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The Magnetic Properties of Naturally Occurring Goethite

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Summary

It has been found that goethite acquires a thermoremanent magnetization (TRM) when cooled in the presence of a magnetic field from 120°C. It is believed that this TRM is due to the presence of antiferromagnetism in goethite with a Neel temperature of 120°C. A few spins have no mates because of small grain size or the presence of imperfections and impurities.

This TRM is related to antiferromagnetism. Similarly, hematite acquires a TRM at its Neel temperature which is due to unbalanced spins. In addition hematite is known to have a 'parasitic ferromagnetism'. Hematite derived from heating goethite above 350°C showed two different types of behaviour. Hematite composed of particles less than $\frac{1}{2}\mu$ diameter showed no spontaneous magnetization, but did show a weak thermoremanence whereas hematite composed of larger particles developed a spontaneous magnetization. These observations indicate that parasitic ferromagnetism exists only in grains larger than $\frac{1}{2}\mu$.

Introduction

It is known that iron oxyhydroxides are common in nature and it is known that some of them have interesting magnetic properties. Various workers have made studies of these properties in the past. In particular, papers by Creer (1962), by Kume (1965) and by Kawai *et al.* (1959) have examined some of the magnetic properties of these materials from the view point of palaeomagnetism. It is possible that in some environments, particularly in moist environments (Schmalz 1959), that goethite forms instead of hematite, as iron silicate grains break down in the weathering environment (Walker 1967). Goethite or other iron oxyhydroxides might therefore be present as an intermediate step in the formation of hematite in red sediments. It is important to have a thorough understanding of the magnetic properties of the oxyhydroxides and of their dehydration products. The purpose of this paper is to discuss the magnetic properties of goethite and hematite formed from it by dehydration and to give a full report on preliminary data already reported (Strangway *et al.* 1967a, b).

Magnetic and thermochemical properties of goethite

Using the Mössbauer effect, various workers (Takada *et al.* 1965; Hrynkiewicz *et al.* 1965; Herzenberg & Toms 1966) have recently shown that goethite is

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antiferromagnetic, with a strong internal field and they believe that there is a double Neel temperature at 63 and 97 °C. Above this temperature, goethite behaves as a simple paramagnetic material.

Several workers have reported on thermochemical experiments with goethite (Francombe & Rooksby 1959; Kulp & Trites 1951; Kelly 1956; Gheith 1952). In general it is found that goethite when heated breaks down between 350 °C and 400 °C to hematite with an endothermic reaction. Huggett (1929) indicated that goethite is paramagnetic at low temperatures and becomes ferromagnetic at 360 °C when heated in air. The process is one of dehydration. Kelly (1956) reports that poorly crystallized goethite can break down to maghemite, and then to hematite, but it is not known whether other workers have found this same situation or not. It is generally believed that the dehydration reactions will proceed at room temperature in environments having low activity of water so that given enough time the end product will be hematite. Creer (1962) indicated that goethite has no spontaneous magnetization, but showed that in very fine particle sizes it has a large susceptibility.

Experimental data

Samples of natural goethite were subjected to a variety of magnetic tests. These include saturation magnetization–temperature curves (*Js–T*), hysteresis tests (*B–H*) and acquisition of thermoremanent magnetization (TRM) after heating to various temperatures. First, the results of these experiments are reported, followed by an interpretation of the observations.

Js–T data

Several samples of goethite, all previously identified by X-ray diffraction, have been studied thermomagnetically by heating them to 700 or 800 °C. The saturation magnetization was measured either on a quartz spring Curie balance or on a vibrating

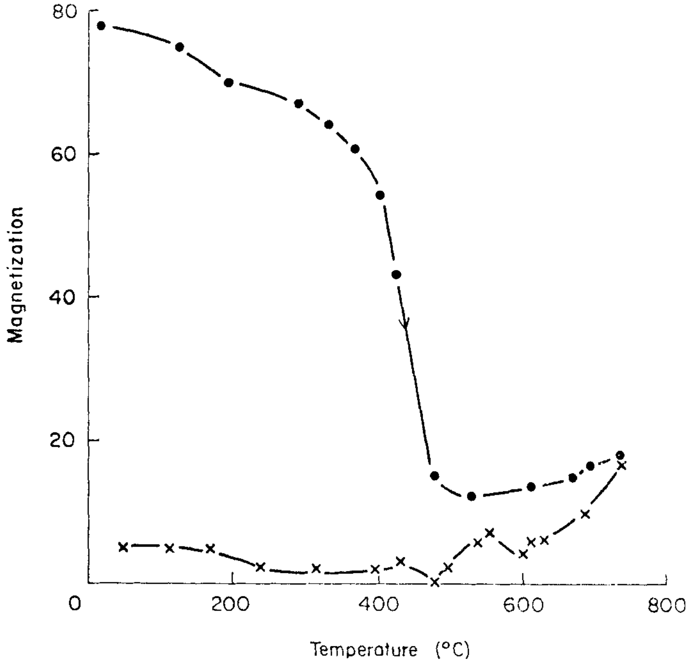

FIG. 1. *Js–T* curve for goethite sample No. 3124 showing loss of magnetization at 350 °C.

Table 1

Magnetic properties of iron oxyhydroxides before and after heating

Sample	Location	Initial material*	Final material*	Initial susceptibility (× 10^{-6} e.m.u./g)	Final susceptibility (× 10^{-6} e.m.u./g)	Hysteresis† initial material	Hysteresis† final material	Peak TRM acquired After heating to 150 °C (× 10^{-6} e.m.u./g)	Peak TRM acquired After heating to 700 °C (× 10^{-6} e.m.u./g)
Part A: Goethite–Weakly Magnetic Hematite									
1	Marquette Michigan	Goethite W.C.	Hematite P.C.	25	20	none	none	5·3	80·0
6								0·0 (acquires TRM in large fields)	60·0
(3114)	Houghton Michigan	Goethite W.C.	Hematite P.C.	29	13	none	none		
(3126)	Harz Mtns. Germany	Goethite P.C.	Hematite P.C.	24	23	none	small	5·8	130·0
(3129)	Michigan	Goethite W.C.	Hematite P.C.	30	17	none	none	14·0	83·0
(3124)	Lake Superior Area	Goethite W.C.	Hematite P.C.	31	22	none	none	45·0	96·0
Part B: Goethite–Magnetic Hematite									
4a	unknown	Goethite W.C.	Hematite W.C.	33	26	none	large	260·0	6100·0
4b	unknown	Hematite M.C. (some Goethite)	Hematite W.C.	40	43	large	large	52·0	5500·0
2	Santa Eulalia Mexico	Goethite P.C. Hematite M.C.	Hematite M.C.	28	28	large	large	94·0	30,000·0
(3113)	Iron Mtn. Michigan	Goethite W.C.	Hematite W.C.	38	28	large	large	6700·0	38,000·0
(3238)	Pikes Peak Colorado	Goethite W.C.	Hematite W.C.	28	28	none	large	210·0	7700·0
Part C: Lepidocrocite									
Lepi	Saxony Germany	Lepidocrocite	Hematite P.C.	32	14	none	none		

* P.C.—Poorly crystallized; M.C.—Moderately crystallized; W.C.—Well crystallized. Based on X-ray.

† Based on fields of 8000 oe.

sample magnetometer. The results fell into two groups. A representative curve from the first of these groups is shown in Fig. 1 and the results are tabulated in Table 1. All samples in this group show a sudden loss of magnetization at about 350 °C. This loss is accompanied by a sudden weight loss, indicating that dehydration and a structure change take place at the same time that the magnetization is lost. It was confirmed by X-ray work that the material formed was hematite. The X-ray powder diffraction of this hematite, however, shows a rather diffuse pattern indicating that the material formed is present as small crystallites.

The second group of goethites have quite different *Js–T* properties, as shown in Fig. 2 and Table 1. On heating, there is often a slight decrease in the magnetization at about 350 °C and a sudden weight loss indicating chemical and structural changes. The magnetization remains high, however, and the sample continues highly magnetic until it loses its magnetization at the Curie temperature of hematite at about 700 °C. On cooling, the sample acquires a magnetization at 700 °C. After cooling, this material is identified as hematite, by X-ray powder patterns. This time the X-ray patterns are sharp indicating that the material is in the form of larger crystals. All samples of natural goethite which we have measured have saturation magnetization-temperature curves similar to one of the two types discussed. Thus upon dehydration, goethites form hematites which possess magnetic characteristics that fall into two groups (Table 1). As will be seen the factor which controls the type of magnetic property is the size of the particles.

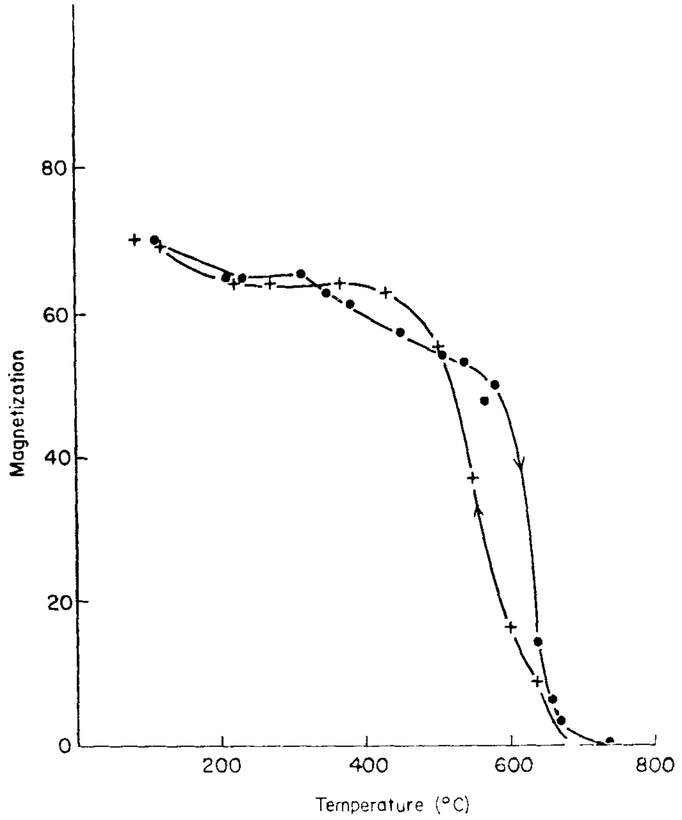

FIG. 2. *Js–T* curve for goethite sample No. 3113 showing magnetization of hematite formed at 350 °C.

Hysteresis properties

The next magnetic property studied was the behaviour in high magnetic fields. Samples were heated to various temperatures and allowed to cool. Then the magnetization was measured as a function of field (*B–H*). Unfortunately the maximum field available was only about 8000 oe so that the true saturation properties could not be measured. The differences found, however, are of sufficient interest to be reported and are distinctive enough to indicate fundamental differences among the materials examined.

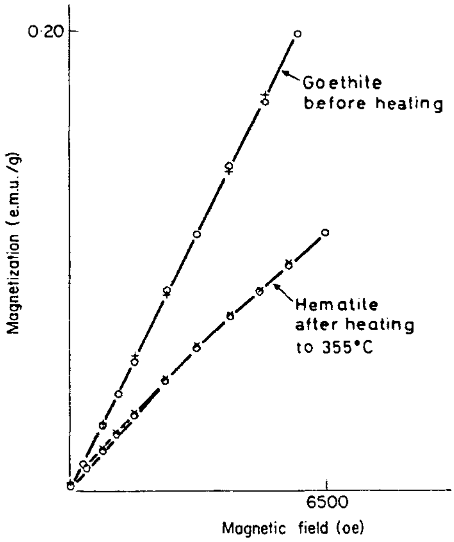

FIG. 3. *B–H* curve for goethite before and after heating.

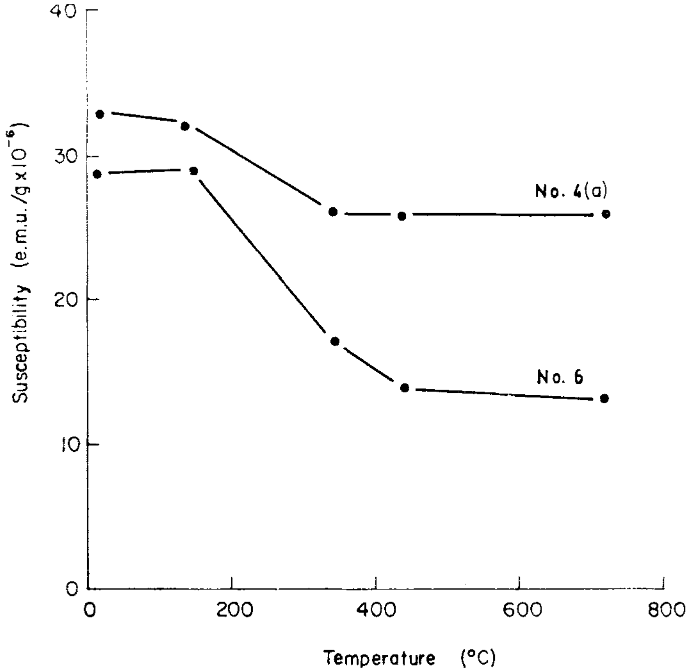

FIG. 4. Susceptibility after heating to increasing temperatures.

The goethite which converts to weakly magnetic hematite has a susceptibility independent of field strength as does also the weakly magnetic hematite which has been formed. This result is shown in Fig. 3 and summarized in Fig. 4. No hysteresis is found in the fields available. Moreover, the sample showed no response on the *Js–T* curve at the normal Curie temperature of hematite. It seems, therefore, that this form of hematite has no spontaneous magnetization.

A similar experiment was done on the goethite which dehydrates to the more magnetic form of hematite at 350 °C. In this case the initial goethite again has a susceptibility that is independent of field strength as shown in Fig. 5. After heating past the dehydration temperature, however, the specimen converts to hematite and acquires a definite hysteresis (Fig. 5). The magnetization in the range of available fields is not strongly dependent on the field and the susceptibility of the hematite is about the same as that for the initial goethite. In this case and in all others like it, it is seen that the hematite formed has a spontaneous magnetization as shown on both *Js–T* experiments and *B–H* experiments.

Thermoremanent magnetization

The final series of experiments that was done was a test on the TRM acquired by various types of materials. These results have proved to be quite interesting and are reported here in some detail.

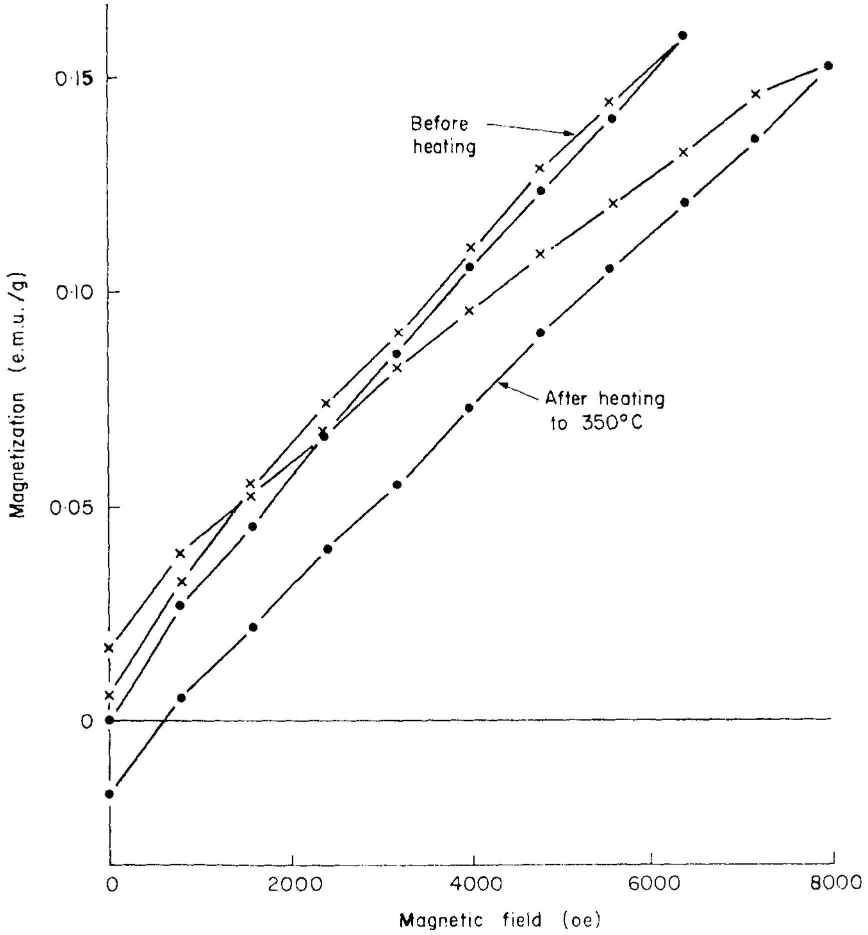

FIG. 5. *B–H* curve for goethite before and after heating.

Goethite inversion to magnetic hematite

The goethite which gives the more magnetic hematite was subjected to a variety of tests. Material from several localities was dispersed in non-magnetic matrices (about 6 per cent) and then heated to various temperatures in air. After each temperature level was attained, the specimen was cooled in the Earth's magnetic

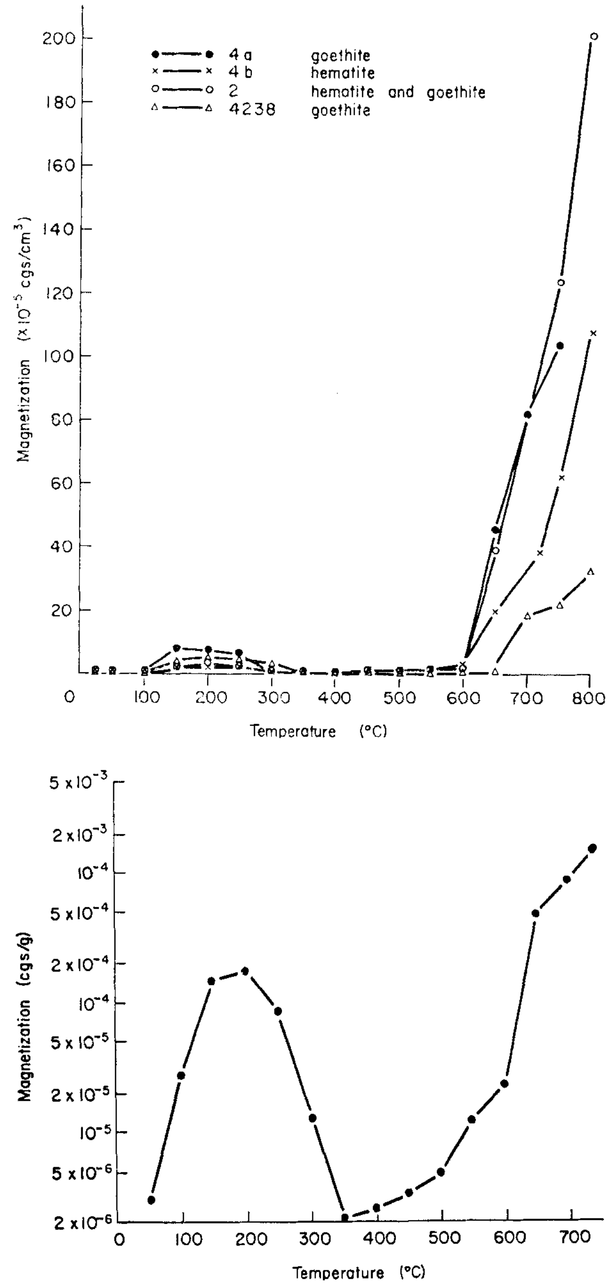

FIG. 6(a). Magnetization acquired by goethite No. 4a, 4b, and 4328 after heating and cooling in the Earth's magnetic field. (b) Magnetization acquired by goethite No. 4a shown on logarithmic scale—emphasizes 120 °C Neel temperature and breakdown at 350 °C.

field and its resulting thermoremanent magnetization measured. In one case, the material came from a specimen containing both goethite (Sample No. 4a) and a mixture of hematite and goethite (Sample No 4b). It is believed that the hematite present is derived from the natural dehydration of the goethite. The results of the heating experiment from these two specimens and the other goethites are shown in Fig. 6(a) and 6(b). At 120 °C a remanent magnetization is developed when the samples are allowed to cool in the Earth's magnetic field. This magnetization is as high as 7×10^{-5} cgs/cm^{-3}. It was first thought that this was a chemical remanent magnetization (CRM) associated with a preliminary stage of dehydration as reported by Kume (1965) and Kawai *et al.* (1959). However, upon reheating specimens and cooling in field-free space, it was found that essentially all of the magnetization is lost. Since the reheating temperature was less than the highest temperature reached during the original experiment, it is unlikely that any further chemical changes took place. When samples were again heated and cooled in the Earth's field, they recovered the original remanent magnetization. It is, therefore, clear that this magnetization is a thermoremanent magnetization (TRM) and is not a result of chemical change. Also there seems to be no CRM developed at 350 °C, the transition temperature for dehydration of goethite to hematite. As the temperature is increased to higher values, the magnetization rises slightly, until finally at about 700 °C, a strong TRM is acquired by the hematite.

Goethite inversion to weakly magnetic hematite

The form of goethite which decays to the weakly magnetic hematite (No. 6, No. 1 and No. 3124) was tested in a similar way (Fig. 7). The curves show a monotonous, steady increase in remanent magnetization with increasing temperature and a significant increase at 120 °C as before in No. 1 and No. 3124 (Table 1). The intensities of TRM after heating to 750 °C are only about 10^{-5} cgs/cm^3 as compared with values of 10^{-3} cgs/cm^3 or more for the other specimens containing the same amount of goethite.

It is interesting that at 350 °C, where the *Js–T* curve shows a breakdown of goethite to hematite (confirmed by X-ray), sample No. 6 shows no obvious changes in the remanent magnetization, indicating that the material does not acquire a CRM at the

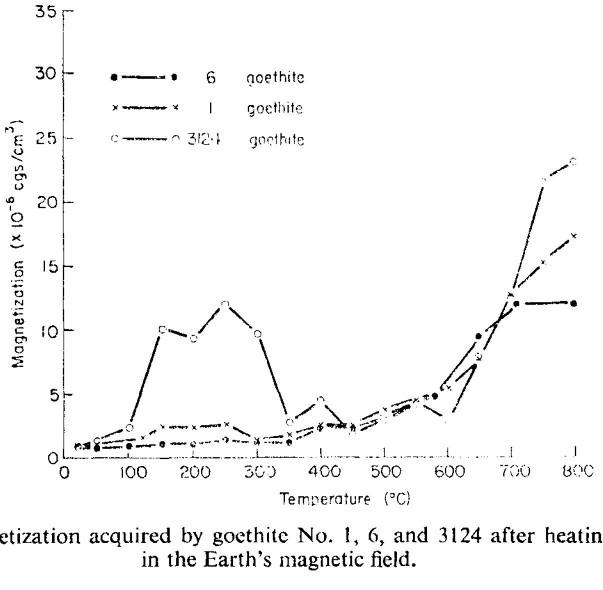

FIG. 7. Magnetization acquired by goethite No. 1, 6, and 3124 after heating and cooling in the Earth's magnetic field.

formation of hematite. When the experiment is done in a field of about 100 oe even sample 3124 acquires a distinct TRM at 120 °C so that all goethites tested acquired a TRM.

The results of the experiments which show the two different kinds of hematite derived from goethite are summarized in Table 2. It was found that the weakly magnetic hematite derived from goethite had small particle sizes as shown by X-ray patterns and by optical examination. Studies of polished sections showed that the weakly magnetic hematite was always in particles of $\frac{1}{2}\mu$ or less in size. A typical photomicrograph is given in Fig. 8.

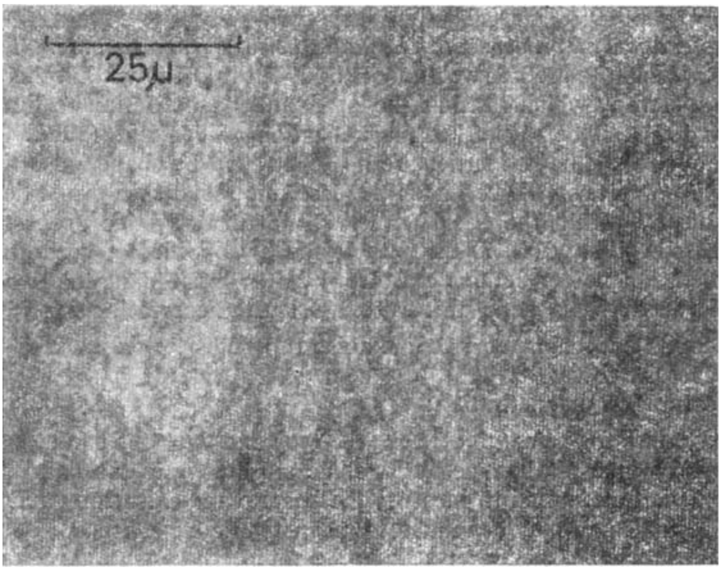

FIG. 8. Photomicrograph at ×1000 of polished surface of weakly magnetic hematite.

Interpretation of results

(a) *Goethite*. There are several possible causes of the weak thermoremanent magnetization in goethite:

1. It may be caused by an unbalanced spin effect due to small grain size, grain imperfections or ion substitution.

2. Goethites may have a parasitic ferromagnetism similar to the one observed in hematite.

3. It could be due to the presence of minute quantities of mineral impurities. In this case the impurity must constitute an extremely small fraction of the sample, as no indication of an additional phase can be detected on the *Js–T* curve or by careful X-ray examination. Chemical analysis of representative goethites revealed no major differences.

The observation that the magnetization appears at 120 °C (close to 100 °C, which is the reported value for the Neel temperature of goethite), and that it disappears at the temperature at which goethite converts to hematite is strong evidence that the magnetization is a property of the goethite itself. It is observed in both well-crystallized and poorly-crystallized goethites. Thus, on the basis of the present evidence the remanent magnetization seems to be due to unbalanced spins in the material.

The problem has been discussed by Neel (1962) and Cohen *et al.* (1962) who show that small grains of antiferromagnetic material can have unbalanced spins accounting for stable permanent magnetization. Neel suggests that for small irregular particles the number of unbalanced spins may be equal to $(N)^{\frac{1}{2}}$ where N is the total number of spins in the grain. As the Bohr magneton number for Fe^{3+} is $5{\cdot}9\mu_B$ the total magnetic moment per grain is approximately $5{\cdot}9\,(N)^{\frac{1}{2}}$. Fig. 9 shows the calculated magnetic moment per unit volume as a function of particle size using data for hematite. The figure suggests that a significant remanent magnetization due to unbalanced spins can exist in grains several hundred Å in diameter. It is probable also that imperfections or impurities in large grains act as centres in which there is local spin unbalance. These sources of spin unbalance are likely to be important in the goethites because both well-crystallized and poorly crystalline samples show a TRM.

(b) *Explanation of properties of hematite derived from goethite.* The magnetic properties of hematite are not well understood, but it is known that there is a strong crystalline anistropy which restricts the remanent magnetization to the basal plane (Chevallier 1951). The saturation magnetization of hematite (about 0·5 e.m.u./g) is weak enough that the properties are not controlled by shape anisotropy or magnetostrictive properties. Since this is the case, the remanence properties must arise from anisotropy within the basal plane. Unfortunately, this property has never been measured. Stacey (1963) using the known properties of hematite, calculated the equivalent magnetocrystalline anisotropy in the basal plane that would give rise to the observed ferromagnetic properties. Using the expression $2K' = HcJs$ where

K' = equivalent magnetocrystalline anisotropy;
Hc = coercive force;
Js = saturation magnetization;

and typical values for hematite of $Hc = 1000$ oe and $Js = 0{\cdot}5$ e.m.u./g give a value of 1250 ergs/cm^3 for the magneto-crystalline anisotropy in the basal plane. Bannerjee (1963) has attempted to measure the basal plane anisotropy and reports that it is quite variable and may be related to magnetostrictive effects.

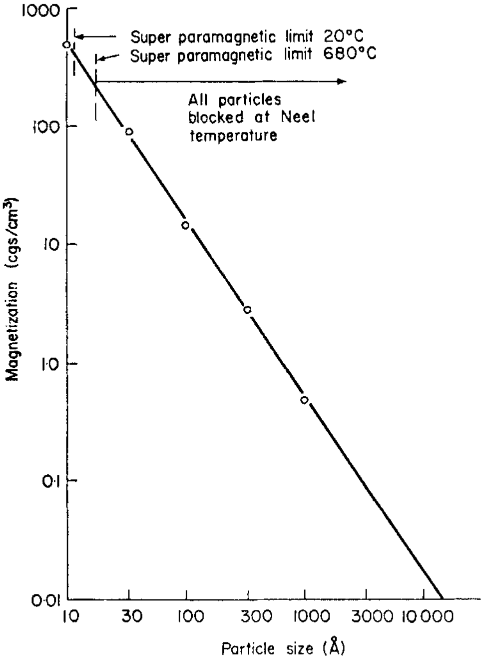

FIG. 9. Expected remanent magnetization as a function of grain size using Neel's model of unbalanced spins.

Using the above value for K' it is possible to make a rough estimate of the size for transition from unstable superparamagnetic to stable single domain behaviour for the parasitic ferromagnetism. Using a time constant of 100 s the value is given approximately by the following formula (Neel 1962):

$$2\,K'V \approx 25kT$$

where V = volume;
k = Boltzmann's constant;
T = absolute temperature.

giving a critical diameter of about $0{\cdot}1\,\mu$.

If, as seems likely, the true spontaneous magnetization is less than 0·5 e.m.u./g the critical diameter would be somewhat larger than $0{\cdot}1\,\mu$.

This rough calculation of the grain size transition is in reasonable agreement with the grain size transition estimated from microscopic examination. If this calculation is correct, it means simply that in larger grain sizes, hematite can have ferromagnetism and that a value of about $\frac{1}{2}\mu$ represents the superparamagnetic limit. That is, below this grain size the thermal disordering energy is greater than the ferromagnetic ordering energy. It seems likely that the magnetic properties of hematite are due to a combination of ' parasitic ' spontaneous ferromagnetism and spin unbalance of its antiferromagnetism. Thus, hematite has a spontaneous magnetization in particles greater than ½ micron in size due to basal plane anisotropy. In particles less than this in size, thermal disordering removes the spontaneous ferromagnetism but the hematite can still have a remanence due to spin unbalance. When the particles are extremely small, thermal disordering starts to disrupt the antiferromagnetic structure and there is a second superparamagnetic limit at about 20Å as discussed by Creer (1961, 1967). This gives a wide range of particle sizes that can carry remanence.

Smith & Fuller (1967) have discussed the problem of unbalance remanence and parasitic ferromagnetism in hematite. They show that the parasitic ferromagnetism is acquired at 680 °C and lost on cooling through the Morin transition −20 °C. The unbalance remanence however is acquired at the Neel temperature of 720 °C and is unaffected at −20 °C. Thus, they have distinguished the two types of magnetism by thermal experiments. The experiments reported here show that the parasitic ferromagnetism is not present in grains smaller than $\frac{1}{2}\mu$ complementing the observations of Smith & Fuller (1967). The results are summarized in Table 2.

Table 2

Summary of characteristics of hematite

	Strongly magnetic	Weakly magnetic
Curie temperature	680 °C	No Curie temperature
Saturation magnetization	High	Low
Coercive force	Large	None
TRM	Strong	Slight
X-ray data	Well crystallized	Small crystallites
Microscopic	Large crystals	½ grain size
Composition	Few impurities	Few impurities
Appearance of initial goethite	Shiny	Dull

(c) *Red bed properties.* Several red bed samples were subjected to similar tests to see if any of them acquired a TRM at 120 °C. Ancient arkose (Fig. 10(a)) and Pliocene mud (Fig. 10(b)) show an acquisition of magnetization as temperature increases similar to that shown by the fine-grained goethite–hematite samples, but there is no indication of a phase with a Curie point at 120 °C. It is probable, therefore, that these samples do not contain goethite and that the magnetization detected is due only to hematite.

A surface sample of Lyons sandstone of Permian age (Fig. 10(c)), on the other

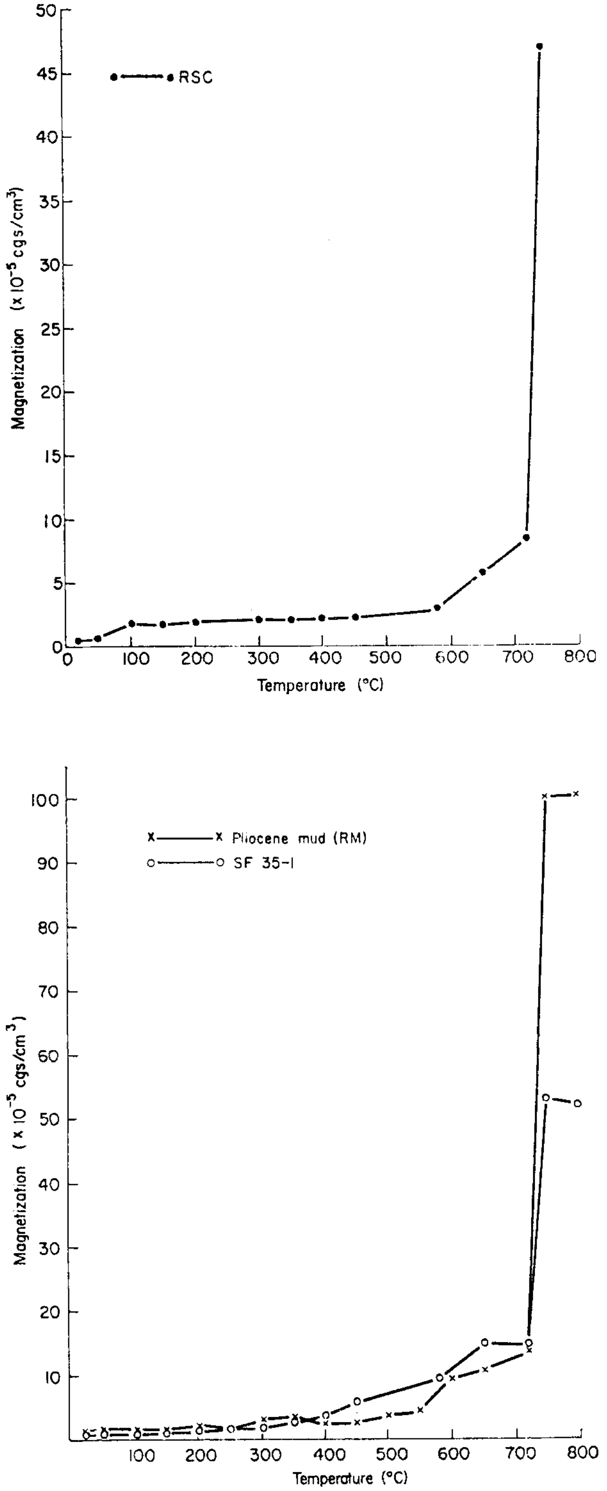

FIG. 10(a). Magnetization acquired by Permian, Maroon red sand-stone. (b) Magnetization acquired by Pliocene sediment after heating and cooling in the Earth's magnetic field.

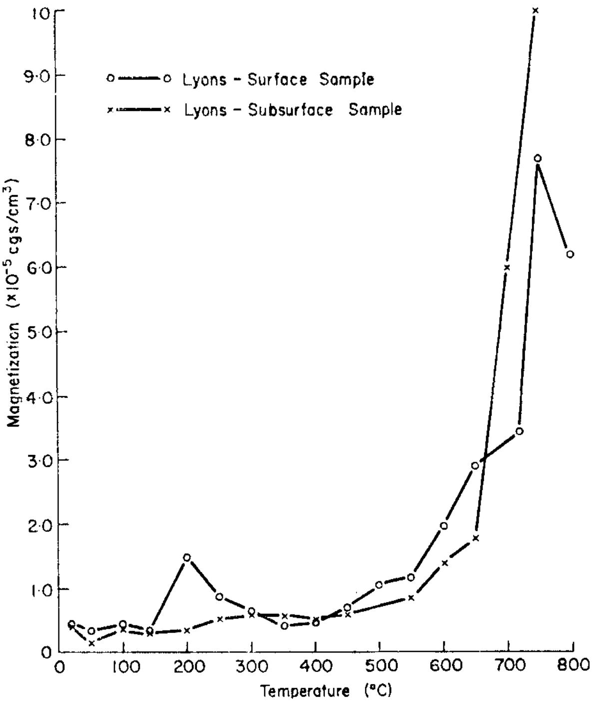

FIG. 10(c). Magnetization acquired by surface and subsurface samples of Permian, Lyons red sandstone.

hand, has a curve which shows the low temperature TRM characteristic of goethite. This sample of Lyons probably contains goethite formed recently by circulating ground water. Spheres of alternating red and bleached zones surrounding limonitic nodules and lightly stained bedding planes testify to recent solution and redeposition of iron oxide in the formation at the outcrop. By contrast, a subsurface sample of the Lyons from a depth of 10 000 feet does not show the low temperature effect (Fig. 10(c)) and has a stable magnetization. Surface samples of the Lyons do not have a measurable, stable magnetization as demonstrated by storage tests and a.c. demagnetization. Thus, the observed NRM which is secondary is easily recognizable. It is significant that Krs (1967) has also noted anomalous directions in ancient porous sandstones.

The low temperature TRM which is attributed to goethite could be an important carrier of stable magnetization. Heating to over 120 °C (or burial depth of about 3 km) would give a TRM in material containing goethite. This could lead to a spurious secondary magnetization which could be removed simply by heating to 150 °C and cooling in field-free space. It is generally considered that goethite is not preserved in ancient rocks. If this is invariably the case, goethite may not be an important source of secondary magnetization, as conversion to hematite, at least in the laboratory, erases the magnetization acquired by goethite. However, until we know more about the occurrence of goethite, the possibility of a low-temperature TRM should be considered a possible source of secondary magnetization.

Conclusions

We conclude that goethite which is antiferromagnetic can acquire a TRM at its Neel point of 120 °C. This TRM is quite weak and variable so that it is not a bulk property of goethite. It is believed that this is a result of a few spins without mates so that the cooling process allows the acquisition of TRM. This is probably a simple property of most antiferromagnetic materials as discussed by Smith & Fuller (1967).

Similarly hematite can be expected to have a weak remanence associated with it. Hematite formed by dehydration of goethite had two types of magnetic behaviour. When grain size is over $\frac{1}{2}\mu$ the hematite shows a characteristic ferromagnetic behaviour. In smaller grain sizes, however, a weak TRM is acquired but the material shows none of the usual ferromagnetic properties. It is thus seen that the parasitic ferromagnetism of hematite has a grain size limit of $\frac{1}{2}\mu$. Smaller particles are superparamagnetic. They still, however, have a remanence carried by unbalance of the antiferromagnetism.

Acknowledgments

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