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A technique for the measurement of thermal changes of magnetic susceptibility of weakly magnetic rocks by the CS-2 apparatus and KLY-2 Kappabridge

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SUMMARY

Techniques for the correction of the effect of the furnace signal on the data measured in the investigation of thermal changes of magnetic susceptibility of weakly magnetic rocks using the CS-2 apparatus and KLY-2 Kappabridge are described. A new method is developed for separating the ferromagnetic and paramagnetic room temperature susceptibility components even for the case in which new magnetite forms during heating.

Key words: magnetic susceptibility, temperature variation.

INTRODUCTION

In palaeomagnetism and magnetic anisotropy investigations a knowledge of carriers of magnetism in the rocks investigated is very important for reliable quantitative interpretation. Techniques for the investigation of magnetic minerals are variable, ranging from mineralogical and petrographic to special rock magnetic methods. Of the later methods, the investigation of thermal changes of magnetic susceptibility (for example, using specially adapted induction bridges, see Stephenson & de Sa 1970; Parma & Zapletal 1991; Parma *et al.* 1993) is very important.

The purpose of the present paper is to develop a technique for the measurement of thermal changes of the susceptibility of weakly magnetic rocks, in which the magnetic signal from the measured specimen is comparable with that of the furnace. This development is orientated towards the CS-2 apparatus (Parma & Zapletal 1991; Parma *et al.* 1993) which, in cooperation with the KLY-2 Kappabridge (Jelínek 1973, 1980), enables the thermal changes of magnetic susceptibility to be investigated with outstanding sensitivity and accuracy.

PRINCIPLE OF THE CS-2 APPARATUS

The CS-2 apparatus is designed for the measurement, in cooperation with the KLY-2 Kappabridge, of thermal changes of low-field magnetic susceptibility of minerals, rocks and synthetic materials. It consists of a non-magnetic furnace and electronic control unit. The specimen measured (mostly powdered), 0.3–0.5 cm^3 in volume, is heated by a Pt winding and its temperature is measured by a Pt–PtRh thermocouple inserted into the specimen. The furnace is cooled by circulating distilled water. The measurement is made in air.

During the measurement process the furnace is moved automatically into and out of the pick-up coil of the KLY-2 Kappabridge. The susceptibility and temperature are measured after each insertion of the furnace and the bridge is zeroed after the furnace is pulled out of the measuring coil. The measurement process is fully automated, being controlled by a personal computer (via a RS 232 C serial channel). The temperature increase and decrease is automatically controlled according to a chosen régime which is set up before measurement, i.e. the maximum temperature, the rate of heating and cooling, and the time of sample annealing at maximum temperature. The result of the measurement is a thermomagnetic curve composed of many discrete susceptibility and temperature determinations; at a standard heating rate of 10 °C min^{-1} from room temperature up to 700 °C and back to room temperature the thermomagnetic curve contains between 500 and 600 pairs of susceptibility and temperature determinations.

CORRECTION FOR THE FURNACE

For strongly magnetic rocks whose magnetic signal is much stronger than that of the furnace, there are no problems with the data processing and the susceptibility values measured can be used directly in the interpretation. Unfortunately, if the signal from the rock specimen is comparable with, or even weaker than, that of the furnace, problems arise from the superposition of these signals.

The following analysis is made in terms of the total susceptibility (introduced by Jelínek 1977), which is more convenient for this purpose than bulk suceptibility, because it provides information about the magnetic signal regardless of the actual volume of the specimen measured. The total susceptibility is the entity given by the measuring instrument regardless of the actual volume of the specimen and is defined as follows:

$$k_T = (V/V_0)k_B, \quad (1)$$

where k_T is the total susceptibility, k_B is the bulk susceptibility, V is the actual volume of the specimen and V_0 is the nominal volume of the specimen (in the case of the KLY-2 Kappabridge with a standard pick up unit $V_o = 10\,cm^3$).

The furnace (with sample holder) of the CS-2 apparatus has a total susceptibility of about -150×10^{-6} (SI) at room temperature. However, its susceptibility is temperature-dependent, showing complex behaviour (Fig. 1). The change in total susceptibility during heating to 700 °C is about 5×10^{-6}.

The volume of the specimen measured in the CS-2 apparatus is 0.3–0.5 cm^3. The signal from this small specimen is therefore more than 20 times weaker than that of a standard (10 cm^3) specimen. Since the bulk susceptibilities of the majority of natural rocks are probably less than 500×10^{-6} (see, for example, Hrouda 1982, 1993; Tarling & Hrouda 1993), which corresponds to the total susceptibilities of less than 25×10^{-6}, it is clear that the direct use of the CS-2 apparatus without correction for the furnace signal cannot give the correct results in these rocks, because their thermal change in total susceptibility is of the same order as the thermal change of total susceptibility of the furnace (5×10^{-6}).

In order to avoid these problems we have developed the following technique. Prior to measuring rock specimens the thermal variation in total susceptibility of the empty furnace is investigated (Fig. 1). Then, the curve of this variation is smoothed using the method of running means (from five points) and the smoothed data are stored in the form of a table. Subsequently, the thermal variation in total susceptibility of the furnace with the specimen is measured. The smoothed thermomagnetic curve of the empty furnace is then subtracted from the thermomagnetic curve of the specimen + furnace.

In this procedure one needs to know the accuracy in the determination of the smoothed empty furnace thermomagnetic curve and the reproducibility in the determination of this curve. In order to reveal them we investigated two furnaces from the first series of the CS-2 apparatus. Two curves of each of the furnaces investigated were measured on different days so that the effect of the absolute calibration error of the KLY-2 Kappabridge could also be evaluated. The results are presented in Fig. 1 showing two curves of the first furnace measured on different days; the curves are very similar to each other. The second furnace shows the same relationship.

To evaluate the mean deviation of the smoothed from the non-smoothed thermomagnetic curve, the following parameter is be used

$$S_s = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(k_{si} - k_{mi})^2}, \quad (2)$$

where k_{mi} is the ith point on the non-smoothed thermomagnetic curve, k_{si} is the corresponding point (at the same temperature) on the smoothed thermomagnetic curve and n is the number of points investigated. The means S_s for both the furnaces investigated are presented in Table 1 and the scatter of the points of the non-smoothed curve with respect to the smoothed curve is also illustrated in Fig. 1.

The reproducibility of the smoothed free furnace curves is evaluated by means of the parameter

$$S_r = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(k_{s1i} - k_{s2i})^2}, \quad (3)$$

where k_{s1i} is the ith susceptibility on the first thermomagnetic curve, k_{s2i} is the susceptibility on the second thermomagnetic curve for the same temperature (the susceptibilities for the same temperatures were obtained through linear interpolation of the neighbouring temperatures), and n is the number of points investigated on a curve. The results are also presented in Table 1.

In addition to the mean deviation of individual points on the first curve and second curve the mean offset of the whole curves (each from the other) is also evaluated as follows

$$S_0 = \frac{1}{n}\sum_{i=1}^{n}(k_{s1i} - k_{s2i}). \quad (4)$$

The results are presented in Table 1.

The S_s, S_r, and S_0 parameters are presented separately for heating curve, cooling curve and the entire curve in Table 1. It can be seen that the scatter of individual susceptibilities along the smoothed curve is very low, being of the order of 10^{-7} which is the measuring error of the KLY-2 Kappabridge on the second measuring range in which the empty furnaces were measured. This scatter is the lowest in the case of the heating curve and the highest in the case of the cooling curve.

The differences between two smoothed curves are also very low, about 2×10^{-7} and again they are the lowest in the heating curve and the highest in the cooling curve.

The offset of the whole curves is extremely low, of the order of 10^{-8} which indicates very good calibration of the KLY-2 Kappabridge in this particular case (much better than guaranteed by the manufacturer).

One can conclude that the errors arising from correction of the thermomagnetic curve of the specimen for the thermomagnetic curve of the empty furnace are probably less than 3×10^{-7} and the thermal changes of susceptibility higher than 5×10^{-7} can be interpreted as resulting from real susceptibility changes and not from measurement inaccuracy.

RESOLUTION OF FERROMAGNETIC AND PARAMAGNETIC COMPONENTS

The accuracy of the CS-2 apparatus and KLY-2 Kappabridge is so excellent that it enables very weakly magnetic rocks to be investigated also. However, as shown by Owens & Bamford (1976), Rochette (1987), Hrouda & Jelínek (1900) and Jover *et al.* (1989) among others, the magnetic susceptibility of weakly magnetic rocks can be affected considerably by the presence of paramagnetic minerals whose susceptibility is temperature-dependent according to the Curie law (see, for example, Nagata 1961)

$$k_p = C/T \quad (5)$$

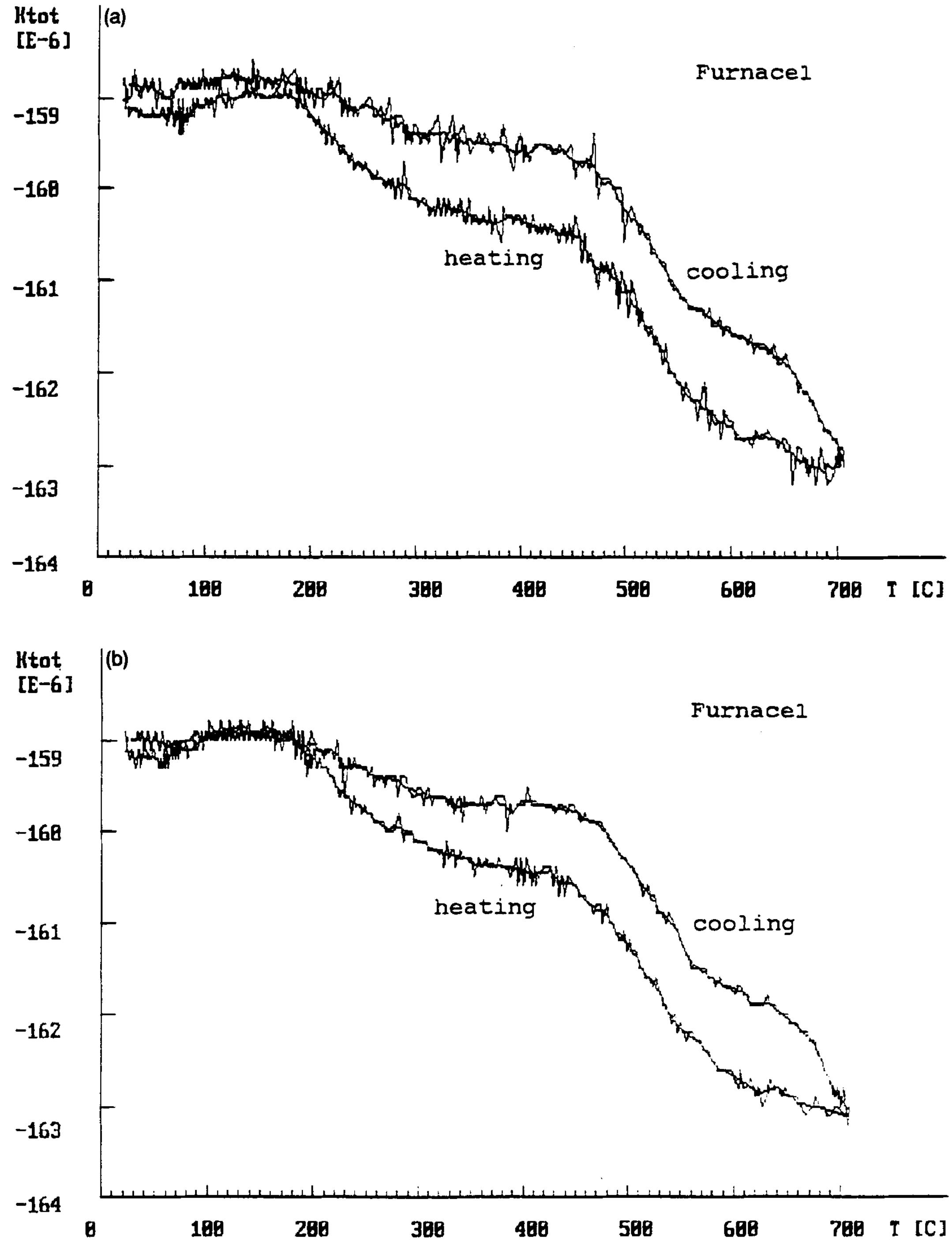


Figure 1. Thermomagnetic curves of the furnace without specimen of the CS-2 apparatus measured on different days. (a) First-day non-smoothed (high-frequency) and smoothed (from five-point running means) thermomagnetic curves. (b) Second-day non-smoothed and smoothed thermomagnetic curves.

where k_p is the paramagnetic susceptibility, C is constant depending on the chemical composition of the mineral and T is the absolute temperature (in Kelvin). The measured thermomagnetic curve of a weakly magnetic rock is composed of the above paramagnetic hyperbola and a complex thermomagnetic curve of ferromagnetic minerals

$$k_r = p_p C/T + p_f k_f, \tag{6}$$

where k_r is the rock susceptibility, p_p is the fraction of paramagnetic minerals in the rock, p_f is the fraction of ferromagnetic minerals, and k_f is the ferromagnetic susceptibility (being a complex function of the absolute temperature, T).

The investigation of various ferromagnetic minerals of variable grain size, made by Dr K. Zapletal and the present author, has shown that in the initial part of the thermomagnetic curve (for example, between room temperature and 200 °C), the susceptibility of ferromagnetic

Table 1. Accuracy of determination of thermomagnetic curves of the furnace without specimen.

Furnace	*Curve*	$S_s[10^{-6}]$	$S_r[10^{-6}]$	$S_o[10^{-6}]$
Furnace1	heating	0.10	0.06	-0.01
	cooling	0.17	0.15	-0.14
	entire	0.14	0.11	-0.07
Furnace2	heating	0.08	0.19	-0.14
	cooling	0.07	0.13	-0.04
	entire	0.08	0.16	-0.09

minerals is either roughly constant or represented by a straight line of very low slope. Eq. (6) then describes a hyperbola offset along the susceptibility axis. If one fits the hyperbola to the initial part of a thermomagnetic curve using the least-squares method, one can determine the constants p_pC and p_fk_f. From the constant p_pC and the absolute temperatures T one can calculate total paramagnetic susceptibility (p_pk_p) at any temperature. After determination of the paramagnetic susceptibility in the entire course of the thermomagnetic curve one can calculate the whole thermomagnetic curve of the ferromagnetic component

$$p_fk_f = k_r - p_pC/T. \quad (7)$$

As the error in the determination of p_pc and p_fk_f constants can be evaluated from the least-squares method, one can easily evaluate the validity of assumptions of eq. (6).

EXAMPLES OF USE

For practical use of the above method, the CUREVAL computer program has been written. Application of this to some weakly magnetic rocks is described. These rocks were heated in air with a standard heating rate of 10 °C min^{-1}.

Figure 2(a) shows the heating and cooling thermomagnetic curves of the specimen of amphibolite from the KTB superdeep borehole, drilled in the German part of the Bohemian Massif. It is clear from the figure that the heating curve has a hyperbolic shape in its initial part and shows a clear Hopkinson peak and Curie temperature in the vicinity of 600 °C indicating the presence of magnetite. The cooling curve shows a conspicuous increase in susceptibility in this temperature interval and much higher susceptibilities in general, indicating the probable creation of new magnetite at high temperatures. Fig. 2(b) shows the initial part of the heating curve, with fitted paramagnetic hyperbola and the results of the resolution for the paramagnetic and ferromagnetic room temperature susceptibilities. The $K_p = p_pk_p$ and $K_f = p_fk_f$ values indicate that it is the paramagnetic fraction that controls predominantly the room temperature susceptibility of this specimen. The low values of the S_p and S_f parameters indicate a high resolution. One can see that the deviations of individual susceptibility points from the fitted hyperbola are really small, indicating the validity of eq. (6) in this case. Fig. 2(c) shows the thermomagnetic curve of the ferromagnetic fraction calculated by the subtraction of the paramagnetic hyperbola shown in Fig. 2(b). This new curve represents the thermal changes of the magnetite only. Both the Hopkinson peak and Curie temperature are more pronounced than in the previous case.

Figure 3 shows thermomagnetic curves of the specimen of a weakly magnetic Devonian shale (bulk susceptibility being 255×10^{-6}) from the Appalachian Plateau, New York. One can see in Fig. 3(a) that the susceptibilities of the cooling curve are almost an order of magnitude higher than those of the heating curve; the heating curve contains extremely high elevation between 400 and 600 °C. This probably indicates intense formation of new magnetite during heating. Despite this, it is possible to resolve the contributions of the paramagnetic and ferromagnetic components (Fig. 3b) to the room temperature susceptibility with acceptable accuracy, if only the initial 200 °C interval is used to fit the paramagnetic hyperbola. Fig. 3(c) shows the separated heating ferromagnetic curve in which magnetite can be well identified; the susceptibility decrease near 700 °C may indicate haematite.

DISCUSSION

The KLY-2 Kappabridge was originally developed for measurement of anisotropy of magnetic susceptibility of rocks and, consequently, shows outstanding accuracy in the determination of relative susceptibility values, with the relative error being 0.1–0.2 per cent of the measured value. If the total susceptibility of the furnace without specimen is about -160×10^{-6}, then the error in the individual susceptibility determination is about $2\text{–}3 \times 10^{-7}$, which corresponds well to the values of the S_s parameter (deviation of the non-smoothed and smoothed thermomagnetic curves of the empty furnace) in Table 1.

However, the error in the absolute susceptibility determination (calibration error) is much higher, about 3 per cent (Jelínek 1980). In the correction of the measured thermomagnetic curve for the susceptibility of the empty furnace one works with absolute susceptibility values and theoretically can introduce errors as high as 5×10^{-6}. This calibration error cannot be illustrated by the repeated measurements of the empty furnace presented in Table 1 where the S_0 parameter values are an order of magnitude lower, indicating outstanding stability of the KLY-2 Kappabridge in this particular case. The calibration error can in some cases give rise to paradoxically negative values of the correted susceptibility values, which have nothing to do with diamagnetism. Consequently, if one wishes to do the above correction as precisely as possible, it is

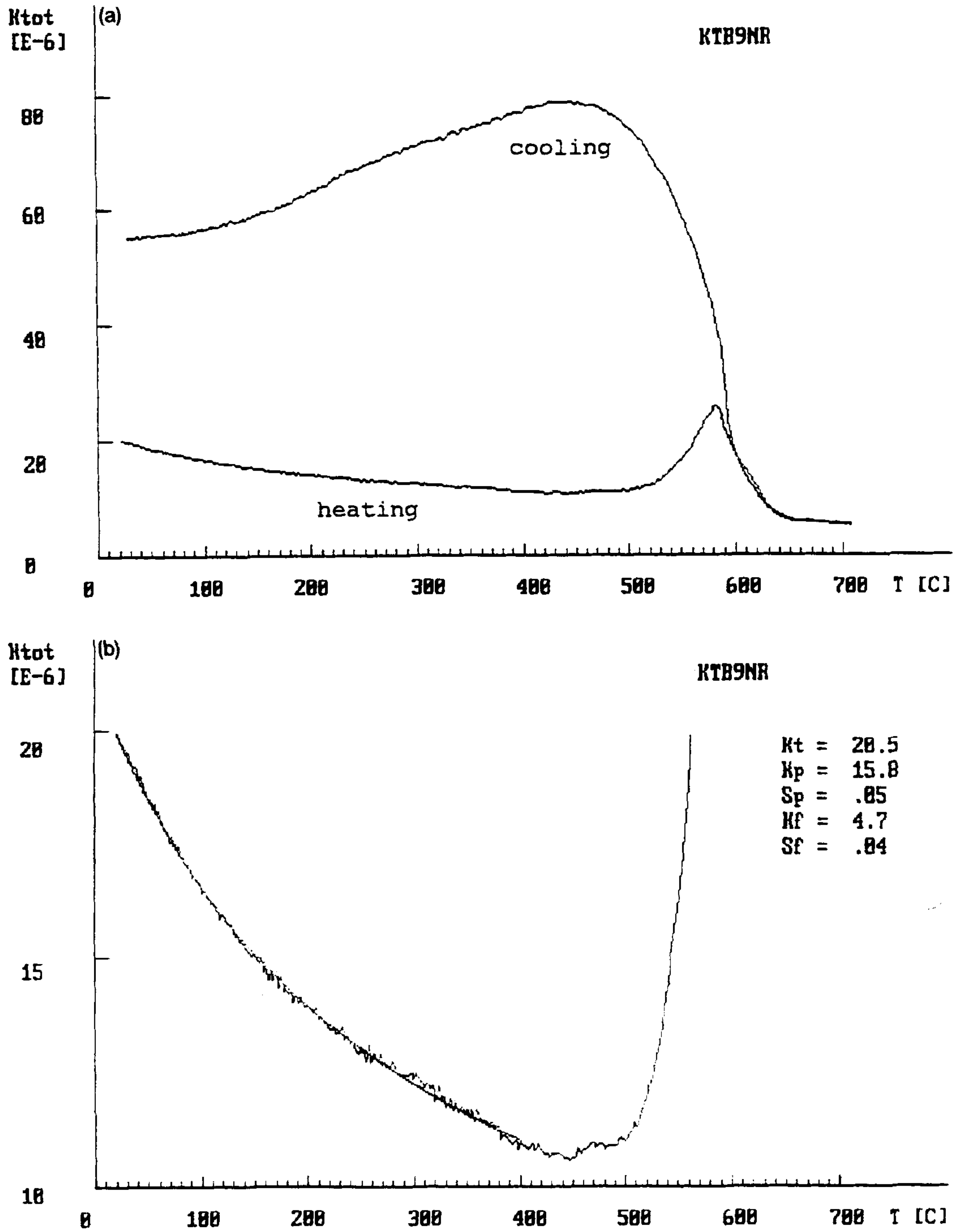


Figure 2. Thermomagnetic curves of the specimen of amphibolite from the KTB borehole, Germany. (a) Heating and cooling thermomagnetic curves corrected for empty furnace. (b) Initial part of heating thermomagnetic curve, with drawn paramagnetic hyperbola (20–400 °C). (c) Heating thermomagnetic curve of the ferromagnetic component only (after subtraction of paramagnetic susceptibility).

recommended that the thermomagnetic curve of the empty furnace and that of the furnace with specimen be measured the same day, without switching off the bridge, in order to profit from the outstanding accuracy in relative susceptibility determination.

The resolution of the room temperature rock susceptibility into its ferromagnetic and paramagnetic components is very important in studies of the anisotropy of magnetic susceptibility, because the ferromagnetic and paramagnetic minerals show different behaviours in various geological situations (for example, see Hrouda 1982; Tarling & Hrouda 1993). The resolution made by the CUREVAL program is based on the assumption that the ferromagnetic susceptibility (k_f in eq. 6) is more or less independent of temperature in the initial part of a thermomagnetic curve. As this is not necessarily true in general, one needs to test whether the above assumption is valid in each particular case. For this purpose, it is recommended to do the

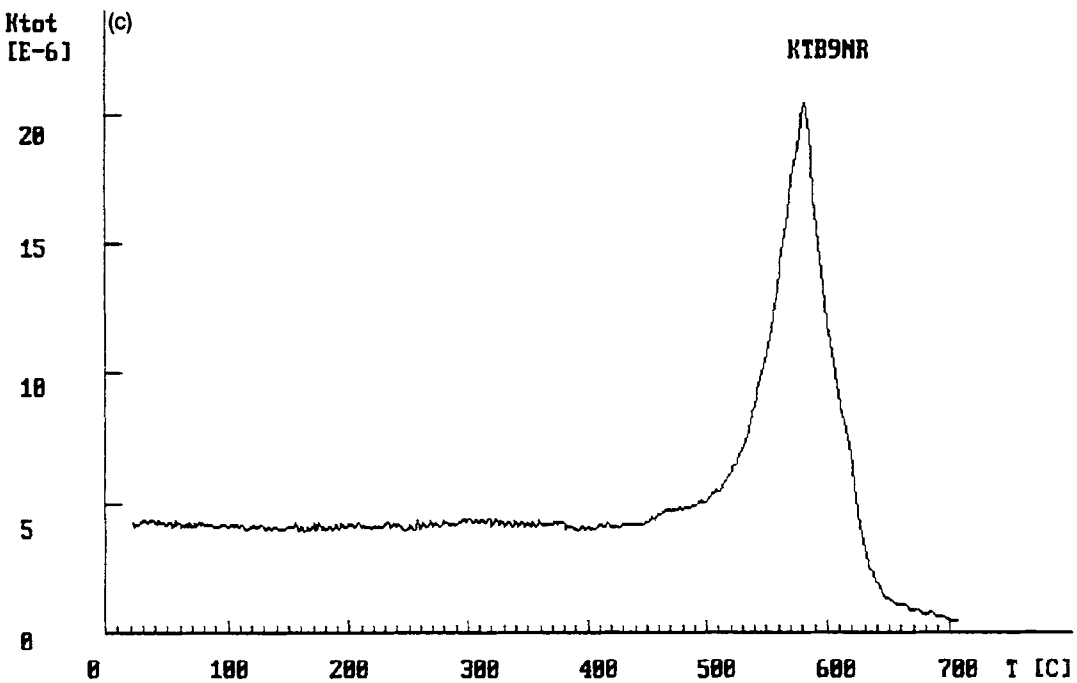


Figure 2. (*Continued.*)

resolution for several different segments of the initial thermomagnetic curve and compare the course of the fitted hyperbola with the measured curve. If the deviations of the individual susceptibility determinations are distributed symmetrically about the hyperbola in the whole course of the fitted part of the thermomagnetic curve (e.g. the 20–400 °C segment in Fig. 2b), the assumption of constant ferromagnetic susceptibility can be regarded as valid from a practical point of view. If the hyperbola lies outside the thermomagnetic curve in a part of the fitted segment, the

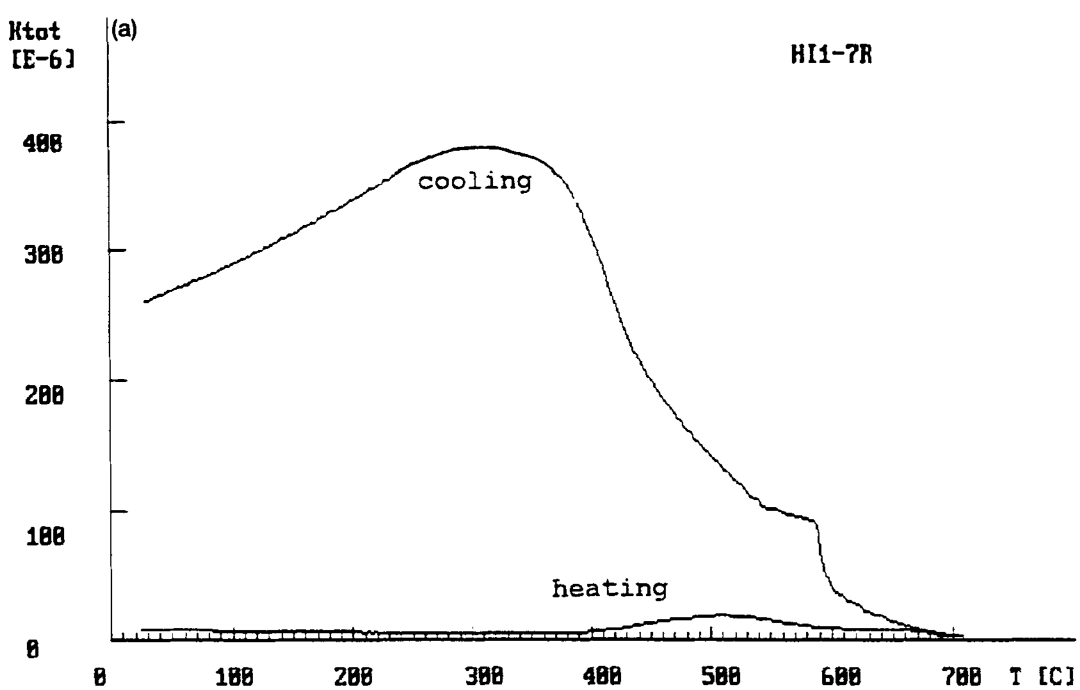
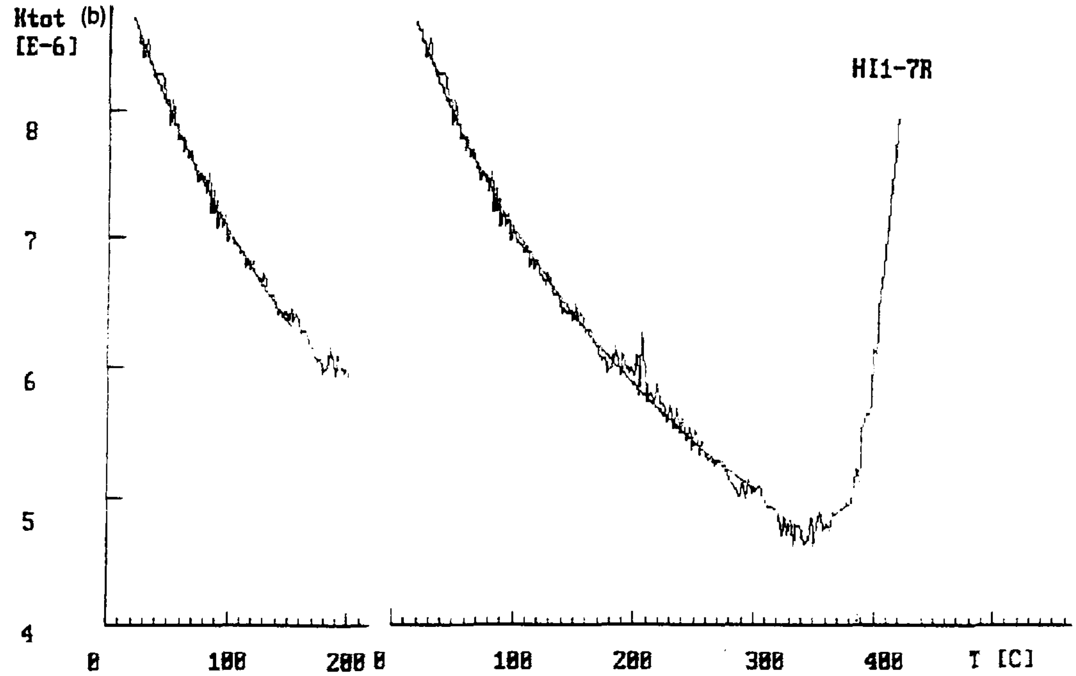


Figure 3. Thermomagnetic curves of a specimen of Devonian shale from the Appalachian Plateau, New York. (a) Heating and cooling thermomagnetic curves corrected for empty furnace. (b) Initial parts of heating thermomagnetic curve, with drawn paramagnetic hyperbolas (20–150°C and 20–300 °C). (c) Heating thermomagnetic curve of the ferromagnetic component only (after subtraction of paramagnetic susceptibility).



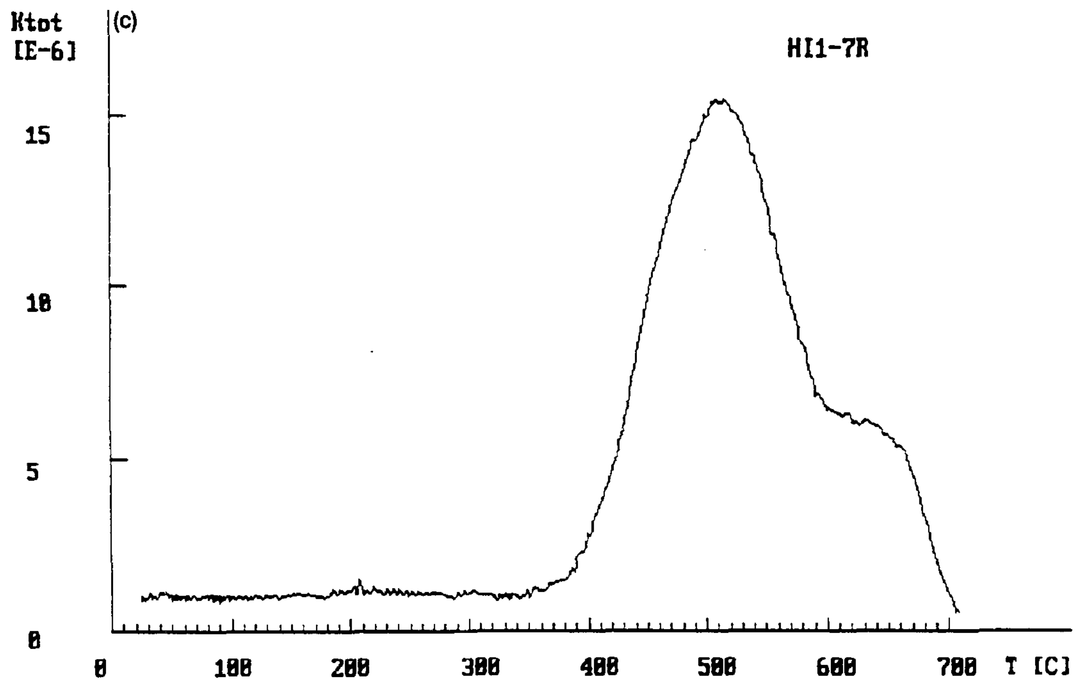


Figure 3. (*Continued.*)

ferromagnetic susceptibility shows systematic changes with temperature and the resolution obtained in this interval is not accurate and should not be used.

The effect of selection of the segment for fitting the paramagnetic hyperbola and subsequent resolution of the susceptibility into the paramagnetic and diamagnetic components on the resolution accuracy is illustrated in Table 2 showing the paramagnetic (K_p) and ferromagnetic (K_f) susceptibilities resolved for variable temperature segments of some specimens. It is clear from Table 2 that in specimens KTB9NR and HI1-7R the resolved paramagnetic and ferromagnetic susceptibilities do not depend very much on the selected temperature segment provided that the upper temperature is lower than 400 °C, while in the specimen FRI8NEU the resolution gives consistent data only at temperatures of less than 300 °C.

The separation of the ferromagnetic thermomagnetic curve from the rock curve is based on the assumption that the Curie law for paramagnetic minerals is valid throughout the whole course of the measured thermomagnetic curve

Table 2. Effect of the selection of temperature segment on the resolution of the room temperature susceptibility into paramagnetic and ferromagnetic components.

	FRI8NEU		HI1-7R		KTB9NR	
Temperature	K_p	K_f	K_p	K_f	K_p	K_f
20 - 100	24.1	4.8	7.9	1.4	16.2	4.3
20 - 150	24.3	4.7	7.7	1.5	16.4	4.2
20 - 200	24.5	4.5	7.4	1.7	16.2	4.3
20 - 250	24.1	4.8	7.3	1.9	16.1	4.4
20 - 300	23.0	5.7	7.4	1.8	15.9	4.6
20 - 350	23.1	5.6	7.5	1.7	15.7	4.7
20 - 400	24.6	4.5	7.0	2.1	15.8	4.7
20 - 450	25.0	4.2	3.3	4.9	15.8	4.7
20 - 500	24.1	4.9	-	-	15.3	5.0
20 - 550	22.2	6.2	-	-	13.7	6.2

Note: K_p and K_f susceptibilities are given in the order of 10^{-6}

(eq. 7). If the paramagnetic minerals are partially changed during heating (new ferromagnetic minerals are created from the iron of paramagnetic minerals), some inaccuracy originates in the separation of the ferromagnetic thermomagnetic curve. This inaccuracy can be estimated from a comparison of the heating and cooling thermomagnetic curves. If only a very small amount of ferromagnetic mineral is created during heating so that the heating and cooling thermomagnetic curves do not differ very much, it is likely that the Curie law is valid and that the separation of the ferromagnetic thermomagnetic curve has been obtained with reasonable accuracy. If the heating and cooling thermomagnetic curves differ very much, indicating the creation of a relatively large amount of ferromagnetic mineral, the high-temperature paramagnetic susceptibility used during the high-temperature part of the ferromagnetic thermomagnetic curve has been underestimated. If one realizes, however, that the decrease in paramagnetic susceptibility due to the loss of iron in paramagnetic minerals is probably an order of magnitude lower than the susceptibility increase due to the creation of new ferromagnetic minerals from the same iron, the underestimation of the high-temperature part of the ferromagnetic thermomagnetic curve can be considered negligible from the practical point of view.

CONCLUSIONS

The curve of thermal changes of magnetic susceptibility of rocks measured by the CS-2 apparatus and KLY-2 Kappabridge is controlled by the following principal factors:

(1) the temperature-dependent susceptibility of the empty furnace;

(2) the susceptibility of paramagnetic minerals in a specimen showing a hyperbolic dependence with temperature;

(3) the susceptibility of ferromagnetic minerals in a specimen showing complex changes with temperature.

While factor (3) is dominant in strongly magnetic rocks and the measured thermomagnetic curves can be interpreted directly, in weakly magnetic rocks it is desirable to separate these factors. Software techniques were developed for the resolution of these factors and the accuracy of the resolution was evaluated as listed below.

(1) The smoothed thermomagnetic curve of the furnace without specimen is determined with an error of less than 2×10^{-7} (in terms of total susceptibility).

(2) The difference between two smoothed thermomagnetic curves of the same empty furnace measured on different days was found to be less than 2×10^{-7} despite the theoretical error of $2–3 \times 10^{-6}$ from the absolute calibration error of the KLY-2 Kappabridge.

(3) The changes in measured thermomagnetic curves greater than 5×10^{-7} can therefore be interpreted as resulting from the thermal change of susceptibility of rocks and not from inaccuracy in correction of the measured curve for the empty furnace.

(4) The initial part of a thermomagnetic curve of a weakly magnetic rock, where the ferromagnetic susceptibility is more or less constant, is represented by a hyperbola shifted along the susceptibility axis. Through fitting a hyperbola to the initial part of the thermomagnetic curve using a least-squares method one can resolve the curve into paramagnetic and ferromagnetic components and determine errors in this resolution. These are usually of the order of 10^{-7}.

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