

Werk

Jahr: 1979

Kollektion: fid.geo

Signatur: 8 Z NAT 2148:46

Digitalisiert: Niedersächsische Staats- und Universitätsbibliothek Göttingen

Werk Id: PPN1015067948_0046

PURL: http://resolver.sub.uni-goettingen.de/purl?PPN1015067948_0046

LOG Id: LOG_0022

LOG Titel: Magnetic rotational hysteresis loss in titanomagnetites and titanomaghemites - application to non-destructive mineral identification in basalts

LOG Typ: article

Übergeordnetes Werk

Werk Id: PPN1015067948

PURL: <http://resolver.sub.uni-goettingen.de/purl?PPN1015067948>

OPAC: <http://opac.sub.uni-goettingen.de/DB=1/PPN?PPN=1015067948>

Terms and Conditions

The Goettingen State and University Library provides access to digitized documents strictly for noncommercial educational, research and private purposes and makes no warranty with regard to their use for other purposes. Some of our collections are protected by copyright. Publication and/or broadcast in any form (including electronic) requires prior written permission from the Goettingen State- and University Library.

Each copy of any part of this document must contain these Terms and Conditions. With the usage of the library's online system to access or download a digitized document you accept the Terms and Conditions.

Reproductions of material on the web site may not be made for or donated to other repositories, nor may be further reproduced without written permission from the Goettingen State- and University Library.

For reproduction requests and permissions, please contact us. If citing materials, please give proper attribution of the source.

Contact

Niedersächsische Staats- und Universitätsbibliothek Göttingen
Georg-August-Universität Göttingen
Platz der Göttinger Sieben 1
37073 Göttingen
Germany
Email: gdz@sub.uni-goettingen.de

Magnetic Rotational Hysteresis Loss in Titanomagnetites and Titanomaghemites – Application to Non-Destructive Mineral Identification in Basalts

A.J. Manson, J.B. O'Donovan, and W. O'Reilly

Department of Geophysics and Planetary Physics, School of Physics,
The University, Newcastle upon Tyne NE1 7RU, Great Britain

Abstract. Magnetic rotational hysteresis loss provides a non-destructive method for the identification of magnetic minerals in rocks provided a catalogue of loss curves is available for well characterized minerals or synthetic analogues. In the present study such loss curves have been determined for synthetic titanomagnetites and titanomaghemites. The effect of the presence of aluminium and magnesium such as is found in naturally occurring minerals has also been determined. One feature of the loss curve, the field at which peak loss occurs (H_p), appears to be independent of the domain state of the material and depends only on chemical composition. The value of H_p may therefore be used to identify minerals in the same way as a value of Curie temperature (T_c), although neither H_p nor T_c alone will give an unambiguous answer. The loss curves of a number of basalts have also been determined and an attempt is made to determine the oxidation state of the titanomagnetites using the data from the synthetic materials.

Key words: Rock magnetism – Magnetic hysteresis – Titanomagnetite – Titanomaghemite.

1. Introduction

Studies of the magnetism of rocks are primarily aimed at providing the physical basis for the assumptions on which the palaeomagnetic method is founded. One basic problem is the identification of the magnetic minerals in rock samples, such minerals often being present in low concentration ($\sim 1\%$) and of submicroscopic grain size ($\lesssim 1\ \mu\text{m}$). The identification and characterization of the magnetic fraction of a rock sample is essential to the interpretation of the magnetic properties of rocks, in assessing the usefulness of rocks as carriers of the palaeomagnetic record and can contribute to our knowledge of the petrological history of rocks.

The magnetic properties of the minerals themselves may provide characteristic 'signatures' from which their presence may be inferred. This requires a catalogue of signatures obtained using well-characterized mineral samples or synthetic analogues. A widely-used measurement in this context is the determination of the temperature dependence of induced or remanent magnetization. The former yields the Curie temperature intrinsic to the magnetic phase. The latter may be used to identify magnetite and haematite by their 'remanence transitions' below room temperature. This method has the advantage of avoiding possible chemical change due to heating at elevated temperatures arising through the oxidizing or reducing conditions existing in the heated rock or inherent instability in the magnetic minerals (providing irreversible changes in the thermomagnetic curve occurring on heating are well understood, such changes can themselves be used to identify minerals). However, the remanence transition occurs only in minerals with a limited range of composition and the transitions themselves are strong functions of extrinsic parameters such as grain size and mechanical strain.

Even under ideal conditions, the results obtained using any single technique do not unambiguously identify the magnetic mineral. A measured Curie temperature, for example, simply locates the mineral on the appropriate contour of the titanomagnetite/titanomaghemite quadrilateral (Readman and O'Reilly, 1972) or on a contour in a titanomagnetite/titanomaghemite subsystem (e.g., O'Donovan and O'Reilly, 1977), or again may indicate a haemo-ilmenite or even a pyrrhotite or goethite if in the appropriate range. A combination of techniques is needed to reduce the field of composition, within which the mineral may lie, to a usefully narrow range.

Another magnetic property which may provide a signature is magnetic anisotropy and anisotropy-related characteristics such as coercive force, remanence coercive force, hysteresis loss, susceptibility and the shapes of magnetization and demagnetization curves. Of special interest among these is the determination of the field dependence of rotational hysteresis loss (Day et al., 1970). This loss is due to the irreversible magnetization changes which occur while rotating a specimen in a fixed magnetic field. There are a number of advantageous features of this method for identifying minerals. First the induced magnetism of the non-ferromagnetic minerals plays no role and cannot mask the characteristic signature of the ferromagnetic phases. Second, the effect depends on the anisotropy rather than the strength of magnetization of the material. Thus although haematite (α Fe₂O₃) is weakly magnetic ($\sim 1/200$ the saturation magnetization of magnetite, Fe₃O₄) the rotational hysteresis loss may be quite large especially if in the finely divided pigment form (of about the same order as that of coarse grain magnetite). Similarly whereas fine grain (pigment) and coarse grain (specularite) haematite have the same Curie temperature, their rotational hysteresis characteristics are different and the two forms of haematite may in principle be distinguished (Cowan and O'Reilly, 1972). Finally the technique is chemically non-destructive. The disadvantage of the technique is that the determination of a rotational hysteresis curve may take many hours and a highly automated instrument is desirable.

Rotational hysteresis loss is measured using a torque magnetometer. A single

crystal specimen suspended in a saturating magnetic field experiences a torque unless the field is parallel to an easy axis of the system, the torque being uniquely determined by the angle between the field and a reference direction. In lower fields the magnetization will lag or lead the field and the resultant torque is no longer unique but, for a certain orientation, will depend on the sense of rotation by which that orientation has been reached. Irreversible changes occur in the orientation of the magnetization during rotation of the field. The curves of the angular dependence of torque for rotation of the field in the clockwise and anticlockwise sense are displaced from one another. The area between these curves has the dimensions of energy and for a rotation $0^\circ \rightarrow 360^\circ \rightarrow 0^\circ$ the area equals twice the hysteresis loss per cycle. A rock specimen contains a dispersion of magnetic grains. In the absence of any 'fabric' the specimen has no bulk easy axis. However even with a random array of crystallite easy axes, the bulk magnetization will lag a non-saturating rotating field, a torque will result and the area between the displaced torque curves gives the loss per cycle of the assemblage.

Theoretical loss curves have been derived for the case of monodomain particles with uniaxial anisotropy, the unique axis being the easy direction (Stoner and Wohlfarth, 1948; Jacobs and Luborsky, 1957). In the model curves, the loss is zero for fields below a critical field ($=K_u/M_s$ for coherent rotation of magnetization where K_u is the anisotropy constant and M_s the spontaneous magnetization). At the critical field the loss rises abruptly to a peak value ($=2.6 K_u$ for an aligned assemblage) and falls steadily to zero at twice the critical field. Owens (1977) has considered the case of uniaxial symmetry in which the unique axis is the hard direction and the unique plane contains a single easy direction. In this case, the field at which the loss will vanish depends on the orientation of the unique plane to the plane of measurement, and can extend to very high fields. We have considered the case of monodomain grains with cubic anisotropy ($K_1 > 0$) and coherent rotation in the (100) plane. Figure 1 shows the resulting variation of rotational hysteresis loss with applied field. The general shape of the curve is similar to the uniaxial case but the critical field for the onset of loss is $1/2(K_1/M_s)$ and the peak loss is $0.908 K_1$ for an aligned assemblage ($0.606 K_1$ for a random array). The loss vanishes at $2K_1/M_s$. Real materials are invariably more complicated than those described in simple idealized models. Nevertheless experimental loss curves (W_R-H curves) are in a general way similar to the model curves. In any event, the important point in the present context, that of mineral identification, is that an observed W_R-H curve can be recognized as belonging to a certain mineral or group of minerals. W_R-H curves are therefore needed for synthetic analogues or well-characterized mineral specimens of the titanomagnetites and their derivatives, produced by oxidation, 'substitution' and post deuteric alteration. These will include magnetite, maghemite, haematite, the titanomaghemites, and haemoilmenites. Other remanence-carrying minerals are the pyrrhotites, goethite and native iron.

The purpose of the present study is to provide some of the required specimen W_R-H curves. The systems studied are fine grain (monodomain) and coarse grain (multidomain) titanomagnetite and the oxidation products of such mate-

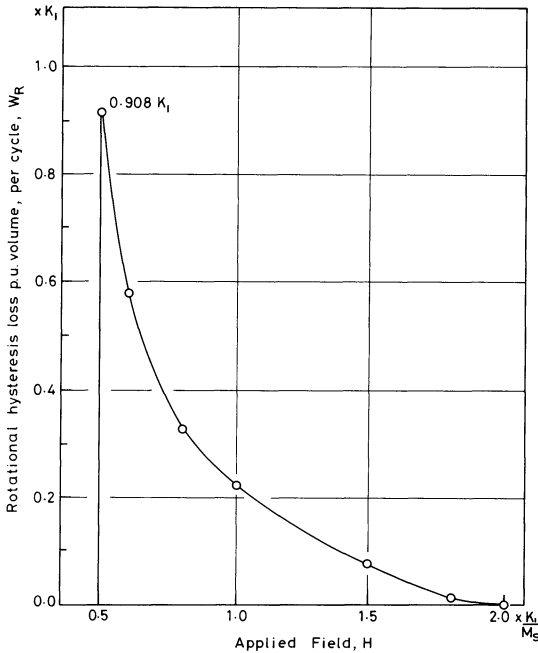


Fig. 1. Model rotational hysteresis loss (W_R - H) curve for aligned monodomain grains with cubic anisotropy ($K_1 > 0$) and coherent rotation of magnetization in the (100) plane. W_R is expressed in units of K_1 and H in units of the ratio K_1/M_s . The curve for a random array of easy axes is similar but with a peak loss of $0.606 K_1$.

rials. The effect of 'substitution' of iron by aluminium and magnesium is also investigated together with the consequent changes in W_R - H curves due to maghemitization in the latter case.

2. Experimental

The rotational hysteresis loss curves were determined using the automatic torque magnetometer of Fletcher et al. (1969) operating at room temperature and in field range 0–20 k Oe. Torque curves for angle $0 \rightarrow 360 \rightarrow 0^\circ$ were plotted on an X - Y recorder at each selected field, the areas enclosed by the curves measured, converted to energy per unit mass, and plotted against field to give the W_R - H curve.

The titanomagnetite specimens were prepared by sintering techniques, the unsubstituted titanomagnetites fired at $1,100^\circ \text{C}$ under self buffering conditions and the substituted materials twice-fired using a technique of partial self buffering at $1,350^\circ \text{C}$. The homogeneity of the specimens was confirmed using X-ray powder pictures and Curie temperature determination. The synthesized material was hand-ground and sieved fractions in the required particle size range prepared.

Fine grain specimens of unsubstituted titanomagnetite were obtained by grinding in a wet slurry in a porcelain ball mill for four days. The finely divided substituted titanomagnetite was obtained by grinding, in high purity methanol, overnight in a tungsten carbide ball mill. Particle size determinations were attempted using X-ray line broadening and the electron microscope. Be-

cause of strain-broadening the former method provides an underestimate of the particle size. The latter method yields an overestimate because of flocculation. The combined measurements gave a particle size of the order of $0.1 \mu\text{m}$.

Oxidation was carried out by heating in air in a thermogravimetric balance, the degree of oxidation being determined from a combination of weight increase data and wet-chemical analysis. Powder pictures of the oxidation products were obtained using Guinier de Wolff and Debye-Scherrer cameras.

3. The Rotational Hysteresis Characteristics

The rotational hysteresis curves of all samples were for the main part of very similar form. A representative suite of curves is shown in Fig. 2. All curves show a sharp rise in W_R to a peak value, followed by a gradual fall, as the applied field increases. The shape of the curves is thus similar to the model curves of Fig. 1 differing in that the measured W_R is not zero at low fields nor does it fall to zero when the applied field is (say) four times the field at which peak loss occurs. Given that the observed measured curves have a similar form to those in Fig. 2 it is not necessary to reproduce the curves themselves but simply to characterize each curve by the value of field, H_p , at which the peak occurs and the height of the peak itself, W_{Rp} .

3.1 Titanomagnetites

The variation of H_p and W_{Rp} for the titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$, $0 < x < 1$) as a function of composition x is shown in Fig. 3. The data refer to material

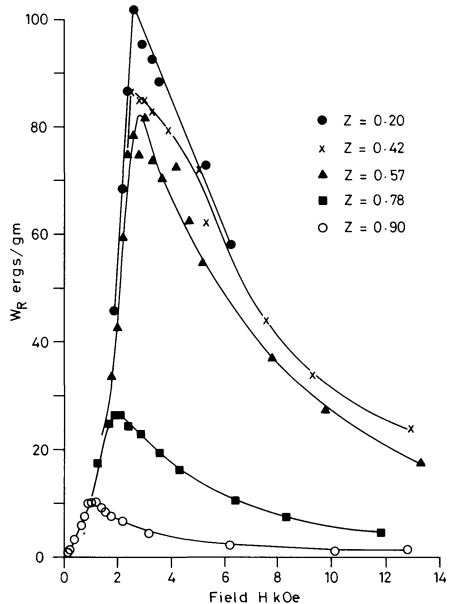


Fig. 2. Representative set of W_R-H curves for a suite of titanomagnhemites (based on $\text{Fe}_{2.25}\text{Mg}_{0.15}\text{Ti}_{0.6}\text{O}_4$) showing the evolution of the loss curve as the degree of maghemitization (z) increases. The field (H_p) at which peak loss occurs falls, as does the peak height (W_{Rp}), as z increases

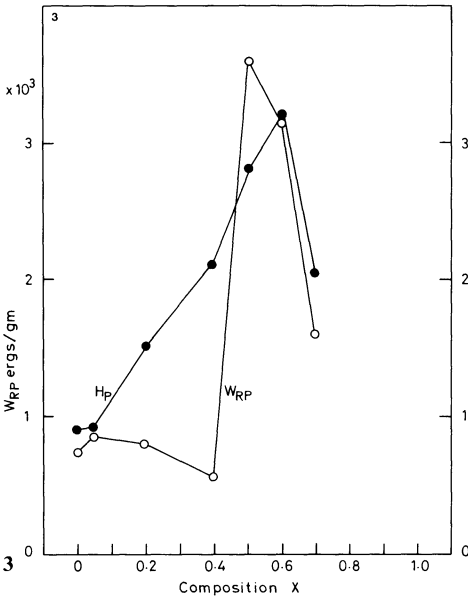


Fig. 3. Variation of H_p and W_{RP} with composition x in the titanomagnetite series $Fe_{3-x}Ti_xO_4$. The data refer to near-stoichiometric samples in the multidomain state, sieved to obtain a grain size range 37–44 μm

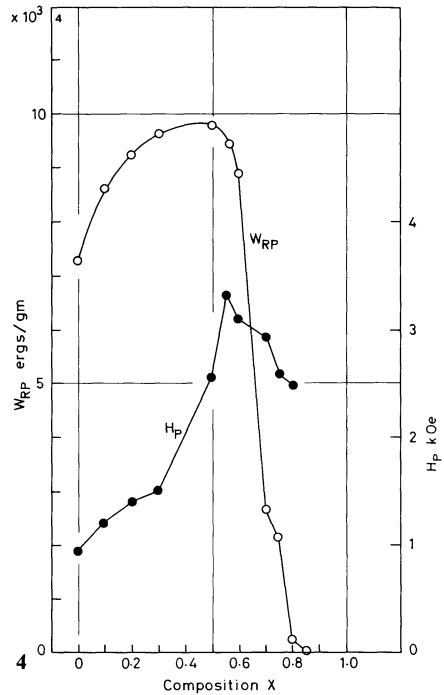


Fig. 4. Variation of H_p and W_{RP} with composition x for ball milled samples of titanomagnetite in the monodomain state. A low degree of non-stoichiometry is introduced by the ball milling. The H_p variation is the same as that in the multidomain samples (Fig. 3) whereas W_{RP} is an order of magnitude larger

which has been sieved to lie in the grain size range 37–44 μm and is expected to comprise mainly multidomain grains. However the possibility of smaller particles, in agglomerates or attached to larger particles cannot be discounted. H_p rises steadily from about 1 kOe for magnetite ($x=0$) to 3 kOe for $x=0.6$. The fall in H_p from $x=0.6$ to $x=0.7$ is associated with the fall in Curie temperature to near room temperature for $x=0.7$ and below room temperature for $x \geq 0.8$. The behaviour of W_{RP} is less systematic, falling from about 700 to 500 ergs/gm as x increases to 0.4 to a peak value of about 3,500 ergs/gm at $x=0.5$ before falling to 1,500 ergs/gm at $x=0.7$.

Figure 4 gives the corresponding data for fine grain ball milled specimens of grain size $\lesssim 0.1 \mu m$ and expected to be in the monodomain state. The values and variation of H_p with composition x are similar to the coarse grain material. However the W_{RP} values now show a more continuous and systematic variation with x and are about an order of magnitude greater than in the multidomain material, rising from about 7,000 ergs/gm ($x=0$) to a peak at about 10,000 ergs/gm ($x=0.5$). The ball milled samples are more non-stoichiometric (cation-defi-

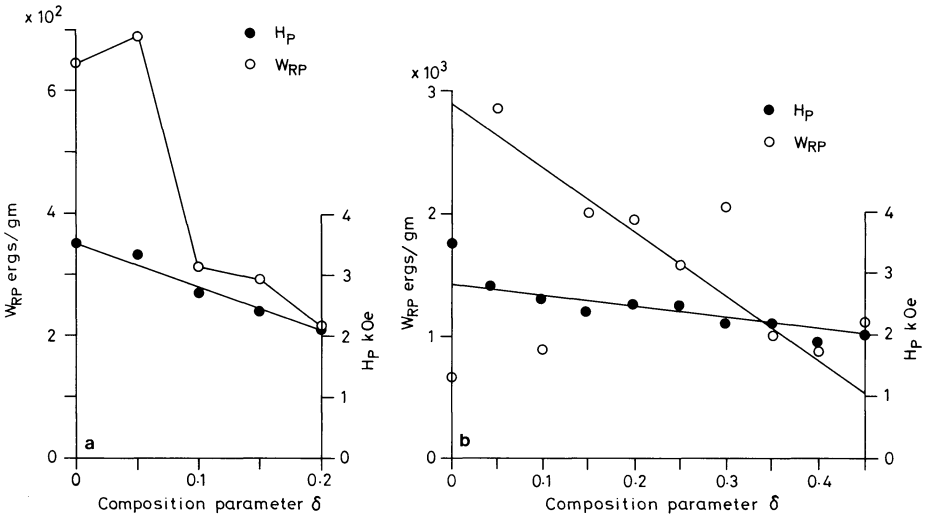


Fig. 5. a Variation of H_p and W_{RP} with composition in the titanomagnetite $Fe_{2.4-\delta}Al_{\delta}Ti_{0.6}O_4$ for multidomain specimens (37–44 μ m). W_{RP} varies erratically with composition whereas the variation of H_p is systematic. **b** Variation of H_p and W_{RP} with composition δ in the titanomagnetite $Fe_{2.4-\delta}Mg_{\delta}Ti_{0.6}O_4$ for multidomain specimens (37–44 μ m). W_{RP} varies erratically with composition whereas the variation of H_p is systematic

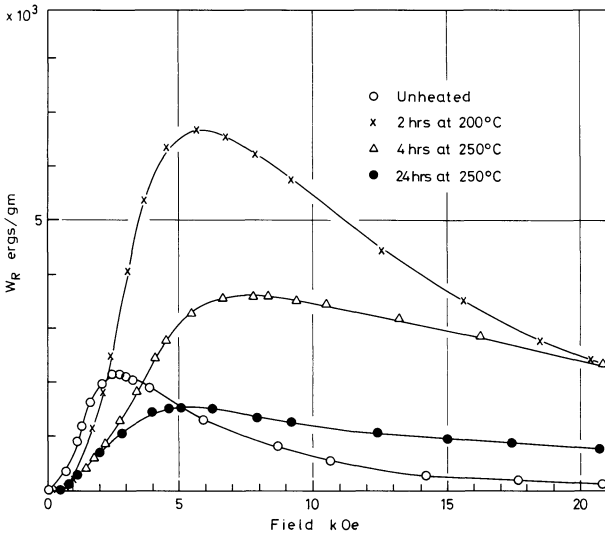


Fig. 6. Evolution of the W_R-H loss curve as a function of heat treatment in air (and increasing degree of maghemitization) of fine grain $Fe_{2.25}Ti_{0.75}O_4$ ($x=0.75$). The starting material has a Curie temperature T_c near to room temperature and, as maghemitization proceeds, the Curie temperature rises. In effect each curve, obtained at room temperature, corresponds to a different 'magnetic isotherm', T/T_c . This behaviour is to be contrasted with that of Fig. 2

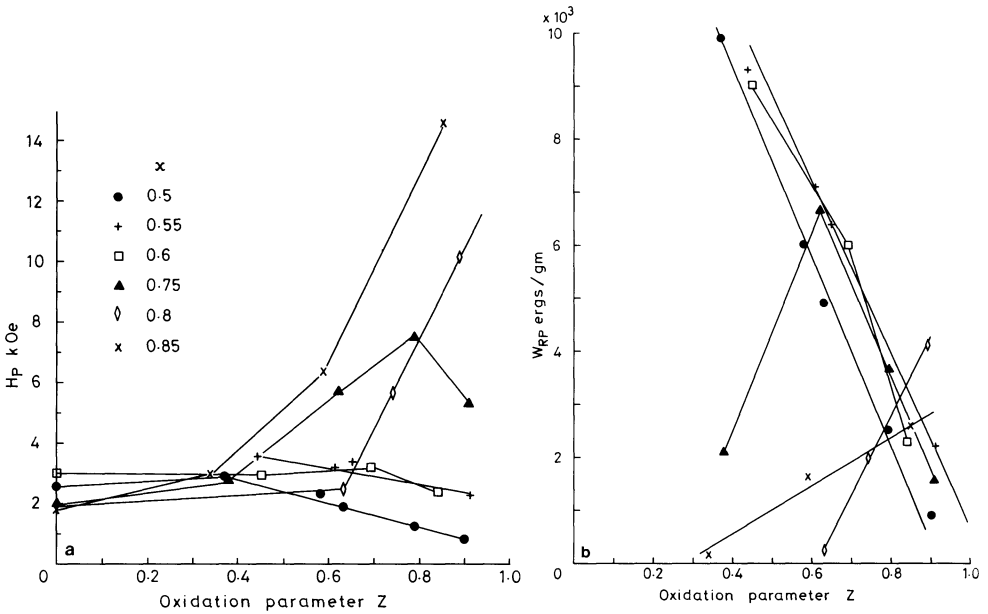


Fig. 7. **a** Variation of H_p with degree of oxidation, z , for maghemitized titanomagnetites of composition $x=0.5, 0.55, 0.6, 0.75, 0.8,$ and 0.85 . **b** Variation of W_{Rp} with degree of oxidation, z , for maghemitized titanomagnetites of composition $x=0.5, 0.55, 0.6, 0.75, 0.8,$ and 0.85 (see legend of **a**)

cient) than the large grain samples and therefore, having higher Curie temperatures, H_p and W_{Rp} persist at room temperature to a higher x value (~ 0.8).

The effect of the presence of cations other than Fe and Ti, such as are found in naturally occurring titanomagnetite has also been studied. The composition $\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$ ($x=0.6$) was chosen as being typical for many basalts and the Fe progressively substituted by up to 0.2 Al ions and 0.45 Mg ions per formula unit. The variation of H_p and W_{Rp} as a function of increasing concentration (δ) of substituting ion is shown in Fig. 5 for coarse grain material (37–44 μm). Al, replacing Fe^{3+} , is more effective in reducing H_p than Mg (replacing Fe^{2+}). Again the W_{Rp} values seem not to depend in a systematic way on composition for these multidomain specimens.

3.2 Titanomaghemites

Because of their relevance to naturally occurring titanomagnetites/titanomaghemites we have concentrated on compositions near to or based on $x=0.6$. The evolution (with respect to degree of maghemitization) of the W_R - H loss curve for a suite of titanomaghemites in which the Curie temperature is well above room temperature is shown in Fig. 2. The behaviour is more complicated when the starting composition is near (or below) room temperature as shown in Fig. 6. This may be described by saying that, at room temperature, the curves

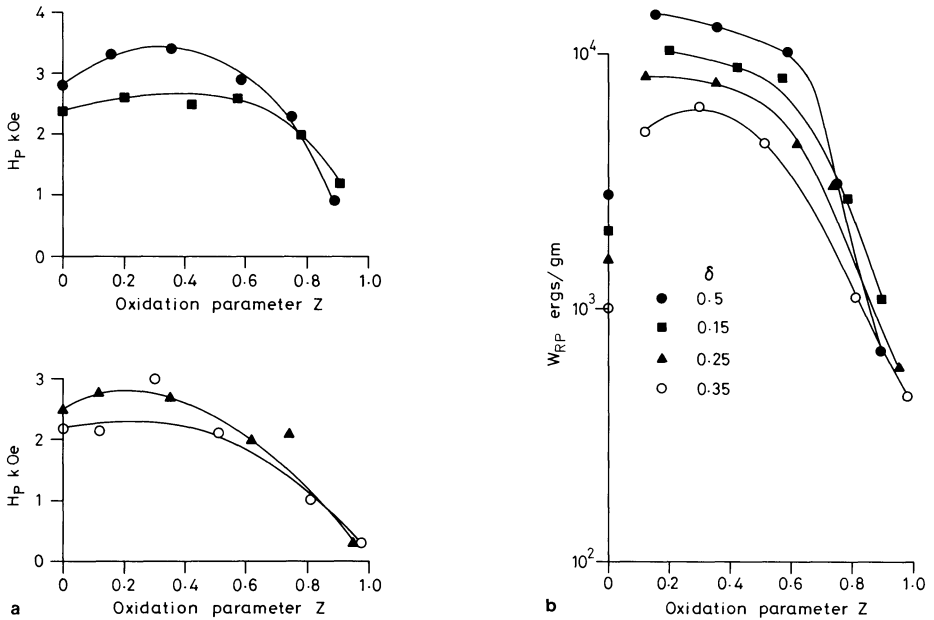


Fig. 8. a Variation of H_p with degree of oxidation, z , for maghemitized titanomagnetite based on $x=0.6$ and containing 0.5, 0.15, 0.25, and 0.35 ($=\delta$) Mg ions per formula unit (for identification of compositions see legend of b). b Variation of W_{RP} with degree of oxidation, z , for maghemitized titanomagnetite based on $x=0.6$ and containing 0.5, 0.15, 0.25, and 0.35 ($=\delta$) Mg ions per formula unit. The data points for $z=0$ refer to unground material in the multidomain state. All other data points refer to fine grain monodomain material

do not correspond to the same ‘magnetic isotherm’, T/T_c . Figure 7 shows the variation of H_p and W_{RP} with degree of maghemitization, z ($0 \leq z \leq 1$, z is the fraction of the Fe^{2+} concentration corresponding to stoichiometry, for a given x , oxidized to Fe^{3+}) for $x=0.5, 0.55, 0.6, 0.7, 0.75, 0.8$, and 0.85 . All the titanomaghemite samples are in the fine grain monodomain state.

The combined effect of magnesium substitution and maghemitization has also been studied, again for ball milled monodomain specimens. The variation of H_p and W_{RP} with z for a subsystem of $x=0.6$ containing up to 0.35 Mg ions per formula unit is shown in Fig. 8.

In all cases, except those complicated by the proximity of Curie temperatures to the measuring temperature (i.e., high x values), maghemitization results in a ‘softening’ of the material with reduced H_p values and W_R levels.

4. Discussion

4.1 Mineral Identification

The observed values of W_{RP} indicate a dependence on some variable parameters such as microstructure rather than chemical composition, especially for multido-

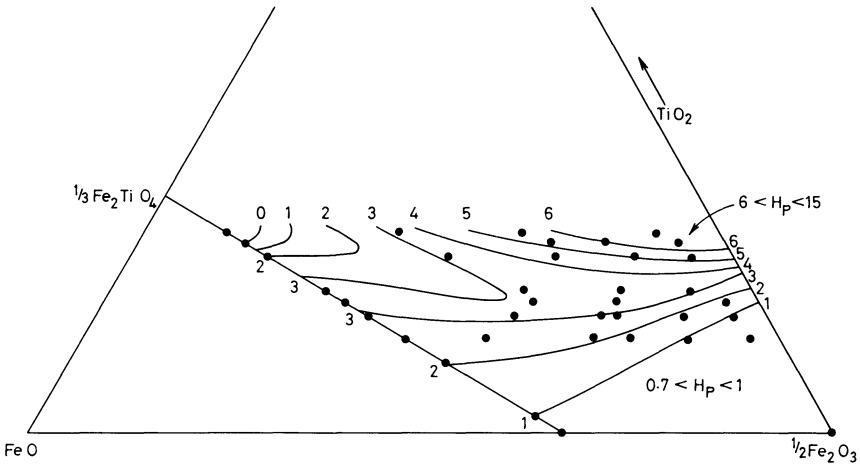


Fig. 9. Contours of constant value of H_p (in kOe) for titanomagnetites/titanomaghemites in the $FeO-Fe_2O_3-TiO_2$ ternary diagram, constructed from the data of Fig. 4 and 7a. Solid circles indicate the compositions of the measured samples

main material. In any event W_{Rp} is an extensive property and would only be useful in mineral identification in rocks if the concentration of magnetic mineral were known. On the other hand, H_p is intensive and has a systematic variation with composition. It appears to be independent of grain size and other extrinsic influences and may be a useful signatory property.

As is traditional, the composition dependence of the characteristic property has been cast in the form of contours on compositional ternary diagrams. Figure 9 shows the H_p contours for the $Fe_3O_4-Fe_2TiO_4-Fe_2TiO_5-Fe_2O_3$ quadrilateral of the $FeO-TiO_2-Fe_2O_3$ ternary diagram. The contours are based on the data of Figs. 4 and 7 and, being derived from a finite number of data points (34), are of necessity a subjective interpretation.

The H_p data of Figs. 5 and 8 have similarly been recast into contours on the relevant quadrilateral (representing Mg substituted and maghemitized $Fe_{2.4}Ti_{0.6}O_4$) in the $FeO-TiO_2-Fe_2O_3-MgO$ tetrahedron (Fig. 10).

The use of ternary diagrams such as those of Figs. 9 and 10 to display the chemical composition of naturally occurring magnetic minerals is not strictly possible unless the concentration of cations other than Fe and Ti is very small, in which case the standard ternary diagram of Fig. 9 may be used. Alternatively if the concentrations of the cations other than Fe and Ti are small except for one species, e.g., Mg, then a specially constructed ternary diagram like the one of which Fig. 10 is a part might be employed. A suite of compositions can be displayed on such diagrams subject to certain constraints on their compositions, e.g., in Fig. 10 all compositions have a constant Ti: (Fe, Mg) atomic ratio. Visual display of compositions is therefore possible only under special circumstances which are unlikely to apply to naturally occurring minerals. It is only possible to describe a composition in terms of its coordinates in multi-dimensional composition space. The coordinates are the molecular fractions of the oxide of each species, preferably referred to one cation. The composition

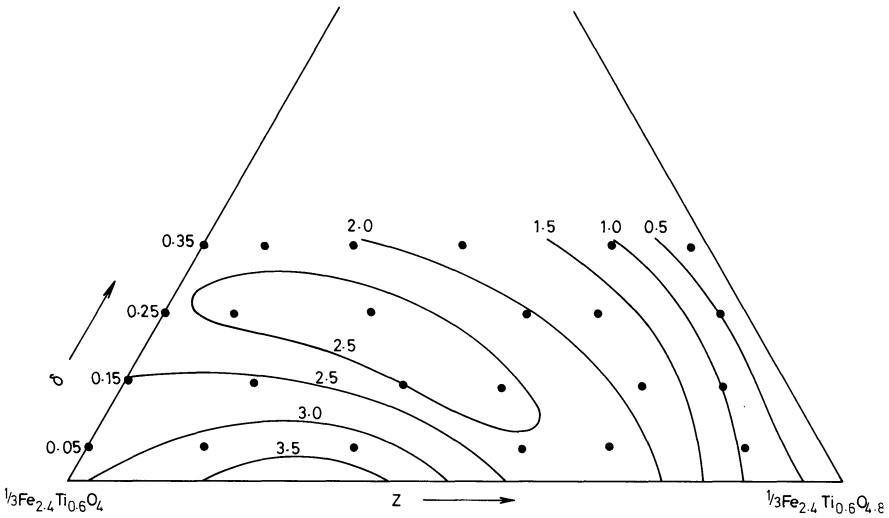


Fig. 10. Contours of constant value of H_p (in k Oe) for a magnesium substituted titanomaghemite subsystem based on $\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$ and containing δ Mg ions per formula unit. The *solid circles* refer to the compositions of the measured samples (see also Figs. 5 and 8)

parameters x and z may still be retained but must be clearly defined (see O'Reilly, 1976). The determination of x and z for titanomagnetite in basalts has been attempted by a number of methods. Chemical analysis for each cation species may be carried out if a refined extract of the magnetic mineral can be made from the rock. Chemical analysis of large enough grains can be carried out in situ using the electron probe microanalyser (EPMA). However this technique cannot determine Fe^{2+} and Fe^{3+} separately, nor oxygen accurately enough to provide a value of z of useful precision. EPMA is therefore combined with the analysis of Fe^{2+} and Fe^{3+} of extracts using conventional chemical analysis, or the Mössbauer Effect, or combined with the determination of some composition dependent characteristic such as Curie temperature. A combination of EPMA and H_p determination could therefore be used.

To this purpose a number of basalt samples were selected which exhibited a single low Curie temperature and were therefore believed to contain only homogeneous unaltered titanomagnetite as the magnetic phase. The six basalts, the titanomagnetite in which had been subjected to EPMA analysis (Creer and Ibbetson, 1970), are listed in Table 1. An attempt had been made to determine the degree of maghemitization of these basalts by comparing their measured Curie temperatures to those expected for stoichiometric titanomagnetites of the indicated composition (Richards et al., 1973). The effect of high temperature oxidation ($> 400^\circ\text{C}$) on the W_R-H curves of these basalts had also been studied (Manson and O'Reilly, 1976).

Column 1 in Table 1 gives the sample number and place of origin. The next four columns give the results of the EPMA analysis. The cation concentrations are expressed as the number of cations per four oxygen ions. Small concen-

Table 1. Rotational hysteresis data $H_p(\text{obs})$ (k Oe) for a number of basalts which exhibit a single, low, Curie temperature and are believed to contain homogeneous titanomagnetite. The microprobe chemical analyses of titanomagnetite grains are taken from Creer and Ibbetson (1970) and the oxidation parameter $z(T_c)$, derived from a consideration of the chemical composition and observed Curie temperature, taken from Richards et al. (1973). $H_p(x, \delta)$ are the values of field at peak rotational hysteresis loss expected from the chemical composition assuming a stoichiometric substituted titanomagnetite. The oxidation parameter based on the rotational hysteresis data, $z(H_p)$ is given in the final column (see text)

Sample	Microprobe Analysis				$z(T_c)$	$H_p(\text{obs})$	$H_p(x, \delta)$	$z(H_p)$
	Fe	Mg	Al	Ti				
RK (Germany)	2.02	0.18	0.29	0.46	0.8	2.4	0.55	?
376 (Argentina)	1.98	0.24	0.15	0.60	0.75	1.6	1.6	low
293 (Argentina)	2.01	0.21	0.14	0.62	0.7	1.9	1.7	low
H21A (Aden)	2.05	0.13	0.15	0.64	0.6	3.5	1.2	~ 1 (?)
G143 (Turkey)	2.15	0.05	0.05	0.72	0.9	2.6	1.75	~ 0.4
D127 (Turkey)	1.99	0.10	0.04	0.85	0.75	2.1	0	0.2

trations of Mn and Cr (up to 0.03 ions per formula unit) were also detected but not listed here. One point of interest is that although the Fe concentration is more or less constant the other species vary widely and in an apparently systematic way. As the Ti concentration increases, the concentrations of Mg and Al decrease. Although the degree of oxidation could in principle be determined from the cation sum, the uncertainty in such a determination would be too large to be useful, and in the present analysis the original data have been normalized to give stoichiometric concentrations (Creer and Ibbetson, 1970).

The x value is simply the number of tetravalent cations per formula unit in a stoichiometric spinel and is therefore found in column 5 of Table 1. The z value of column 6, $z(T_c)$, was derived (Richards et al., 1973) using the Curie point data of synthetic materials. The Curie point corresponding to the stoichiometric composition of the indicated x value was reduced according to the concentrations of Al and Mg and the Curie temperature so derived compared to that observed. The observed Curie temperature was the higher in all cases and, knowing that maghemitization would increase the Curie temperature, this mechanism may be invoked to explain the difference. The degree of maghemitization is then estimated from the measured Curie temperatures of maghemitized synthetics. The same process has been applied in the present study using the H_p values. Column 7 of Table 1 gives the measured H_p values, $H_p(\text{obs})$, for the six basalts. The data for substituted synthetic titanomagnetites obtained in the present study is then used to obtain the H_p expected for a stoichiometric substituted titanomagnetite, $H_p(x, \delta)$. The difference between $H_p(\text{obs})$ and $H_p(x, \delta)$ may then be explicable in terms of maghemitization. Good agreement between $H_p(\text{obs})$ and $H_p(x, \delta)$ is found for two of the samples, 376 and 293 which may indicate near stoichiometric titanomagnetite. The value of oxidation parameter deduced from the rotational hysteresis measurements, $z(H_p)$, in column 9 is therefore considered to be low. For the other samples $H_p(\text{obs})$ is significantly

higher than $H_p(x, \delta)$. Inspection of the data of Figs. 7 to 10 shows that maghemitization does increase H_p values for high x (>0.6). Making the approximation that a given degree of maghemitization will produce the same elevation in H_p in both substituted and unsubstituted compositions a value of $z(H_p)$ may be derived. Thus samples G143 and D127 may be assigned $z(H_p)$ values of 0.4 and 0.2 respectively. $H_p(\text{obs})$ of H21A is not so easily explained as the H_p seems to be constant, independent of z for $x=0.6$ (Fig. 7). However the contours for high z (Fig. 9) are closely spaced for $x \gtrsim 0.6$ and it may be that for $z \sim 1$, H_p will increase for $x=0.6$. $z(H_p)$ for H21A may therefore be tentatively taken as being ~ 1 . $H_p(\text{obs})$ for the remaining sample, RK, seems inexplicable. The large concentration of Al, together with Mg, depresses $H_p(x, \delta)$ to $0.55 k$ Oe whereas $H_p(\text{obs})$ is $2.4 k$ Oe. The effect of maghemitization on low x values (see $x=0.5$, Fig. 7) is to further depress the value of H_p . It might be concluded that the titanomagnetite in RK is near-stoichiometric but has an anomalously low H_p . RK is a much-studied basalt (see Petersen, 1962; Soffel, 1969) which is considered to contain unoxidized titanomagnetite and to be typical in many ways of continental basalts. However the EPMA analysis indicates a very large concentration of cations other than Fe and Ti. In fact with a total of 0.47 ions of Mg and Al per formula unit it might be arguable whether it qualifies as a 'titanomagnetite'. This high concentration of diamagnetic ions also presents problems in interpreting the observed Curie temperature. The 'compositional' Curie temperature for RK should be $\sim 90^\circ \text{C}$ (Richards et al., 1973) whereas the observed value is 250°C . The high degree of maghemitization needed to bring the 'compositional' and observed Curie temperatures into line is not indicated by, for example, thermomagnetic curves. The role of the 'minor cation species' in naturally occurring titanomagnetites remains unclear.

4.2 Magnetic Anisotropy

It has been noted that H_p varies in a systematic way with composition, regardless of the domain state of the specimens. It is seen, for example, that H_p of a titanomagnetite of a given composition is about the same for coarse and fine grain specimens. However, the W_{Rp} values for the fine particles are about an order of magnitude bigger than for coarse grains of the same composition (Sect. 3.1). It appears that whereas H_p is a function of the intrinsic properties of a material W_{Rp} depends on extrinsic properties or microstructure. Similarly the coercive force of fine-particle, ball-milled titanomagnetites is (at about $2 k$ Oe for $x=0.6$) an order of magnitude bigger than that of coarse grain material.

According to the monodomain theory (Sect. 1) the peak rotational hysteresis loss, W_{Rp} , is proportional to the anisotropy energy per unit volume, as is the product of H_p and M_s , the spontaneous magnetization. The ratio $W_{Rp}:(H_p M_s)$ should then be constant for a given symmetry and type of anisotropy regardless of chemical composition. The magnesium substituted fine grain titanomaghemite specimens (Sect. 3.2) are in the monodomain state and range in W_{Rp} from about 500–15,000 ergs/gm, a factor of about 30 and in H_p by a factor of about 10 ($0.3\text{--}3 k$ Oe). The ratios $W_{Rp}:(H_p M_s)$ for this system of

18 compositions lie between 0.1 and 0.2, relatively constant compared to the range in W_{Rp} . As W_{Rp} seems to depend on microstructure or extrinsic properties in the same way as coercive force, H_c , it seems likely that the ratio $W_{Rp}:(H_c M_s)$ may have a value nearer to a constant. This is indeed found to be the case for the suite of magnesium substituted titanomaghemites. Taking the H_c data for this system (O'Donovan and O'Reilly, 1977), this ratio has a value of 0.30 varying by about $\pm 10\%$ except two specimens out of the 18 which have values of about 0.20. The ratio does therefore appear to be a constant for the system. The actual values however are rather lower than predicted by the monodomain, coherent rotation, models which give 1.21 (cubic anisotropy) and 1.8 (uniaxial) for a random array of easy axes.

No model expressions for W_{Rp} and H_p are available for multidomain materials, however it is of interest to form the $W_{Rp}:(H_{p,c} M_s)$ ratios for the suite of 15 multidomain specimens of Al and Mg substituted $Fe_{2.4}Ti_{0.6}O_4$ (Sect. 3.1). The values of the two ratios are quite different. The $W_{Rp}:(H_p M_s)$ values for the Al substituted system lie between 0.005 and 0.007 and between 0.025 and 0.035 (with one value at 0.013 and one at 0.043) for the Mg substituted set. Using the H_c instead of the H_p values gives ratios over a closer range for both sets (0.5–1.7) having the same order of magnitude as for the monodomain system, although the degree of constancy is much poorer.

Magnetic 'hardness' whether expressed in terms of H_c , H_p , or W_{Rp} seems in the titanomagnetite system to be associated with the presence of Fe^{2+} . Thus as x increases, magnetic hardness increases. Similarly as z increases, magnetic hardness decreases. This effect is obscured at high x values where the Curie temperatures are low and measurements at room temperature appear to indicate a contrary variation of hardness with x and z . However this variation is due to variation in the magnetic isotherm (T/T_c) at room temperature. Of especial interest are the high values of H_p for the high x , high z , compositions (Fig. 7). It appears that the small residual concentrations of Fe^{2+} in $x=0.8$, $z=0.9$, and $x=0.85$, $z=0.85$ in the presence of the high Ti and vacancy concentrations make a large contribution to the anisotropy possibly via magnetostriction. It could be that a higher degree of oxidation would see the anisotropy fall for these samples as appears to be happening for $x=0.75$. Compositions in this area of high Ti concentration of the titanomaghemite quadrilateral of the ternary diagram seem to be the magnetically hardest part of the system. In nature, although the remanence carried by such material may be extremely stable, the near-stoichiometric first-formed titanomagnetite would not acquire a thermoremanent magnetization. The remanence would be acquired during subsequent maghemitization. However maghemitization is generally considered to occur fairly rapidly in nature ($\sim 10^6$ years) and although this would preclude using reversals of the geomagnetic field as a petrological tool (i.e., to infer rates of maghemitization from the polarity of the titanomaghemite), the chemical remanence, so acquired, would have palaeomagnetic usefulness.

5. Conclusions

The identification of the magnetic minerals in the rock samples or artefacts used in any investigation of the palaeomagnetic field is of fundamental impor-

tance. No single technique is available by which this may be done. Magnetic rotational hysteresis loss measurements can contribute to the identification of minerals, in situ, without danger of bringing about chemical change and may also give some indication of the domain state of the mineral if its concentration can be estimated. The rotational hysteresis loss curves obtained for synthetic analogues in the present study would form the basis for such investigations of rock samples.

Acknowledgments. This work forms part of NERC sponsored research programmes 'Rock and mineral magnetism' and 'Thermoremanence in titanomagnetites'. Two of the authors (A.J.M. and J.B.O'D.) have been in receipt of NERC studentships. Some of the samples were provided by Dr. P.W. Readman and we also thank Dr. Z. Hauptman for invaluable assistance in the preparation and analysis of materials.

References

- Cowan, B.K., O'Reilly, W.: The effect of heat treatment on magnetic minerals in red sandstones, studied using the technique of rotational hysteresis. *Geophys. J. R. Astron. Soc.* **29**, 263–274, 1972
- Creer, K.M., Ibbetson, J.D.: Electron microprobe analyses and magnetic properties of non-stoichiometric titanomagnetites in basaltic rocks. *Geophys. J. Roy. Astron. Soc.* **21**, 485–511, 1970
- Day, R., O'Reilly, W., Banerjee, S.K.: Rotational hysteresis study of oxidized basalts. *J. Geophys. Res.* **75**, 375–386, 1970
- Fletcher, E.J., De Sa, A., O'Reilly, W., Banerjee, S.K.: A digital vacuum torque magnetometer for the temperature range 300°–1,000°K. *J. Phys. Earth* **2**, 311–314, 1969
- Jacobs, I.S., Luborsky, F.E.: Magnetic anisotropy and rotational hysteresis in elongated fine particle magnets. *J. Appl. Phys.* **28**, 467–473, 1957
- Manson, A.J., O'Reilly, W.: Submicroscopic texture in titanomagnetite grains in basalts studied using the torque magnetometer and electron microscope. *Phys. Earth Planet. Inter.* **11**, 173–183, 1976
- O'Donovan, J.B., O'Reilly, W.: The preparation characterization and magnetic properties of synthetic analogues of some carriers of the palaeomagnetic record. *J. Geomagn. Geoelectr.* **29**, 331–344, 1977
- O'Reilly, W.: Magnetic minerals in the crust of the Earth. *Rep. Prog. Phys.* **39**, 857–908, 1976
- Owens, W.H.: Rotational hysteresis in haematite. *Geophys. J. Roy. Astron. Soc.* **49**, 282 (Abstract), 1977
- Petersen, N.: Untersuchungen magnetischer Eigenschaften von Titanomagnetiten im Basalt des Rauhen Kulm (Oberpfalz) in Verbindung mit elektronen-mikroskopischer Beobachtung. *Z. Geophys.* **28**, 79–84, 1962
- Readman, P.W., O'Reilly, W.: Magnetic properties of oxidized (cation-deficient) titanomagnetites (Fe, Ti, □)₃O₄. *J. Geomagn. Geoelectr.* **24**, 69–90, 1972
- Richards, J.C.W., O'Donovan, J.B., Hauptman, Z., O'Reilly, W., Creer, K.M.: A magnetic study of titanomagnetite substituted by magnesium and aluminium. *Phys. Earth Planet. Inter.* **7**, 437–440, 1973
- Soffel, H.C.: The origin of thermoremanent magnetization of two basalts containing homogeneous single phase titanomagnetite. *Earth Planet. Sci. Lett.* **7**, 201–201, 1969
- Stoner, E.C., Wohlfarth, E.P.: A mechanism of magnetic hysteresis in heterogeneous alloys. *Philos. Trans. R. Soc. Ser. A*: **240**, 559–640, 1948

Received May 24, 1979; Revised Version August 6, 1979; Accepted August 11, 1979

