The Magnetic Balance and Its Application to Studying the Magnetic Mineralogy of Igneous Rocks

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A magnetic balance operating between \(-196^\circ\text{C}\) and \(800^\circ\text{C}\) with magnetic fields up to \(1.2\ \text{MA m}^{-1}\) is described. The typical noise level of the instrument corresponds to a sample dipole moment of \(1.6 \times 10^{-7}\ \text{Am}^2\) (the moment of \(1.7\ \mu\text{g}\) of magnetite magnetized to saturation at room temperature or about \(200\ \mu\text{g}\) of typical basaltic rock). Small samples may be used which leads to consistency between the calibration figure for both ferrimagnetic and paramagnetic minerals coexisting in the same sample and also allows rapid temperature change. An important feature is a programmable temperature-time regime. Above room temperature heating rates between \(2^\circ\text{/min}\) and \(100^\circ\text{/min}\) can be selected, and the influence that heating rate can have on the form of the thermomagnetic curve is demonstrated.

The magnetic balance operating in high field is the principal instrument for Curie point temperature determination. However, the balance has much wider application than this one task. The balance is a powerful tool in magnetochemistry or in monitoring temperature-induced structural transformations. We present here results which, for the first time, show the temperature dependence of the inversion process by which the cation-deficient magnetic minerals in submarine basalts transform to other magnetic phases. It may be that inversion proceeds at a slow rate under submarine conditions. Such inversion, which is accompanied by a change in saturation magnetization and grain size, will inevitably affect the intensity of remanent magnetization and magnetic susceptibility of the submarine crust.

1. Introduction

The remanent magnetization of rocks provides a means of studying the time dependence of the geomagnetic field and the motions of the crust of the Earth over geological time. Advancing technology allows progressively more rapid and effortless execution of those operations which constitute a palaeomagnetic study. The measurement of large numbers of rock samples is an effective strategy only when random errors are important. To confront the inevitable systematic error (i.e. the difference between a conceived model of a system and reality) experimental work is

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needed; in addition to being used as a message-carrying medium, the rocks must also be studied. A first step is to determine the composition of the constituent magnetic phases and to detect any change in the composition during the laboratory heating which attends palaeomagnetic and palaeointensity procedures. The microstructure of the magnetic medium has an equally important role in the magnetization process, and the concentration (or its change during heating) may also need to be determined. A summary of the dependence of the magnetic “observables” on composition, concentration and microstructure is given in Table 1.

It can be seen that all measurable observables depend on composition. Only thermomagnetic properties depend only on composition. These include Curie point temperature \( \left( T_\text{c} \right) \) and magnetic signatures which accompany heat-induced structural or chemical changes (e.g. inversion of cation deficient spinels, dehydration of hydrated minerals). The thermomagnetic observables concerned can only be measured unambiguously in high magnetic field. The temperature dependence of low-field susceptibility or remanence, which are microstructure-dependent magnetization process parameters, will not suffice. An instrument measuring the high-field magnetization over a wide temperature range is a crucial component of any study of the magnetic properties of rocks.

In this paper we describe the latest version of our high-field thermomagnetic balance and investigate the effect of heating rate on the form of the thermomagnetic

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<td>( T_\text{c} ), ( M_F/M_M ), other thermomagnetic signatures</td>
<td><strong>intensive properties</strong>—( T_\text{a} ), ( T_{\text{trans}} ), ( H_\text{c} ), ( H_{\text{cr}} ), ( H_\text{p} )</td>
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<td><strong>extensive properties</strong>, ( M_M ), ( \chi_{\text{HF}} )</td>
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The observables:

\( T_\text{a} \), Curie point temperature; \( M_F/M_M \) ratio of magnetization after and before thermomagnetic run; \( T_{\text{trans}} \), blocking temperature (e.g. the Morin transition); \( H_\text{c} \), coercive force; \( H_{\text{cr}} \), coercive force of remanence; \( H_\text{p} \), field for peak rotational hysteresis loss; \( M_M/M_M \), ratio of saturation remanence to saturation magnetization; \( Q \), Königsberger ratio \( (\chi H \text{ remanence}) \); \( M_M \), saturation magnetization; \( \chi_{\text{HF}} \), high field susceptibility; \( \chi_\circ \), initial susceptibility; \( W_{\text{cr}} \), peak rotational hysteresis loss; \( M_\ast \), saturation remanence; * remanences also depend on blocking condition.

**A system has microstructure by virtue of not filling the whole Universe with a perfect crystal structure.** The shape of the surface of the magnetic phase, the volume enclosed by the surface (including “internal” surfaces enclosing non-magnetic regions or voids) and the volume and shape of the space surrounding adjacent bodies, are included under the general heading of “microstructure” along with other crystal defects.
(M, T) curves of some igneous rocks. We also consider the contribution of the paramagnetic constituents (olivines, feldspars, etc.). The thermomagnetic behaviour of the ferrimagnetic phases may be obscured if such contributions are not removed.

In further experiments to illustrate the wide applicability of the instrument, oceanic basalts are held at isotherms and M, t curves produced. This allows the study of the kinetics of the inversion of titanomagnetics and contributes to an understanding of the role of this process in the magnetization of the oceanic crust.

2. The Thermomagnetic Balance (Figure 1)

The principal new features of the balance compared to earlier versions (e.g. CREER and DE SA, 1970) are an improved displacement transducer and a microcomputer controlled temperature-time regime. Previously we have used a (non-linear) capacitative displacement sensor. This has been replaced by a commercially available linear variable displacement transformer.

2.1 The detection of displacement and the automatic restoring system

A horizontal beam suspended by a 4-wire semi-kinematic system is free to move along the x-axis. The beam carries a quartz sample holder which is positioned between the poles of a 7" Newport electromagnet. Shaped pole pieces produce a uniform product H_y(dH_y/dx) (the y-axis passes through the centre of the poles and

Fig. 1. Schematic block diagram of the thermomagnetic balance. A detailed description is given in the text (Section 2).
the x-axis is the horizontal axis along which the sample is free to move; \( H_y \) is the component of the electromagnet field in the y-direction. The sample experiences a force \( F_x = \mu_0 m_y \left( \frac{dH_y}{dx} \right) \) where \( m_y \) is the y-component of the dipole moment of the sample; \( m_x \) and \( m_z \) are ideally zero in the symmetry of the system. The beam is, therefore, displaced in the x-direction when the electromagnet is energized.

The beam is automatically restored to its zero position by a second order closed loop feedback mechanism (e.g. DE SA and WIDDOWSON, 1974). The position of the beam is sensed by a linear variable displacement transformer (Sangamo controls type DF/5/S) which has its slug attached to the beam. The transducer provides the error signal which passes via a voltage amplifier, with a lead-lag compensation network for stabilizing the feedback loop, and power amplifier to two pairs of gradient coils. Two identical permanent magnets are fixed to the beam and lie along the axes of the gradient coils. The magnets are orientated back-to-back ensuring that a force is not exerted by the field gradient of the nearby electromagnet. The gradient coils carry current in the appropriate sense to provide the restoring force. A metering resistance \( R \) in series with the coils produces the voltage analogue of the sample magnetic moment. The response time of 0.25 s allows the balance to record rapidly changing magnetic moments in the vicinity of the Curie point.

2.2 Temperature control and the sample environment

A cylindrical 600 W furnace (Fig. 1) enclosed in a water jacket raises the sample temperature to a working maximum of 800°C. The temperature of the sample is sensed by a thermocouple. The furnace receives power via a temperature controller (Eurotherm 810) which has the facility for external control and, in a standard run, is driven by an externally generated voltage-time ramp. A motorola MC 68705P microprocessor with 1.8 kbytes of EPROM and 112 bytes of RAM is used to generate the voltage ramp via a D/A converter. The slope and duration of the ramp are programmed by means of a keypad. A typical slope is 0.125 V min\(^{-1}\), giving a heating or cooling rate of 20°C min\(^{-1}\) to and from a programmed maximum temperature.

There is no provision for evacuating the sample environment within the furnace. This would involve a vacuum chamber large enough to enclose the suspension system, with no guarantee that the oxygen pressure in equilibrium with the composition of the sample was achieved at all temperatures. The preferred system adopted here is to use, as sample holder, an evacuated quartz ampoule (at pressure 10\(^{-4}\) T). Thus the sample is self-buffering. This does not necessarily prevent oxidation of the magnetic fraction of a rock sample which contains water or other volatiles. Nor, of course, does it prevent a structural change such as inversion (Subsection 3.2) taking place.

For measurements below room temperature the water jacket is drained and refilled with liquid nitrogen. Measurements are best obtained during a warming cycle when the furnace element is employed to accelerate and control the heating rate.

2.3 Calibration and performance

During the runs the field at the centre of the electromagnet gap is maintained at chosen constant values up to 1.2 MA m\(^{-1}\) by a current regulated power supply (2
Farnell H60/50 units in series). The profile of the field $H$, as a function of position $x$, the gradient of the field $dH_y/dx$, and the product $H_y(dH_y/dx)$ can be determined by, respectively a Hall effect probe, a readily saturated ferromagnetic sample and a paramagnetic sample. Operating points can then be chosen suitable for the materials to be investigated. At the standard operating position chosen for measuring igneous rock samples (34.5 mm from the pole piece apexes) a maximum field of 0.8 MAm$^{-1}$ with a gradient of 11 MAm$^{-2}$ is experienced by the sample and the balance sensitivity is $(1.28 \pm 0.03) \times 10^5$ V A$^{-1}$m$^{-2}$. The typical noise level of $\pm 2$ mV corresponds to a sample dipole moment of $\pm 1.6 \times 10^{-5}$ Am$^2$ (the moment of 1.7 $\mu$g of magnetite magnetized to saturation at room temperature, or about 200 $\mu$g of typical sea-floor basalt). Signal to noise ratios of the order of $10^3$ are, therefore, readily realized, and the small size of the samples used ensures that the same calibration figure obtains for both the paramagnetic constituent (which requires $H_y$, $dH_y/dx$ constant) and ferromagnetic constituents (which requires a constant $dH_y/dx$) of a sample, and that a near constant temperature over the sample and adjacent thermocouple junction is achievable with conveniently fast heating and cooling rates. The thermal mass of the thermocouple is adjusted empirically to match that of the sample holder and typical sample by setting the position of the ceramic sleaving around the thermocouple.

An example of a thermomagnetic run between liquid nitrogen temperature and 750$^\circ$C heated at 20$^\circ$C min$^{-1}$ is shown in Fig. 2. The sample is a composite containing

![Fig. 2. Thermomagnetic curve between $-196^\circ$C and 750$^\circ$C, at a heating rate of 20$^\circ$C mm$^{-1}$, of a composite sample containing 6 titanomagnetites of different Curie point temperatures ranging from $-150^\circ$C to 580$^\circ$C.](image-url)
synthetic Fe₂TiO₄ (Curie point temperature $T_c \sim -150^\circ$C), Fe$_{2.2}$Ti$_{0.8}$O$_4$ ($T_c \sim 0^\circ$C), Fe$_{2.4}$Ti$_{0.6}$O$_4$ ($T_c \sim 200^\circ$C), Fe$_{2.6}$Ti$_{0.4}$O$_4$ ($T_c \sim 340^\circ$C), Fe$_{2.8}$Ti$_{0.2}$O$_4$ ($T_c \sim 470^\circ$C) and Fe$_3$O$_4$ ($T_c \sim 580^\circ$C). An inflexion on the curve is evident at each of the six Curie points of the sample.

A general discussion of the design criteria of magnetic balances is provided by COLLINSON (1983).

3. Measurements with the Balance

3.1 The effect of heating rate

Compositional and structural changes may take place in magnetic minerals when heated above room temperature. When the progress of such changes is linearly related to the observed saturation magnetization at the measuring temperature, the thermomagnetic balance becomes a powerful magneto-chemical tool, e.g. for the study of inversion (Subsection 3.2). In seeking the composition of the magnetic mineral in rocks, a simple Curie point temperature does not define a unique composition, and the information contained in the thermomagnetic run as a whole should be valuable.

A basic requirement of palaeomagnetic and palaeointensity work is to suppress chemical changes taking place on heating. The magnetic balance provides the means by which the conditions necessary to suppress the change may be sought. In chemical applications the form of the thermomagnetic curves depends on the interplay of the balance heating and cooling rates, the $M_s$-$T$ curves of the magnetic phases and the reaction or transformation rates at each temperature. Close control of the balance heating and cooling rates is necessary to pursue a systematic study of a particular chemical problem. Figure 3 illustrates the variation in form of a thermomagnetic curve which may be found. Here three samples from a DSDP Leg 73 minicore (522B-5-2, 30) (Housden et al., 1984) sealed in evacuated capsules (at a pressure $10^{-4}$ Torr) are heated at different rates—at 2°C/minute, 20°C/minute and 100°C/minute. The forms of the three curves are quite different although the inferred Curie point temperatures on the lower part of the heating runs are the same. It is not our intention to discuss at this point the processes underlying this different thermomagnetic behaviour but to show the need for a flexible and reproducible programmable temperature-time regime in thermomagnetic analysis.

3.2 Isothermal runs—a study of inversion kinetics

During inversion a cation deficient titanomaghemite with spinel structure irreversibly transforms without change in chemical composition to a more compact structure; the simplest example is the transformation of $\gamma$Fe$_2$O$_3$ (maghemite) to $\alpha$Fe$_2$O$_3$ (haematite). The observation of inversion as a magnetic signal during thermomagnetic runs on basalts from the submarine basement has been widely used to show that maghemitization is a widespread submarine alteration process (e.g. Ozima et al. (1968) and many subsequent studies by several authors). Inversion presumably also takes place in nature as well as in the laboratory if the temperature
Fig. 3. Thermomagnetic curves of vacuum-encapsulated samples of a DSDP basalt heated at (a) 2°C/min, (b) 20°C/min and (c) at 100°C/min. The forms of the three curves are quite different and depend on the heating rate employed.

and pressure (KUSHIRO, 1960) are high enough. Early studies of the laboratory inversion of titanomaghemites in basalts are described by WASILEWSKI (1968) and OZIMA and LARSON (1968), and work on synthetic titanomaghemite by READMAN and O'REILLY (1970). A recent study of the inversion of synthetics may be found in ÖZDEMIR (1987). During laboratory experiments inversion temperatures commonly lie in the range 300–400°C at atmospheric pressure. In nature, ample time may be available for the inversion of the metastable titanomaghemite to a stable assemblage at lower temperatures. Beneath the oceans, hydrostatic pressure may well also accelerate the process.
DSDP Leg 73 minicore 522B-5-2, 20 was employed as the medium in which to study the kinetics of inversion. Encapsulated samples were rapidly heated (at 100°C/min) to isotherms (300, 360 and 410°C) and the magnetization measured as a function of time (Fig. 4). To avoid overshoot the temperature controller slows the rate of temperature rise as the set temperature is approached. Thus the times taken to reach the isotherms were about 3, 4 and 4.5 min respectively. This means that inversion starts before the isotherm is reached (Fig. 4).

To convert the measured magnetization into a fraction of reaction ($y$), the inversion is supposed as a direct transformation of an initial phase to a product phase without intermediate compositions. Thus at the isotherm the magnetization, $M$, is taken to vary linearly with the fraction of reaction. At the beginning of the reaction ($y=0$) $M = M_i$, and when the reaction is complete ($y=1$) $M = M_F$. Then $y = (M - M_i) / (M_F - M_i)$. $M_F$ and $M_i$ were determined from a straight thermomagnetic run, $M_F$ on the assumption that inversion had progressed to completion after heating to 600°C. This is suggested by the repeatability of the thermomagnetic curve after heating to 600°C had been accomplished. In the case of synthetic titanomaghemites, oxidation of encapsulated material is negligible in laboratory time. However, the magnetic phase in rock samples is not necessarily self-buffering when the rock contains volatiles. To reduce any unwanted chemical alteration to a minimum the run was carried out at a heating and cooling rate of 100°C/min to minimise the effect of any oxidation which might take place in the basalt sample. The resultant thermomagnetic curve is shown in Fig. 5. The normalized values of $M_F$ at the three isotherms are

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**Fig. 4.** Thermomagnetic analysis of vacuum encapsulated DSDP basalt, each sample heated at 100°C/min to an isotherm (300, 360 and 410°C) at which it is held for two hours. The crosses mark the points at which inversion would be complete after a long enough time, these points being inferred from the straight run to high temperature shown in Fig. 5.
The Magnetic Balance and Its Application

Fig. 5. The $M_f$-$T$ curve for the DSDP basalt of Fig. 4 heated at 100°C/min to 600°C and cooled at the same rate. It is assumed that the cooling curve corresponds to a completely inverted sample. The initial magnetizations ($M_i$) at the three isotherms are given by the intersections of the vertical dashed lines and the heating curve; the final magnetizations ($M_f$) by the intersections of the vertical dashed lines and the cooling curve. Note that Fig. 3(c) is the $M_r$-$T$ curve for the whole rock whereas the data of the heating curve of this Figure has the paramagnetic fraction removed (see Subsection 3.3).

indicated. We note that $M_f/M_i$ at room temperature is 5.6, the Curie point temperature of the titanomaghemite is 355°C and that of the inversion product 555°C. The data of Fig. 5 correspond only to the ferromagnetic fraction in the basalt; the inferred contribution to the high field magnetization of the paramagnetic fraction has been removed (Subsection 3.3).

The inferred progress of the transformation expressed as $y$, the fraction of reaction, against elapsed time at the set temperatures is shown in Fig. 6. The zero of
The progress of inversion of titanomaghemite in the DSDP basalts expressed as a fraction of reaction plotted against the elapsed time at the three isotherms. The inference is that the transformation would take place at ambient temperatures at a (presently unknown) slow rate.

The curves for the higher temperatures has been obscured by the onset of the transformation before the time zero at the isotherm. This prevents an adequate close fit of the data to model rate equations. Therefore, a usefully accurate analysis of the reaction kinetics can not be made using the present data. However, it is clear that the rate of transformation is temperature dependent, and the conclusion is that inversion will take place at an unknown slow rate at ambient temperatures in the submarine basement provided there is no threshold temperature below which the cation deficient structure is stable. The inversion may have profound effects for the magnetism of the Earth’s crust as both the composition and microstructure of the magnetic phase will be changed. Further experiments are planned using the balance to produce data in which the systematic errors are reduced so that models can be used to quantitatively interpret the experiment. The reason for presenting these presently inconclusive results is again to show the power of the developed thermomagnetic balance as a tool to study the materials which can potentially reveal so much information about the history of the Earth.

3.3 The contribution of paramagnetic minerals to thermomagnetic curves

The importance of the contribution of paramagnetic minerals to thermomagnetic curves depends on the relative concentrations of the paramagnetic and ferromagnetic fractions and on the composition of the latter. In magnetically dilute rocks such as sediments, and even some igneous rocks, the information about the ferromagnetic fraction contained in the thermomagnetic curve is obscured.

An example of such a rock is the allivalite of the Central Layered Intrusion, Isle of Rhum, Scotland, the thermomagnetic curve of which is shown in Fig. 7(a). Above
the Curie point of the magnetic fraction, the magnetic moment in the presence of the field is still large at about 30% of the moment at room temperature. This high temperature moment is almost entirely due to non-ferromagnetic iron-bearing minerals. Analysis of the room temperature hysteresis loop determined using a vibrating sample magnetometer (VSM) (e.g. COLLINSON, 1983) suggests that the allivalite contains 0.01% of magnetite whereas 4% by weight consists of iron in the non-ferromagnetic state. This latter deduction is based on a high field magnetic susceptibility of $1.29 \times 10^{-7} \text{ m}^3 \text{ kg}^{-1}$, measured in fields higher than that required to saturate the magnetite. The composition of the magnetic phase is established in a detailed magneto-petrological study of the Central Layered Intrusion (HOUSDEN, 1986).

The susceptibility of magnetically disordered materials follows the law $\chi = C/(T+\theta)$, where the asymptotic Curie temperature, $\theta$, may be negative or positive. For paramagnetic minerals $\theta$ may be as high as several tens of degrees. In the case of the ferromagnesian olivines, $\text{Fe}_{2x}\text{Mg}_{2-2x}\text{SiO}_4$ ($0 < x < 1$), $\theta = -87x$ K approximately (HOYE and O'REILLY, 1972). For the Rhum allivalite the two unknowns $C$ and $\theta$ are determined from the room temperature susceptibility (via the VSM) and 600°C susceptibility (via the balance) ($=0.42 \times 10^{-7} \text{ m}^3 \text{ kg}^{-1}$). The results are $\theta = -27$ K and $C = 1.77 \times 10^4 \text{ m}^3 \text{ kg}^{-1}$ K. The curve for the moment of the paramagnetic fraction in field applied during the thermomagnetic run is computed (the smooth curve in Fig. 7(a)) and subtracted from the measured moment to reveal the thermomagnetic curve of the ferromagnetic fraction alone (Fig. 7(b)). After removal of the paramagnetic...
contribution the form of the ferromagnetic $M_s-T$ curve is revealed and the Curie point temperature more sharply defined.

We note in passing that the coercive force of the magnetic mineral in a rock such as the allivalite can also be accurately determined only by subtracting the paramagnetic contribution from the hysteresis loop of the bulk rock.

4. Conclusions

The magnetic balance has been the principal instrument for the measurement of Curie point temperature which, if determined via the magnetization process, can only be easily defined in high magnetic fields. The magnetic balance has a much wider application than this single task and provides a powerful and, in its developed form, a versatile means for studying many aspects of the magnetism of materials. For such applications a controllable and reproducible temperature-time regime may be essential. This is especially so in magnetochemical problems with temperature dependent reaction rates.

We have illustrated the usefulness of the magnetic balance in monitoring the process of inversion by which metastable nonstoichiometric magnetic phases transform without bulk chemical change into other phases. The results described of experiments on submarine basalts may have important implications for the magnetism of the submarine crust. Processes which take place on the geological time scale can, of course, never be observed under the same conditions in the laboratory. It is always necessary to extrapolate from the laboratory conditions to the conditions believed to obtain in nature. If there is no threshold temperature between the temperature of our laboratory experiments and the temperature of the submarine basement, such an extrapolation suggests that the process will operate at an, as yet undetermined, slow rate under submarine conditions.

In the case of magnetically dilute materials, the definition of the Curie point temperature and other features of the thermomagnetic curve can be greatly enhanced by correction for the contribution, to the high field moment of the sample, of the paramagnetic phases coexisting with the ferromagnetic material.

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