
weight of Fe/molecular weight of Fe$_3$O$_4$, one finds the equivalent mass of
Fe for such mass of magnetite. This turns out to be $\sim 2.3\times 10^{19}$ g of elemental
Fe. Assuming Trendall & Blockley's (1970) estimate to be correct in order
of magnitude we can speculate that if only one quarter to one half of this
mass of Fe is bound by magnetite, then such an iron formation could serve
as a source of a regional magnetic anomaly. A similar estimate for the
iron formations of the Kursk magnetic anomaly is given by Alexandrov (1973),
of $5\times 10^{19}$ g. In the Quadrilatero Ferrifero of Minas Gerais, Brazil, an
intense regional magnetic anomaly is found (Bosum, 1973); the interpretation
is that this feature is caused by the immense iron formation of that
district. It is very difficult to prove any of these interpretations as
we are working with a tremendous slab of crust, $\sim 2\times 10^{20}$ cm$^3$. Even so we
may speculate that if one of these vast iron formations has been meta-
morphosed to medium or high-grade under moderately reducing conditions
(relative to the Fe$_3$O$_4$-Fe$_2$O$_3$ buffer) and structurally reconfigured into
a true and dimensional body it could serve as the source of a more intense
regional magnetic anomaly such as that of Kursk, the Quadrilatero Ferrifero,
or perhaps even that of Central Africa.
Part II

Phase Equilibria of Magnetite in Orogenic Magmas

The principal carrier of magnetization in crystal rocks is magnetite. The abundance of this phase in plutonic rock depends critically on the order of its appearance in the sequence of crystallization. If magnetite appears early in the sequence it may be modally significant, while if it appears late in the sequence most of the iron may have been taken up by pyroxenes and olivine and magnetite will be sparse. The position of magnetite in this sequence depends critically on the fugacity ($f_{O_2}$) of oxygen in the system. A high $f_{O_2}$ promotes magnetite stability while a low $f_{O_2}$ reduces its thermal stability relative to the silicate minerals. This stability has been previously shown by R. N. Thompson for an iron-rich rock, and his results are shown by Figure 1.

This composition is not particularly similar to that of orogenic magmatic bodies which largely make up the crust. And we originally proposed to carry out a similar study on a basaltic composition from an active island arc; the Aleutian island arc. The method we used consisted of sealing the powdered rock in an evacuated silica glass tube containing a chemical to buffer the $f_{O_2}$. The charge was then heated to magmatic temperatures in a horizontal resistance furnace and held at that temperature for several days. Counting the runs necessary in developing the technique, thirty four runs were made over the period of one year.
The starting composition in all runs is:

<p>| | |</p>
<table>
<thead>
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<tbody>
<tr>
<td>SiO₂</td>
<td>49.05</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.89</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.32</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.0</td>
</tr>
<tr>
<td>FeO</td>
<td>6.52</td>
</tr>
<tr>
<td>MnO</td>
<td>0.18</td>
</tr>
<tr>
<td>MgO</td>
<td>3.91</td>
</tr>
<tr>
<td>CaO</td>
<td>10.44</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.36</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.89</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.27</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>99.14</td>
</tr>
</tbody>
</table>

The buffering materials were Ni-NiO, Co-CoO, and MnO-Mn₃O₄. Each of these pairs fixes the fO₂ to vary with temperature along a curve that is similar to what is actually observed in magmas. The charges were quenched from magmatic temperatures, the rock-glass powdered and inspected under a microscope in oils to determine the presence or absence of magnetite. These results are shown by Figure 2; each symbol represents two runs, solid = magnetite, open = no magnetite.

It is clear from these results that magnetite stability is indeed strongly affected by fO₂. The critical range of fO₂ is in the region slightly above the Ni-NiO buffer. To determine the stability limit of magnetite in
in an actual magma, the prevailing magmatic $f_{O_2}$ must be known.

The determination of $f_{O_2}$ in a magmatic assemblage is most commonly done using chemical thermodynamics and less commonly through direct sampling with an oxygen probe. Basalts from the ocean ridges typically have an $f_{O_2}$ near that described by the quartz-magnetite-fayalite (QFM) reaction. Continental lavas like rhyolites have an $f_{O_2}$ near that described by the MnO-M$_3$O$_4$ reaction, and island arc lavas have an $f_{O_2}$ in between these two extremes. In fact, orogenic (island arc) lavas generally have phenocrysts of magnetite, while ocean ridge lavas rarely do.

The importance of this effect cannot be overemphasized in terms of its importance to magnetization of the crust. A magma crystallizing at depth under these conditions will produce an abundance of magnetite. This magnetite will be coarse-grained and will acquire a weak remanent magnetization upon cooling through the Curie point. The magnetic susceptibility of the resulting rock is directly proportional to its magnetite content as is shown by Figure 3.

Conclusions

The stability of magnetite in crustal rocks is intimately dependent on the sequence of crystallization of the original magma as well as subsolidus metamorphic reactions. The position of magnetite in the sequence of crystallization depends to a great extent on the prevailing fugacity of oxygen, which is fairly high. Because of this, phenocrysts of magnetite can be expected early in the crystallization sequence. Should these rocks form a large part of the lower continental crust they could easily amount for much of its magnetization.
References


Figure 1: The $f_{O_2}$-Temperature plot for one-atmosphere melting experiments on a tholeiite (after Thompson, 1973). L is liquid, P1 is plagioclase, Mt is magnetite, O1 is olivine. NNO is the Nickel-Nickel Oxide buffer curve and QFM is the Quartz-Fayalite-Magnetite buffer curve (after Ewart, 1979)
Figure 2: Experimental results obtained under this grant on the stability of magnetite in the orogenic composition AT-6.
Figure 3: Variation of magnetic susceptibility with magnetite content (from H. Mooney).