CHEMICAL AND CRYSTAL CONTROLLED
MAGNETIZATION OF ROCKS

LYNN G. HOWELL

Humble Oil & Refining Company, Houston Research Center, Houston, Texas

ABSTRACT. In large part this review is intended to show the role of chemical magnetization among the principal processes by which rocks become magnetized. Chemical magnetization can occur at any time during the geological history of a formation. The high coercive force of hematite makes for a stable magnetization; thus, red beds have been investigated extensively. However, the extent to which red beds are chemically magnetized has not been established. Since the hematite crystal shows a strong magnetic anisotropy, being ferromagnetic in the basal plane and only slightly, if at all, ferromagnetic along the c-axis, preferred crystallographic orientation can exert a control as to the direction of magnetization. In the Allard Lake hemosiderite ore of Quebec, the preferred orientation seems to exert a controlling influence on the direction of magnetization. Also, such an influence may exist to a less extent in the Clinton iron ore of Alabama. On the other hand, chemically magnetized hematite from concretions in the Wilcox beds of Texas shows no appreciable preferred crystallographic orientation as found by both X-ray and magnetic susceptibility measurements. Thus, in this case at least, hematite crystals could grow without control of orientation by the Earth's magnetic field.

INTRODUCTION

In paleomagnetic measurements the main objective is to determine the direction of magnetization of a rock with the assumption that this direction represents the direction of the Earth's field at a definite time in geological history, usually the time of formation of the rock (Irving, 1959; Cox and Doell, 1960).

In these studies there are three principal processes by which rocks become stably magnetized: (1) thermal, (2) depositional, and (3) chemical. In the thermal magnetization process, a heated rock becomes magnetized in the Earth's field when it cools through a critical temperature, called the Curie point. A common value of this temperature is of the order of 600°C. In general, thermal magnetization occurs in igneous and baked (contact-metamorphosed) rocks. As to depositional magnetization, it is assumed that the fraction of sedimentary particles that are already magnetized are aligned in the Earth's field either in settling or in resting in a soft mud on the bottom; thus, the rock as a whole becomes magnetized in a direction close to that of the Earth's field. In the chemical process, the magnetic minerals are magnetized in the Earth's field as they form chemically.

Although the thermal and depositional processes have been recognized for a long time, it is only in recent years that the importance of chemical magnetization in paleomagnetism has been demonstrated. Koenigsberger (1938) early suggested the possibility of a chemical magnetization and referred to it as "crystallization remanence".

FIELD RESULTS OF CHEMICAL MAGNETIZATION

Doell (1956) and Martinez and Howell (1956) published specific results of magnetization of rocks along with evidence for the chemical origin of the remanence. Doell studied blue sandstones of upper Miocene age occurring in California. He presented evidence that the magnetization lay principally in the
blue coating of the grains, since at a temperature of about 200°C both the coating and the magnetization were destroyed. The main evidence for chemical magnetization, which Doell called "crystallization magnetization", was the increase of intensity with an increase in cementation, a postdepositional chemical action. It should be pointed out that the Earth's field in late Miocene time was not appreciably different from the present. Thus, a question might be posed as to the time of magnetization of these sediments. The question of stability was investigated by a heating treatment to wash out isothermal remanent magnetizations. After such a treatment, a hard component seemed to persist which was consistent.

Martinez and Howell measured the direction of magnetization of calcareous concretions (fig. 1) occurring in the Barnett shale of Mississippian age in the Llano Uplift area of Central Texas. These concretions, thought to be syngenic, contained hematite formed by oxidation of pyrite. It was suggested that the hematite may have been the principal magnetic mineral. At any rate, detrital matter was very scarce and could hardly have accounted for the remanence. It was concluded that the magnetization was probably acquired during the chemical processes. The authors noted that, in the case of this type of magnetization, the problem of realignment of particles upon settling to the bottom and through compaction does not exist; actually, this problem has not seemed to be serious. Also, they pointed out the stability of such a magnetization, a factor of the highest importance in paleomagnetic studies.

Strong evidence for stability of the magnetization was offered in that the direction was consistent for samples obtained over a large area with distances of separation up to 70 miles and was quite different from the direction of the present field; the pole locations calculated from the data agreed with other Carboniferous pole locations in the literature, those of Belshe (Runcorn, 1955) from samples in England and those of Runcorn (1955) from samples in Arizona; one location at which the remanence was reversed yielded closely agreeing pole locations of opposite polarity; and finally, good agreement in magnetization was found from rocks of different lithology: limestones, shales, limy shales, and concretions.
Although stable magnetization by the thermal process in igneous rocks and by the depositional process in sediments in general takes place at the time the rock is formed, such may not be the case with chemical magnetization. As the magnetic minerals can be formed chemically at any time during the existence of the formation. Thus Howell and Martinez (1957) pointed out that in the case of Sawatch samples of Cambrian age from Colorado the magnetization may well have taken place near the end of Paleozoic times: the time could not be pin-pointed due to the restricted sampling. The reasoning was based on the position of the poles computed from the magnetic data, their locations being far removed from the expected Cambrian poles and consistent with the much later time. The Sawatch samples consisted largely of sandy ferruginous dolomites containing both glauconite and hematite. The petrographic evidence indicated that the hematite was formed at the time of dolomitization. Hence, the remanence may have been due in main to the chemical magnetization of the hematite taking place at the time of dolomitization. Thus, palaeomagnetism offers a possible tool for dating such post-depositional changes, when the directions of the Earth's field are known in geological time.

However, the presence of chemical magnetization may not be welcome in many cases. For example, the chemical changes may take place slowly over a long period of time or even incompletely so that no definite answer is furnished. Again surface formations may have suffered weathering that has changed the old magnetization to a new chemical magnetization of little interest. Howell, Martinez, Frosch, and Statham (1958) showed an example of late oxidation.

Fig. 2. Remanent vectors for unweathered Weches formation represented by solid dots on upper hemisphere of net, for weathered samples represented by open circles on lower hemisphere (Howell, Martinez, Frosch, and Statham, Geophysics, 1960, reprinted by permission).
and chemical magnetization from the Weches formation of Eocene age in East Texas. The unweathered glauconite of the Weches was found to be reversely magnetized; probably the Earth's magnetic field was reversed in Weches time. However, as seen in figure 2, the weathered Weches containing limonite was found to be magnetized in a direction close to that of the present Earth's field and not far from that of the ideal dipole at the Earth's center pointing along the polar axis. Thus, recent chemical magnetization was indicated for the weathered zone.

LABORATORY RESULTS OF CHEMICAL MAGNETIZATION

Both Haigh (1958) and Kobayashi (1959) have produced chemical magnetization in the laboratory. In each case, magnetite was formed by heating hematite in a reducing atmosphere at a temperature of about 300°C in a magnetic field; the samples were then cooled in a field-free space. Both Haigh and Kobayashi carried out magnetizations at various field strengths and found the chemical magnetization to be strong, in fact, intermediate between thermal remanence and isothermal remanence. Isothermal magnetization is that produced by subjecting the sample to a field at a given temperature, in the one case being room temperature (Haigh) and in the other, 340°C (Kobayashi).

Haigh (1958) suggested a mechanism for chemical magnetization following the theory of Néel (1949, 1955) for single-domain magnetic particles. For such particles the rate of magnetization in a magnetic field or of demagnetization in zero field is related to a characteristic "relaxation time" \( \tau_o \) for a given particle. Thus for a particle in zero field the decay relationship for the magnetic remanence \( J_r \) at a given time \( t \) is given by:

\[
J_r = J_o \exp \left( -t/\tau_o \right)
\]

where \( J_o \) is the remanence in the beginning. For a particular magnetic mineral,

\[
\frac{1}{\tau_o} = C \exp \left( -A \frac{v}{T} \right)
\]

where \( v \) is the volume of the single-domain particle; \( T \) is the temperature; \( A \) and \( C \) are essentially independent of \( v \) and \( T \). In the chemical process it is assumed that the individual crystals grow in size from very small nuclei. Thus, the small crystals with short relaxation times are immediately magnetized in the Earth's field. As the crystals grow, the relaxation time increases with \( v \), and in the end with sufficiently large crystals the relaxation time becomes extremely long and the magnetization is frozen in.

THE IMPORTANCE OF RED BEDS

Blackett (1956) suggested a frequent occurrence of "chemical magnetization" and attributed the remanence of most red sandstones to such an origin. However, there may be some argument in many cases as to whether the magnetization of red sandstones is chemical or depositional. Intergranular cementation processes can, of course, produce chemical magnetization as mentioned by Blackett. Reference to these points will be made in the following discussion.

Creer, Irving, and Runcorn (1954) and Clegg, Almond, and Stubbs (1954) have carried out magnetic studies of hematite-bearing sandstones in Great Britain. Creer and his colleagues obtained samples from the Torridonian
and the Longmydian of Precambrian age, from the Old Red Sandstone (Devonian) and from New Red Sandstone (Triassic). The magnetic matter was separated from samples from the formations in the form of black detrital particles identified as hematite by X-ray analysis. The Curie point was found to be 680°C, a further indication of the presence of hematite. Also, to destroy the saturation magnetization a reverse magnetic field $H_b$ of 1600 oersteds was required. For the field samples of whole rock, $H_b$ covered a range of 2000 to 10,000 oersteds. Thus, as will be seen also from the work of Clegg, hematite-bearing rocks came to be recognized as desirable for paleomagnetic studies because of their high coercive force and consequent magnetic stability.

In laboratory tests, Creer and his colleagues came to the conclusion that these rocks were magnetized with a hard component (probably associated with detrital grains) and with a soft component (probably in part at least associated with fine-grain hematite cementation). Here the particle size determined the relaxation time and hence the stability and the hardness of magnetization. In the Torridonian and in some cases in the Old Red Sandstone, the fine-grain rocks showed less scatter of direction of magnetization in a particular sample than did the coarse-grain rocks. This was offered as evidence “consistent with a depositional magnetization”; presumably the fine grains were deposited with less turbulence and thus under more favorable conditions for magnetic alignment; of course the grains were still not sufficiently small to have short relaxation times.

Clegg and his colleagues found the Triassic New Redstone samples to be stably magnetized. The arguments were: The magnetization over a wide area of sampling was consistent and quite different in direction than that of the present Earth’s field; about half the sites produced samples of reverse magnetization, the line of magnetization, neglecting the sense, being consistent; and, finally, the magnetization in a tilted bed with respect to the bedding plane was consistent with flat-lying beds. Also, the magnetization was stable even when the samples were subjected to A-C magnetic fields up to 300 oersteds, as was also found by Creer (1957) with some of his hematite-bearing samples. On the other hand, the samples could be magnetized with a viscous component in a D-C field of a few oersteds. Thus, this work also suggests the possibility of both hard and soft magnetization components in the case of red beds.

On the basis of experiments with settling of powdered samples in the Earth’s field. Clegg and his group found laboratory evidence consistent with a depositional origin of the magnetization. However, they could not exclude the possibility of the magnetization taking place at a higher temperature at a time of burial of the formation.

Thus, the role of hematite is very important in paleomagnetic studies because of its magnetic stability. Moreover, hematite is quite common in chemically magnetized sediments as other iron minerals can be readily oxidized to hematite: here the time of the chemical action is very important.

**MAGNETIC PROPERTIES OF HEMATITE**

The hematite crystal, rhombohedral in form, is extremely anisotropic as to magnetic properties. At temperatures below its Curie point of 675°C and
above a transition temperature of about $-20^\circ$C, it is ferromagnetic in the basal plane, and weakly, if at all, ferromagnetic along the c-axis. Shull, Strauser, and Wollan (1951) found by means of neutron diffraction that for a magnetic cell, the directions of the magnetic moments of the iron ions are parallel to each other and to the basal plane in the $-20^\circ$ to $675^\circ$C range but that these directions turn through an angle of $90^\circ$ below $-20^\circ$C and become parallel to the c-axis: in both states the ions are arranged in regular opposing directions to set up an antiferromagnetic grouping. For the room temperature case, figure 3 shows the directions of magnetic moment of the iron ions along the c-axis related to the rhombohedral structure.

Thus, for a single crystal of hematite the remanent vector normally lies in or very close to the basal plane. Also, the magnetic susceptibility is much higher in directions parallel to the basal plane than along the c-axis. For the case of powdered hematite, Morin (1950) and Guillaud (1951) demonstrated a weak ferromagnetism in the upper temperature state and an absence of ferromagnetism (antiferromagnetism) in the lower temperature state. Chevallier (1951) found that powdered magnetite loses its ferromagnetism when the particle size is reduced to a diameter of about one micron. This observation is interesting because Li (1956) suggested that the ferromagnetism resides in the structure of the domain wall. The one-micron particles are probably single domains with no walls between domains to supply ferromagnetism.

THE ROLE OF THE HEMATITE CRYSTAL IN CHEMICAL MAGNETIZATION

With these properties in mind, Howell, Martinez, and Statham (1958) raised several questions concerning hematite-bearing rocks such as: (1) Is the crystallographic orientation of hematite controlled by the direction of the Earth's field as it grows chemically? (2) If the basal plane is preferentially oriented by the field or other means, is the remanence vector restricted to this plane? (3) Can the remanence be destroyed in outcrops exposed to temperatures below $-20^\circ$C?

As to the last question, it was found that a single crystal of hematite cooled in frozen CO$_2$ lost a fraction of its remanent magnetism but not enough to cause any alarm concerning outcrops exposed to low temperatures.
As to question (1), Howell, Martinez, Frosch, and Statham (1960) found that hematite can be formed chemically in the Earth’s magnetic field with no significant preferred crystal orientation. Samples of chemically formed hematite were obtained in Central Texas from the Wilcox of lower Eocene age, where they occurred in large concretions or concretionary lenses, which probably consisted primarily of siderite originally. The few samples collected were magnetized in a direction intermediate between that of the present field and that of the ideal dipole centered along the Earth’s spin axis. Thus the chemical magnetization could have taken place in recent times.

Magnetic susceptibility measurements were made in different directions with these samples and no appreciable anisotropy was observed. Thus no significant preferred crystal orientation of the hematite was indicated. As a further check on a possible orientation, X-ray diffraction observations were made with sample slabs cut in different planes. Thus the sections labeled in table 1 include a vertical north-south surface, which is close to a plane including the Earth’s magnetic field, whereas the surface of the section dipping 35° to the south is close to the plane perpendicular to the Earth’s field. The relative peak heights for the reflections from the (211) crystal plane and from the (110) plane are shown, the (211) making an angle of about 38° with the basal plane and the (110) being parallel to the c-axis. The peak height of the (211) was arbitrarily chosen as 1.00 for each slab. There is no X-ray reflection from the basal plane of hematite.

<table>
<thead>
<tr>
<th>Reflecting Planes</th>
<th>Relative Peak Heights</th>
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<tbody>
<tr>
<td></td>
<td>(211)</td>
</tr>
<tr>
<td>Sample 2A</td>
<td></td>
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<tr>
<td>Vertical N-S Section</td>
<td>1.00</td>
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<tr>
<td>Horizontal Section</td>
<td>1.00</td>
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<tr>
<td>Section Dipping 35° to S</td>
<td>1.00</td>
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<tr>
<td>Sample 3A</td>
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<tr>
<td>Vertical N-S Section</td>
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<tr>
<td>Horizontal Section</td>
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<tr>
<td>Section Dipping 35° to S</td>
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From these measurements there were no large changes in relative heights of the two peaks for the different sections, but this is not the case with samples that showed preferred crystal orientation, as will be noted later. Thus, no preferred crystal orientation of significance is indicated by both the X-ray and the magnetic susceptibility observations.

Here, then, is an example of chemical magnetization in which the crystals grew in the Earth’s field without preferred orientation but with a very strong resultant magnetization in the direction of the Earth’s field. The value of $Q$, which is the ratio of the remanent magnetism to the magnetism induced by the Earth’s field, varied from 10 to 40 for these samples, values which are high even for many igneous rocks with thermal remanence. Hence, the evidence
here is consistent with Haigh’s (1958) mechanism of a strong freezing of the remanent magnetism in chemical magnetization. It should be pointed out that for an individual crystal the magnetic vector would be expected to lie in or close to the basal plane in a direction of maximum component of the Earth’s field in the plane; Hargraves (1959) found evidence for such a mechanism in the case of hemo-ilmenite ore grains, as will be discussed later. For the variously oriented crystals, then, the direction of the vector sum of the individual magnetizations for the rock as a whole would be essentially that of the Earth’s field. This magnetizing field apparently has no crystal-orienting effect in the chemical growth.

CRYSTAL CONTROLLED MAGNETIZATION

For the Clinton iron ore of Alabama, another formation containing chemically formed hematite, Howell, Martinez, and Statham (1958) reported a susceptibility anisotropy with the plane of maximum susceptibility oriented very near to the bedding plane of the formation. Also, the remanent vectors lay close to the planes of maximum susceptibility as shown in figure 4.

X-ray measurements reported by Howell, Martinez, Frosch, and Statham (1960) indicated a preferred crystal orientation of the hematite as seen in table 2.

<table>
<thead>
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</tr>
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<tbody>
<tr>
<td></td>
<td>(211)</td>
</tr>
<tr>
<td><strong>Sample A</strong></td>
<td></td>
</tr>
<tr>
<td>Normal-to-Bedding Section along Strike</td>
<td>1.00</td>
</tr>
<tr>
<td>Normal-to-Bedding Section along Dip</td>
<td>1.00</td>
</tr>
<tr>
<td>Bedding Section</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Sample F</strong></td>
<td></td>
</tr>
<tr>
<td>Normal-to-Bedding Section along Strike</td>
<td>1.00</td>
</tr>
<tr>
<td>Normal-to-Bedding Section along dip</td>
<td>1.00</td>
</tr>
<tr>
<td>Bedding Section</td>
<td>1.00</td>
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</tbody>
</table>

(Howell, Martinez, Frosch, and Statham, 1960)
In this case, the sections were cut along the bedding and perpendicular to the bedding. Here the reflection from the (110) plane was abnormally high in the sections cut at right angles to the bedding plane. Hence it was indicated that the (110) planes tended to lie perpendicular to the bedding plane, and still further that the basal planes of the crystals tended to lie in the bedding plane. There was agreement thus between the X-ray results and the susceptibility measurements, showing a variation of about 5 percent between the maximum and minimum susceptibility.

Although the sampling was too meager to make definite conclusions, there was a possibility indicated that the dip of the remanent vector was too small, a possibility based on the pole positions computed from the remanent data for these Silurian rocks. The poles would have been expected to lie closer to the equator. This situation can, of course, be justified by the preferred orientation of the basal planes along with the strong tendency of the remanent vector to lie in the basal plane.

On the one hand the Wilcox containing chemically formed hematite showed no preferred crystal orientation and no susceptibility anisotropy, whereas the Clinton iron ore also containing chemically formed hematite showed both preferred crystal orientation and susceptibility anisotropy. Howell and his associates suggested the possibility that stresses in the older Clinton iron ore may have accounted for the preferred crystal orientation.

The conclusion that the remanent vector can be influenced in direction by physical or chemical factors other than the magnetizing field is backed by studies of metamorphic and igneous rocks. Howell, Martinez, and Statham

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**Fig. 5.** Upper hemisphere plot of remanent vectors, traces of planes of maximum susceptibility, and trace of plane of foliation, Valley Springs gneiss (Howell, Martinez, and Statham, Geophysics, 1958, reprinted by permission).
(1958) showed two examples of metamorphic rocks for which the plane of maximum susceptibility lay near to the plane of foliation, and, furthermore, the remanent vector lay close to both these planes. Figure 5 shows a plot of results obtained from the Valley Springs gneiss of Texas. The trace of the plane of foliation and the traces of the planes of maximum susceptibility along with the remanent vectors for three samples are shown on the upper hemisphere of a Schmidt net.

Hargraves (1959) found a pronounced anisotropy of magnetic susceptibility in the case of hemo-ilmenite ore in the Allard Lake region of Canada. The ratio of maximum to minimum susceptibility ranged as high as 3.8. Also, with polished sections, the titanhematite lamellae showed a preferred plane of orientation of crystals falling in the plane of maximum susceptibility. Thus, the susceptibility anisotropy was interpreted on the basis of the magnetic properties of the hemo-ilmenite grains for which ferromagnetism exists in the basal plane and is practically absent along the c-axis. Further, there was a tendency for the remanent vector to lie near the plane of maximum susceptibility, and it was suggested that the crystals were magnetized in the basal plane by the "resolved component" of the Earth's field. Hargraves presented data that suggest this hypothesis: in general, the intensity of remanence decreased as the angle increased between the plane of maximum susceptibility and the indicated direction of the Earth's field. He suggested as one possibility that the titanhematite lamellae were magnetized at the time of exsolving in the cooling process. It should be mentioned that Hargraves did point out that from his data alone it would be hard to decide whether the grain "shape" or the crystallographic structure dominates in fixing the direction of the remanence. Either or both could influence the susceptibility anisotropy.

Stacey (1960) investigated the possible deviation of the remanent vector from the direction of the magnetizing field caused by magnetic anisotropy in the case of igneous samples. He has applied the torquemeter as a tool for analyzing the portion of the anisotropy due to the particle shape orientation and that due to the crystallographic orientation. This method is especially applicable to rocks containing magnetic crystals of the cubic type such as magnetite.

CONCLUSIONS

We have pointed out the importance of chemical magnetization in studies of rock magnetism, a mechanism which is now receiving general recognition. We have also pointed out the role of hematite in controlling the direction of remanent magnetization in the case of single crystals and in the case of preferred crystallographic orientation of mineral assemblages of crystals. The role of shape structure of particles in magnetic anisotropy has also been mentioned.

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REFERENCES


