Werk

Jahr: 1978
Kollektion: fid.geo
Signatur: 8 Z NAT 2148:45
Digitalisiert: Niedersächsische Staats- und Universitätsbibliothek Göttingen
Werk Id: PPN1015067948_0045
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LOG Id: LOG_0067
LOG Titel: On the presence of titanomagnetite in basalts
LOG Typ: article

Übergeordnetes Werk

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On the Presence of Titanomagnetite in Basalts

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Abstract. Observed magnetic properties such as the apparent Curie point of magnetite occurring in association with titanium in basalts are usually explained on a titanomagnetite solid-solution model. A possible alternative is to invoke grain size effects, for example if very fine, stable single-domain (SD) particles of *magnetite* become superparamagnetic on heating to temperatures several hundred degrees below the Curie point of magnetite. It is shown that measurement of the magnetic hysteresis at different field strengths and temperatures may enable one to distinguish between these alternatives. Moreover, magnetic properties due to multi-domain (MD) magnetite in rocks should be distinguishable from those due to MD titanomagnetite, for example in measurements of the temperature dependence of low-field susceptibility. Extensive studies carried out with these techniques on basalts from different continents and oceans showed surprisingly that a magnetic behaviour attributable to 'true' titanomagnetite was very rare in the continental samples. In only one case of a young ($< 30,000$ years old) marine pillow basalt were the properties of the dominant magnetic mineral found to be compatible with SD *titanomagnetite*. These results can be interpreted in terms of a possible compositional instability of original titanomagnetites with time and of associated changes in the effective grain size and magnetic properties of basalts.

Key words: Titanomagnetites – Magnetic domain state – Magnetic granulometry – Basalts – Curie points.

1. Introduction

From studies on synthetic samples, it has long been known (e.g., Chevallier et al., 1955; Uyeda, 1958) that iron-titanium oxides form series of solid solutions of which titanomagnetite (TM) has the most important direct bearing on the understanding of the magnetic properties of basalt. The magnetic properties of oxidized or cation-deficient titanomagnetites, sometimes called titano-

maghemites (TMh), have been studied, also on synthetic samples, as a function of Ti content and degree of oxidation (e.g. Readman and O'Reilly, 1972).

Serious difficulties may be encountered in applying these solid-solution properties based on synthetics to actual rocks. For example, Mössbauer studies by Jensen and Shive (1973) of magnetite-rich ($x \leq 0.20$) synthetic TM have suggested that most of the titanium resides in submicroscopic clusters of Ti-rich material surrounded by nearly pure magnetite, and that the size and composition of these clusters may be affected by the method of sample preparation. Also, attempts by several workers (Ade-Hall, 1964; Smith, 1967; Creer, 1971) to correlate the Curie points (T_c) of basalts determined by experiment with those calculated from chemical composition of the magnetic minerals have revealed large discrepancies. For one particular synthetic TM of composition 0.6 $Fe_2TiO_4 \cdot 0.4\ Fe_3O_4$ (hereafter called TM60) a scatter of 70°C in T_c data of different workers was reported (Hauptman, 1974). Even when only one magnetic mineral is present, such uncertainties could result from grain-size effects (Radhakrishnamurty et al., 1972); thus if the magnetite or TM occurs as very fine particles dispersed in the basalt, the loss of ferromagnetic properties observed at a relatively low temperature may be partly or entirely due to thermal agitation, as distinct from the disappearance of spontaneous magnetization. Then T_c is an apparent Curie point rather than the true Curie point corresponding to some TM mineral composition.

In this paper we propose a few criteria for distinguishing the presence of 'true' (solid-solution) TM from magnetite in titaniferous basalts, and we show from measurements on nearly 400 continental and oceanic basalts that cases of magnetic behaviour which can be attributed unquestionably to the presence of true TM were virtually absent. Unfortunately, this very fact makes it difficult to provide an adequate experimental test of the above-mentioned criteria, which therefore remain somewhat speculative.

2. Curie Points in Basalts

The Curie point is one of the important parameters for ferromagnetic materials and it can be determined to a very high degree of accuracy in the case of pure metals like iron, cobalt and nickel, or of stoichiometric compounds such as magnetite. For magnetic alloys it may not be possible to measure T_c as accurately, because minor variations in synthesising conditions could cause variations in observed T_c values of a few degrees between different samples. In the case of rocks containing magnetic minerals having a broad blocking temperature spectrum, the measurement of T_c may be subject to greater errors. Sometimes the procedure of heating rocks to determine the Curie points of the minerals in them will cause progressive and irreversible changes whereby any values experimentally obtainable may have an ambiguous relationship to the original minerals.

The two most common methods for the determination of T_c are (i) measurement of temperature dependence of saturation magnetization (J_s) or maximum

undersaturated magnetic moment (M) of the sample in fields of a few thousand oersteds, referred to as the $J_s - T$ or $M - T$ method, and (ii) study of thermal variation of susceptibility (k) measured in low fields and termed the $k - T$ method. In the $J_s - T$ or $M - T$ method a signal proportional to J_s which decreases with increasing T for a given material is measured, for example in Curie point balances. In the $k - T$ method the measurement involves a signal that sometimes increases with T and attains a peak value just below T_c because of the Hopkinson (1889) effect. Only the $J_s - T$ ($M - T$) methods will generally ensure that the Curie points measured are representative of the medium to high coercive force (H_c) fraction. However, $k - T$ curves can be highly diagnostic of the properties especially of soft components. Since basalts commonly exhibit a broad H_c spectrum of magnetite or TM, the most effective procedure for obtaining the Curie points of two or more components present in a sample is to employ high-field and low-field measurements (including those of hysteresis) jointly. Successful combined applications of these methods to mixed-component basalts have been reported (Radhakrishnamurty and Deutsch, 1974; Deutsch and Pätzold, 1976; Murthy et al., 1976).

3. Effects of Oxidation and Grain Size on Curie Point

In view of the widespread occurrence of a mineral with composition around TM60 in marine basalts, its magnetic properties have special significance for understanding marine magnetic anomalies. It is also important to know how TM60 alters and what the alteration products are, for a proper interpretation of magnetic anomalies associated with somewhat weathered rocks. In the work of Ozima et al. (1968) and Ozima and Larson (1970) it is implied that TM and TMh are distinguishable by heating. From studies of synthetic samples they conclude that heating stoichiometric TM's to 600° C in either air or vacuum tends to produce nearly reversible $J_s - T$ curves, whereas in the case of TMh such heating produced a sharp irreversible increase of both J_s and T_c. Although these authors showed that this criterion worked in some marine basalts, it is doubtful whether it applies to all basalts, especially when the moisture and gas content of different samples could vary widely.

It is, in any case, a widely observed fact (Wilson and Smith, 1968; Ozima and Larson, 1970) that the thermomagnetic curves of many basalts are highly irreversible, often with T_c increasing to 580° C or higher temperatures upon heating. Such behaviour is consistent with relatively unoxidized magnetite or TM becoming (more) cation-deficient to produce CD magnetite, TMh or maghemite as the case may be.

When a magnetic material can be obtained in bulk form and remains unchanged on heating, its T_c can be determined accurately. This is the case even when large multidomain (MD) grains of such a sample are dispersed in a non-magnetic matrix. However, if the grains are very fine single-domains (SD), then thermal disordering might have caused the blocking temperatures (T_b) to be substantially lower than T_c; in that case, measurement of magnetization of the grains at temperatures much higher than T_b may be difficult and

hence determining T_c may involve some uncertainty. That grain-size effects can be important is underlined in an extreme example: Sato et al. (1971) report that the apparent magnetization of 150 Å and 100 Å grains of manganese ferrite and $Mn_{0.6}Co_{0.4}Fe_2O_4$, respectively, was zero in both cases even in an applied field of 9.2 Koe when measured at room temperature where these materials are ferrimagnetic in bulk.

In the case of magnetite, Feitknecht and Gallagher (1970) postulated that heating to 200° to 300° C provokes ferrous ion migration and this mechanism causes oxidation of small grains to maghemite. One consequence of this cation migration in magnetite on heating is that, whereas it may interfere with magnetization measurements on fine grains at high temperature, it will have negligible effect in large grains and hence should not impede a precise determination of T_c based on large grains. A far-reaching implication of this phenomenon is that it establishes a measurable criterion for distinguishing MD magnetite from MD titanomagnetite dispersed in rocks (see below). Another important aspect of heating magnetite grains is that a protective coating of hematite may form on the surface of the grains and complete conversion to hematite is prevented even by prolonged heating in air. This mechanism could account for the observation that some basalts are affected very little in their magnetic properties even after being heated in air at 100° C for 24 h (Radhakrishnamurty and Sahasrabudhe, 1965).

The above features need careful consideration, and grain size as well as oxidation effects on the observed magnetic properties of basalts have to be recognized before these can be interpreted in terms of TM or TMh solid solution models.

4. Criteria for Distinguishing MD Magnetite From MD Titanomagnetite

In Fig. 1, a $k - T$ curve characteristic of large MD grains of magnetite (Radhakrishnamurty and Deutsch, 1974) is compared with that inferred for a titano-
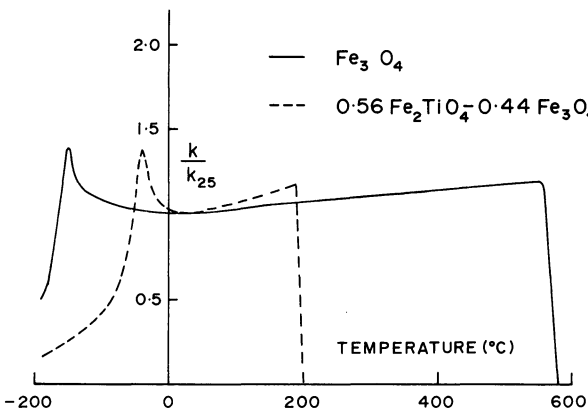

Fig. 1. Thermal variation of susceptibility for large multidomain grains (schematic). The magnetite curve is a composite based on experimental results from magnetite ore and very old basalts. The titanomagnetite curve is constructed from data available in the literature

magnetite of composition 0.56 $Fe_2TiO_4 \cdot 0.44\ Fe_3O_4$ ('TM56'). The magnetite curve (solid) is based on combined experimental observations on magnetite ore and on very old basalts. The curve is nearly or (as depicted) entirely reversible and shows an abrupt drop of k at the Curie point of magnetite and a sharp peak near the isotropic point $(-155°C)$ that would be suppressed in SD magnetite owing to the predominance of shape anisotropy over other forms of anisotropy. Also, with SD grains, the curve may be more highly irreversible and its high-temperature portion should be less blocky. The 'magnetite' curve is almost identical to that obtained (Murthy et al., 1976) on a sample of young (9 m.y.) peridotite from Leg 37 of the Deep Sea Drilling Project, which exhibited MD characteristics in a Lowrie-Fuller test and could therefore be regarded as material in a 'true' multi-domain rather than pseudo single-domain (PSD) state (Johnson et al., 1975).

The $k-T$ curve for TM56 (dashed line) is constructed from magnetic data available for it in the literature and by making use of the analogy it bears to magnetite. Our reason for depicting here an inferred rather than experimental curve is simply that curves of this type based on synthetic MD titanomagnetite, as distinct from magnetite, apparently have never been reported in the literature. A possible cause of this lack of data is suggested by the results of some recent experiments we undertook using coarse, single-phased synthetic TM's, in which the samples failed to show obvious MD properties. That the dashed curve nevertheless conforms to a realistic expectation for natural rock is clear from the known properties of the MD state and from the measured variation of isotropic and Curie points in titanomagnetite. Thus Syono and Ishikawa (1964) obtained a set of isotropic temperatures on homogeneous TM crystals grown in the laboratory, including a value of about $-40°$ C for TM56. Curie point values of TM56 or of material close to this composition quoted by different workers (see Hauptman, 1974) vary over a range of about 50° C and for the present purpose T_c is taken as 200° C. By further extrapolation, one could expect similar curves for other members of the TM series with k-peaks at their respective isotropic points, though in TMh the transition is probably absent (see 'Discussion'). Because of the expected appearance of such peaks in the curves of TM56 and similar material, it is again implicit that they apply only to a truly multi-domain state.

It follows that, *in the multi-domain state only,* variations of (i) T_c and (ii) the isotropic point observed in $k-T$ curves can serve as two criteria for distinguishing magnetite from titanomagnetite in rocks. Widely different intermediate members of the TM series, if they occur as MD's, could be similarly distinguished from one another. Single-domain criteria are discussed later.

5. Results of Measurements

In a study at the Tata Institute and Memorial University, several hundred basalt samples from different parts of the world were subjected to measurements of thermomagnetic and hysteresis properties.

The $k-T$ curves were obtained on standard cylindrical specimens of about 20 g, heated and cooled in air in the temperature range $-196°C$ to 650°C, and the signal noted at regular intervals. Using the equipment described earlier (Radhakrishnamurty and Likhite, 1970; Pätzold, 1972), the procedure was to measure k first in the range $-196°C$ to 20°C during the natural heating of samples after immersion in liquid nitrogen. Between 20° and 650°C both heating and cooling curves are traced at rates of 6–10°C per minute, then the -196

to 20° C measurement is repeated so that each 'cooling' curve actually consists of cooling and heating sections coinciding at 20° C. Since in this way the heating rate is not controlled between −196° and 20° C, some rocks, especially among those with low (≦300° C) apparent Curie points, were treated more rigorously below 20°C so as to produce both cooling and heating curves, each kind with rate-control. The technique is standard, using a furnace and cool N_2 gas under regulated pressure down to –180° C, whereby cooling or heating can be slowed as desired so as to equalize temperatures over the specimen volume. This was important near the isotropic point of magnetite (–155° C) or titanomagnetite where, in the $k - T$ curves, the susceptibility peak characteristic of MD material (Fig. 1) might be suppressed by the presence of significant thermal gradients within the specimen. Careful application of these procedures has satisfied us that, in all cases where diagnostic features such as transition peaks were not observed, their absence is due to other than experimental causes.

Rayleigh loops (hysteresis in 10 oe) and high-field (1500 oe) hysteresis at 25° C and −196° C for all the samples were also observed, using instruments

Table 1. Prominent magnetic state of some submarine and continental basalts samples. None of the samples indicated a magnetic behaviour unambiguously attributable to a titanomagnetite. Most of the samples are mixtures of two or three states, but a sample is placed under the inferred most prominent state of the mixture. MD: multi-domain, SD: single-domain, SP: superparamagnetic and CD: (strongly) cation-deficient state of magnetite grains. In some cases (e.g. Refs. A,B), column 3 cites fewer samples than were reported in the original study, after omitting those whose magnetic state could not be clearly established

Formation or source	Age	Number of samples (+) or sites (@)	Prominent magnetic state				Ref.
			MD	SD	SP	CD	
1	2	3	4	5	6	7	8
Leg 34, DSDP	15, 30, and 40 m.y.	37+	−	6	31	−	A
Leg 37, DSDP	3.5, 10, and 13 m.y.	18+	1	9	1	7	B
Columbia River basalts	Miocene	8+	−	2	6	−	C
Western Iceland basalts	12 m.y.	29+	−	11	10	8	D
Northern Ireland basalts	Tertiary	26+	−	3	15	8	D
Hungary basalts	Tertiary	6+	−	1	4	1	D
Mull dykes	Tertiary	16@	−	6	9	1	D
Mull and Skye basalts	Tertiary	82+	6	24	35	17	D
Dykes, England and Wales	Tertiary	11+	−	3	4	4	D
Deccan traps	60 to 65 m.y.	36@	−	3	12	21	C
Hungary basalts	Cretaceous	6+	−	3	2	1	D
Rajmahal traps	Cretaceous	17@	−	11	4	2	C
Scotland basalts	Carboniferous	24+	5	7	−	12	D
Newfoundland ophiolites	Ordovician	56+	31	1	23	1	C
Bijiwar traps	Precambrian	6@	5	−	−	1	D
Cuddapah traps	Precambrian	15@	14	−	−	1	C
Basic dykes, India	Precambrian	6@	6	−	−	−	C

A: Deutsch and Pätzold (1976)
B: Murthy, Deutsch, and Pätzold (1976)
C: Radhakrishnamurty and Deutsch (1974)
D: Radhakrishnamurty, Raja, Likhite, and Sahasrabudhe (1972)

and procedures given in earlier papers (Likhite and Radhakrishnamurty, 1966; Radhakrishnamurty, Likhite and Sastry, 1971). $M-T$ curves were obtained on powders heated in a vertical Curie point balance in air at 1300 oe (Deutsch and Pätzold, 1976), as a supplementary study.

A striking result of these measurements, using the criteria proposed above, is that not a single $k-T$ curve that could be attributed to large MD grains of titanomagnetite was found. Instead almost all old (Precambrian) basalts and some younger ones showed characteristic MD curves with Curie points and isotropic points of magnetite (Fig. 1, solid curve). A summary of available results showing the inferred domain states in these basalts is given in Table 1. These results suggest that large TM grains behaving magnetically as multi-domains occur very rarely in basalts.

Next, a detailed study was made of two marine basalt samples dredged from the Mid-Atlantic Ridge 45° N and kindly provided to us by Dr. J.M. Hall of Dalhousie University along with photomicrographs of their polished surfaces (Fig. 2). Figure 2a is that of sample HU56-3-20 taken from a pillow basalt of age less than 30,000 years (reported age $12,000 \pm 18,000$ years; Aumento, 1969) and Fig. 2b is for a sample, HU74-003-6-1, believed to have come from the interior of a flow whose age may be a few million years. Both the photographs were taken at $\times 900$ in oil. The opaque grains in both the samples have compositions around that of TM60 (J.M. Hall, private communication, 1974).

In Fig. 3 the $k-T$ curves and Rayleigh loops of the two samples are given. It is interesting to note that, while the $k-T$ curves are similar in the 20°–600° C range, HU74-003 shows a Rayleigh loop (Fig. 3d) and the other sample (Fig. 3c) does not.

Figure 4 shows the high-field hysteresis loops of the samples both at 25° C and $-196°$ C. Sample HU56-3 is weak and hence parameters like coercive force (H_c) and relative remanence (ratio of remanent to maximum intensity, J_r/J_m) obtainable from the hysteresis loops are approximate. However, it is clear that the loop characters of the two samples are distinctly different from
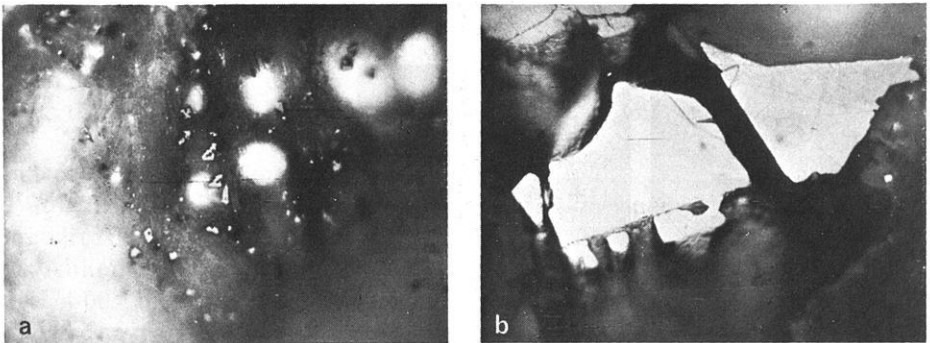

Fig. 2a and b. Photomicrographs of polished surfaces of two optical marine basalt samples, taken at $\times 900$ in oil. (a) is for a pillow basalt, HU56-3-20 and (b) for HU74-003-1, a fragment believed to have come from the interior of a flow. The samples and photomicrographs were provided by Dr. J.M. Hall of Dalhousie University
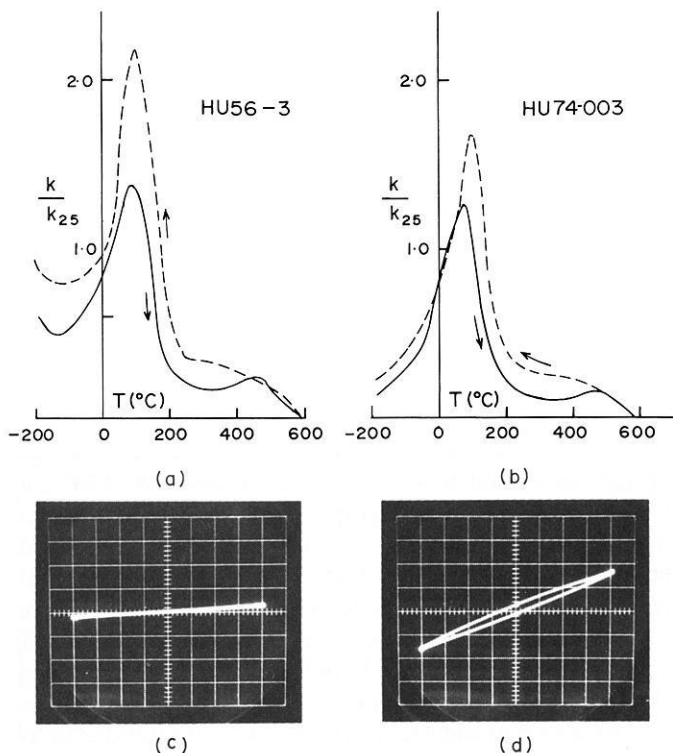
Fig. 3a–d. $k - T$ curves and Rayleigh loops for the two samples of Fig. 2. Rayleigh loops were obtained from (c) 11.2 g of HU56-3-20 and (d) 13.9 g of HU74-003-6-1. Scales for (c) and (d) are the same: X-axis, one small division = 0.5 oe; Y-axis, one small division = 0.013 emu
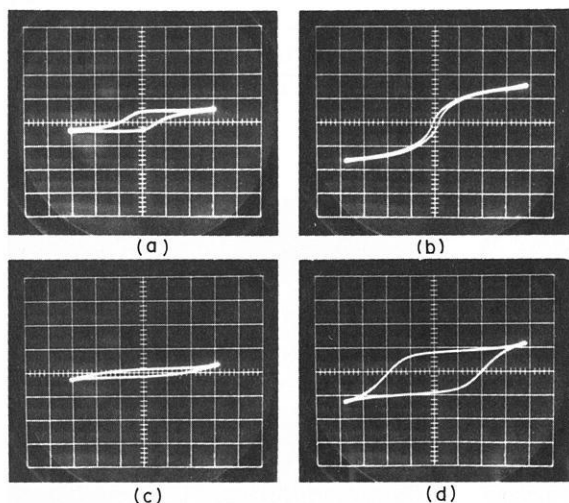

Fig. 4a–d. High-field hysteresis loops for the samples whose Rayleigh loops are given in Fig. 3. (a) and (c) are for HU56-3 at 25°C and −196°C respectively; (b) and (d) are for HU74-003 at the two temperatures. Scale (same for all loops): X-axis, one small division = 75 oe; Y-axis, one small division = 1.17 emu. The distortion at some of the loop extremities is due to instrumental noise superimposed on a weak signal
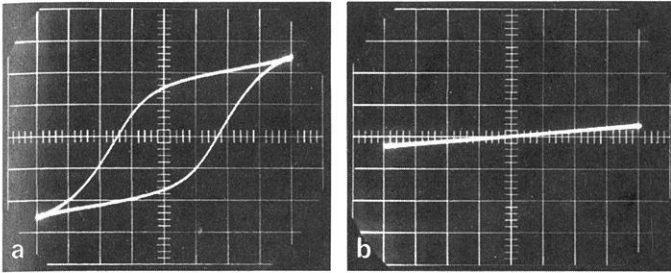
Fig. 5a and b. Medium-field (400 oe) hysteresis loops for a large disc of sample HU56-3. (a) is at 25°C and (b) is at −196°C. Scale: X-axis, one small division = 20 oe; Y-axis, arbitrary

one another at 25° C (Fig. 4a and 4b), though both show a considerable increase in H_c at −196° C (Fig. 4c and d). The J_r/J_m value for HU56-3 is more than 0.5 at 25° C (Fig. 4a), which may imply a substantial contribution from magneto-crystalline and/or stress-induced anisotropy of the grains. To show this feature clearly, medium-field (400 oe) hysteresis loops, for which a larger sample and higher instrument sensitivity could be used, are given in Fig. 5. The J_r/J_m value is a little over 0.6 for this sample even in a field of 400 oe at 25° C (Fig. 5a). The sample has a coercive force of more than 700 oe at −196° C (Fig. 4c) and hence an observable hysteresis could not be excited in 400 oe (Fig. 5b); no minor loop is seen since the differential susceptibility is small even in low fields. On the other hand, J_r/J_m for HU74-003 is about 0.2 at 25° C (Fig. 4b) and 0.7 at −196° C (Fig. 4d) and the respective H_c values are 50 oe and 675 oe.

6. Criteria for Distinguishing SD Titanomagnetite From Hyperfine Magnetite

The characteristic features of HU74-003, namely a $k-T$ curve with spectacular 'Hopkinson' peak and a tail, a Rayleigh loop at 25° C, and having the high-field hysteresis parameters quoted above, are compatible with the presence of fine, predominantly superparamagnetic (SP) interacting particles (Radhakrishna-murty et al., 1971) that become stable SD on cooling to low temperatures. In a study of 46 basalt cores recovered by the Deep Sea Drilling Project (Leg 34) from the Nazca Plate (Deutsch and Pätzold, 1976) about two-thirds were found to have properties such as these, termed 'type 1', as did also a single core out of 46 available from DSDP Leg 37 in the North Atlantic (Murthy et al., 1976). In most of these type 1 samples, the $k-T$ and hysteresis parameters are virtually identical to those of HU74-003.

Although above 0° C the $k-T$ curves of HU56-3 are similar to those of HU74-003, the hysteresis properties are quite different. The properties of HU56-3 may be explained by postulating the presence of SD grains of composition like TM60, for in such a material the contribution to hysteresis properties from magnetocrystalline anisotropy (K_1, K_2), and especially from stress-induced anisotropy (K_σ), can exceed that due to uniaxial shape anisotropy of the grains

because of the low saturation intensity. For comparison, J_s decreases from 93 emu/g for magnetite to about 24 emu/g for TM60; the corresponding decrease of K_1 is slightly less, from -1.4×10^5 to about -0.4×10^5 erg/cm^3, whereas K_σ increases from about $+0.6 \times 10^5$ ergs/cm^3 for magnetite to about 2.2×10^5 ergs/cm^3 for TM60 (all values at 17° C, taken or extrapolated from Y. Syono, quoted by Nagata, 1965). Hence K_σ/J_s for TM60 is roughly 15 times as large as the same ratio for magnetite.

The above composition-dependent properties can explain the observed large values of J_r/J_m and H_c and the absence of a Rayleigh loop in sample HU56-3 if its composition were that of a high-Ti titanomagnetite. On the other hand, the observed hysteresis parameters are incompatible with a very-fine particle explanation based on magnetite, where one would expect to observe small hysteresis parameters and an open Rayleigh loop. It seems reasonable that the converse argument applies to sample HU74-003. Then the $k - T$ curve for HU56-3 above room temperature may be explained as being due to SD titanomagnetite particles, indicating a T_c of about 200° C which would correspond to a composition a little closer to magnetite than TM60. We can offer no clear explanation for the minima in k near $-150°$ C for sample HU56-3. Some changes have taken place on heating the two samples as revealed by comparing the heating and the cooling curves. HU56-3 showed a thin Rayleigh loop after cooling, which can be attributed to some 'SP' particle formation. The susceptibility of both samples had increased after cooling, but the $k - T$ curves corresponding to their virgin and heated states are similar in trend.

These results suggest two criteria for distinguishing stable-SD titanomagnetite from extremely fine-grained ('SP'-sized) magnetite in rocks where in either case the true or apparent Curie point is less than that of magnetite. *Criterion 1:* At a temperature just below the blocking temperature range as indicated for example by $k - T$ curves, the sample probably is an SD titanomagnetite if hysteresis experiments show that J_r/J_s is large (≥ 0.5) and the coercive force also is large (several hundred oersteds). *Criterion 2:* SD titanomagnetite, like SD magnetite, does not show low-field hysteresis (a Rayleigh loop). Conversely, magnetite (or TM) in a predominantly SP state is indicated if the high-field hysteresis is small (Criterion 1) and if a Rayleigh loop is observed (Criterion 2). Let us now re-formulate the two criteria proposed earlier. *Criterion 3:* A sample is MD titanomagnetite rather than MD magnetite if its $k - T$ characteristics are of 'multi-domain' type and T_c is less than for magnetite. *Criterion 4:* MD titanomagnetite is indicated if the isotropic point, as shown for example in $k - T$ curves, differs from that of magnetite. Conversely, a sample having multi-domain characteristics is magnetite rather than titanomagnetite if its Curie point is close to 578°C (Criterion 3) and its isotropic point is close to $-155°$ C (Criterion 4).

According to Ade-Hall, Johnson and Ryall (1976) most of the DSDP Leg34 samples identified as 'type 1' by Deutsch and Pätzold (1976) contain magnetic grains of composition around TM60, a deduction based on $J_s - T$ curves and chemical analysis of the magnetic grains using the electron microprobe. However, Ade-Hall, Johnson and Ryall (1976) designated some samples as TM's and others as TMhs using the Ozima, Ozima and Kaneoka reversibility criterion.

They also report that a sharply defined T_c was absent even though a nitrogen atmosphere was used for getting the $J_s - T$ curves for the samples. This was also generally observed from $M - T$ curves obtained in air by Deutsch and Pätzold (1976). Ade-Hall et al. (1976) further found a factor of 20 variation in k values when they expected a factor of three among the samples on the basis of grain-size effects and mineral abundance. For all the observed discrepancies cation-deficiency of the TMs, attributed to low-temperature oxidation, was proposed as the main reason.

It should be noted, however, that discussions involving cation-deficiency in the deep-sea basalts, whether of low- or high-temperature origin, are relevant only to samples having T_c values generally above 175°–225° C (Johnson and Hall, 1978). For example, in the study of DSDP Leg 37 basalts (Table 1), all but two of the samples exhibited 'type 2' behaviour attributed to single-domain particles of magnetite or titanomagnetite, which in some cases appeared to be moderately to strongly cation-deficient ('type 2b'; Murthy et al., 1976). On the other hand, the 'type 1' basalts forming the majority of samples in the Nazca Plate study (Leg 34, Table 1) yielded T_c values exclusively below 200° C, along with more or less reversible $k - T$ and $M - T$ curves (Deutsch and Pätzold, 1976). This agrees with thermomagnetic results for other Nazca Plate samples of composition close to TM60 (Ade-Hall et al., 1976; Johnson and Hall, 1978). In each case the carrier is an unoxidized spinel of stoichiometric titanomagnetite (Johnson and Hall, 1978) or magnetite (Deutsch and Pätzold, 1976). Hence, in the type 1 basalts at least, there are no considerations of serious cation-deficiency to complicate the interpretation here presented: namely that low observed T_c values may represent a grain-size effect in hyperfine magnetite, as distinct from a 'true' Curie point in titanomagnetite.

7. Discussion

The main points of observation may be summarized as follows:

(i) Although chemical compositions close to high-Ti titanomagnetite (e.g., TM60) commonly occur in basalts, the magnetic properties vary widely even between samples of similar composition.

(ii) Magnetic behaviour that could be attributed to large MD grains of true titanomagnetite has not been found among the samples so far studied by us.

(iii) Only one sample (HU56-3), from a submarine pillow basalt less than 30,000 years old, has been shown to have properties expected of TM60-like material.

(iv) Many marine basalt samples show the magnetic behaviour attributable to fine single-domain including SP particles, and this feature has been observed even when the physical grain-size of the iron oxide minerals was large enough to form multi-domains.

(v) Samples with sharply indicated Curie points are uncommon, except in some old basalts containing MD magnetite.

The above points seem to suggest that some mechanism or mechanisms operated on the grains of previously TM60-like material in the marine basalts which fundamentally altered their magnetic behaviour. One possible way of explaining the above features is to hypothesize the formation of homogeneous grains of TM60 when the lavas were extruded, and subsequent subdivision into SD and SP particle sizes insofar as the magnetic behaviour is concerned. If the TMs are unstable, time alone can change their magnetic behaviour, with other physical and/or chemical processes speeding up the alteration. Since, in this presumed subdivided condition, our observations indicate mostly properties attributable to pure or nearly pure magnetite, it may be postulated that most of the titanium is able to exsolve submicroscopically in some form or other from the original TM, given enough time. What we regard as single-domain behaviour due to TM could be inferred in only one sample less than 30,000 years old, compared with 93 other marine basalts (HU74-003 plus 46 samples each from Legs 34 and 37), all but one of which are also of single-domain nature but are much older (3 to 20 m.y.). Therefore it is possible that the compositional stability of true titanomagnetites may be limited to time periods of less than a million years. For the present this hypothesis must remain somewhat speculative.

The lack of observed cases of multi-domain TM may imply that, even if large titanomagnetite grains had been common at the time the basalts originated, they were not homogeneous enough in terms of their magnetism to show MD behaviour, probably because of defects, strains or impurities in the grains.

Alternatively, if one considers that all cases of a sharp drop in $J_s - T$ or $k - T$ curves represent an approach to the true Curie point of a TM phase, then the different hysteresis properties found for such samples may have to be attributed to some unknown magnetic properties of these phases. Although the isotropic points of all the members of the TM series are not yet known, from the few available it seems reasonable to assume (e.g. data by Syono and Ishikawa, 1964) that transition points exist up to TM60 or TM70. Since maghemite has no low-temperature transition like that of magnetite, it may not be unreasonable to assume TMhs also to be without transitions. As for highly-cation-deficient titanomagnetites, they may have peculiar magnetic properties like those reported for cation-deficient magnetite (Radhakrishnamurty et al., 1971). However, most of the marine basalts studied by Deutsch and Pätzold (1976) and Murthy et al. (1976) indirectly showed low-temperature transitions in terms of an increase in H_c and J_r/J_m values at $-196°$C compared to their respective values at $20°$ C; it is therefore difficult to see how they could be strongly cation-deficient TM as was deduced by Johnson and Hall (1978).

Finally, it might be argued that the presence, typical in oceanic basalts, of minor cation impurities (Al, Mg, Mn) in titanomagnetite may have affected the magnetic properties of our samples sufficiently to cause a misdiagnosis of the domain state. By this argument, the presence of such impurities in multi-domain grains conceivably could have suppressed the isotropic peak seen otherwise in the $k - T$ curves of 'pure' samples; then, assuming that some samples identified by us as single-domained actually have an MD structure, this could explain our failure to identify such MD's. This possibility is difficult to assess, in view of the nearly complete absence of relevant

experimental data. The effect of minor cations on the isotropic points of titanomagnetite such as TM60 does not appear to have been studied, as distinct from their effect on other magnetic properties of sea-floor basalts (Petersen et al., 1979). A total $Al + Mg + Mn$ contribution of about 2% by weight in TM60 is characteristic, for example in Nazca Plate basalts (Bunch and Laborde, 1976), which applies to the samples measured by Deutsch and Pätzold (1976). As we have pointed out, however, most of these samples do show indirectly the low-temperature transition in (titano) magnetite, and we argue therefore that the presence of the minor impurities is unlikely to have had a critical effect on those magnetic properties measured by us that relate to domain structure.

Unfortunately, the hysteresis properties of TMs and TMhs have not been studied and recorded systematically by workers who synthesised them for comparison with the properties of marine basalts. Nevertheless, to ignore the hysteresis and susceptibility properties of basalts, especially when they strongly indicate the presence of SP and/or SD particles, in preference to the results of optical and chemical studies, may lead to error in inferring their magnetic state.

In support of the view that even large ferromagnetic grains may be effectively subdivided in terms of their magnetic properties, Jacobs and Bean (1963) recorded: '... an interesting example has been recently described in a mixed cobalt-zinc ferrite by Booth and Crangle (1962). Superparamagnetic behaviour was observed despite the fact that the material was in bulk, essentially single phase, polycrystalline form'. Thus it seems reasonable to propose that magnetic behaviour expected from effective SD/SP particles occurs in apparently large magnetite or titanomagnetite grains in marine basalts, which could then account for the observed magnetic properties of the iron oxide grains.

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