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Rockmagnetic Studies of Upper Jurassic Limestones From Southern Germany*

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Abstract. Acquisition of isothermal remanent magnetization (IRM) and the behaviour of IRM during high and low temperature treatment indicate that magnetite, goethite and minor quantities of hematite determine the magnetic properties of the Upper Jurassic limestones in Southern Germany. The direction of natural remanent magnetization (NRM) of magnetite is of detrital, synsedimentary origin, whereas the goethite, although its NRM is extremely stable against AF cleaning, has been magnetized only partly during the Jurassic. Part of the goethite NRM is interpreted to be of Tertiary (pre-Upper Miocene) age being formed during a period of Karstification in the Lower Tertiary. The apparent polarity sequence described earlier (Heller, 1977) is not of Jurassic age.

Key words: Rockmagnetism – Palaeomagnetism – Limestones.

1. Introduction

Recently the palaeomagnetic record preserved through a 160 m thick Late Jurassic limestone sequence from Southern Germany (Franconia, Swabia: Lat. N: 49°, Long. E: 11°) has been described (Heller, 1977). The well bedded, shallow water marine sediments do not show signs of major sedimentation breaks or essential later folding and seemed therefore to be suitable for the development of a reversal stratigraphy during the Oxfordian to Lower Kimmeridgian (Malm α–δ), the time when the limestones were deposited.

Only normal polarities have been observed in the older part of the section (Oxfordian) and the older portion of the Lower Kimmeridgian (Malm α–γ). Thus a period of normal polarity of the geomagnetic palaeofield could be established which lasted at least about 6 my. The younger part of Lower Kimmeridgian limestones (Malm δ) contained many reversely magnetized

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samples and yielded a polarity stratigraphy which tentatively has been correlated with the Mesozoic oceanic magnetic anomalies M25–M24 (Larson and Hilde, 1975).

During the previous work the interpretation of the stable remanence, and therefore the palaeomagnetic significance of the data, remained ambiguous to a certain extent. The purpose of this paper is to establish the significance of the palaeomagnetic record by rockmagnetic studies as well as optical, electron microprobe and X-ray analysis of the ferromagnetic minerals contained in the limestones. Five characteristics of the magnetic stratigraphy need to be discussed in the light of an improved knowledge of the rockmagnetic properties of the limestones.

1. The palaeopole position of the normal polarity sequence differs from that of the mixed polarity sequence, the latter being very close to European Tertiary palaeopole positions. The statistically significant difference was previously interpreted as possibly resulting from apparent polar wandering, but it could not be ruled out that the type and time of acquisition of the stable remanence were different in the upper and lower part of the section. The magnetization in the higher portion perhaps originated more recently than the time of deposition of the sediments.

2. Occasionally within the mixed polarity sequence normally magnetized as well as reversely magnetized individual specimens have been found in the same sample. What kind of magnetization process caused this curious directional behaviour of the remanence?

3. Two closely neighbouring sections (Heller, 1977, Fig. 6), situated in the mixed polarity zone and exposing exactly the same stratigraphic limestone sequence, do not yield exactly corresponding reversal patterns. There are several limestone beds in the two sections in which different remanence polarity has been observed at nearly the same stratigraphic level within one bed. This, of course, could be ascribed to a high reversal frequency of the palaeofield, but the complexity of the reversal pattern which is generated when plotting a combined polarity profile, casts doubt on whether the stable remanence actually was acquired at the same time in both sections.

4. The initial natural remanent magnetization (NRM) intensities are very weak. They average around 2×10^{-7}. Gauss and depend on the stratigraphic position or, what turns out to be equivalent, on the limestone facies. At the bottom of the section which is shown in Figure 1, marls and marl-rich limestones (Malm $\alpha(+\beta)$) are predominant. They have the highest initial NRM intensities of the order of 1×10^{-6} Gauss. Proceeding into higher parts of the profile the limestone facies changes to very pure micritic limestones (Malm β–γ). At the same time the NRM intensity decreases gradually to a value of about 6×10^{-8} Gauss. The youngest portion of the section showing mixed polarities of NRM directions is built up by a sponge facies known as bafflestones (Wilson, 1975). These limestones (Malm δ) have a slightly increased NRM mean intensity of about 2×10^{-7} Gauss. The correlation between facies and NRM intensity is certainly related to varying intrinsic rockmagnetic properties of the limestones, as the formation of the ferromagnetic minerals depends on the syn- or postdepositional environment of these sediments.

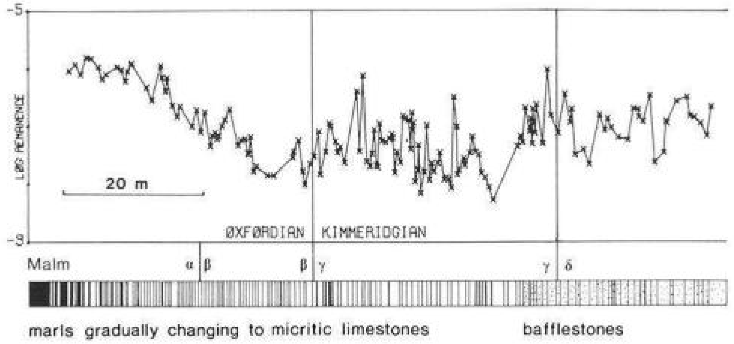

Fig. 1. Correlation of NRM intensity and limestone facies. Thick and thin marl beds are indicated by black shading; marl-rich and pure micritic limestones are the white layers; bafflestone layers are dotted. Bottom of the section to the left. Remanence intensities given in Gauss

5. Within the mixed polarity sequence zones of marl deposition are found especially in Swabia. These marl beds are always normally magnetized, whereas the under- and overlying bafflestones carry mixed polarities of stable remanence.

In order to elucidate the problems and questions raised above, the following experiments and investigations have been carried out.

2. Rockmagnetism

2.1. Magnetic Identification of Ferromagnetic Minerals

The limestones contain only very small amounts of ferromagnetic minerals, their weight percentage ranging up to about 0.05%. Dissolution of the limestone matrix by means of diluted formic acid and subsequent heavy liquid separation unfortunately did not yield enough material for thermomagnetic analysis. Therefore all the rockmagnetic studies had to concentrate on the characteristics of remanent magnetization, measured in standard one-inch solid rock specimens. Besides AF demagnetization of natural remanence, acquisition curves of isothermal remanent magnitization (IRM) have been measured at a constant temperature of 0° C in fields up to 50 kOe using a superconducting magnet. Furthermore, the temperature dependence of IRM measured in zero field has been observed by using a modified Digico spinner magnetometer (Heiniger and Heller, 1976). This magnetometer enables continuous measurement of the remanence vector between liquid nitrogen temperature and 700° C. Some additional temperature dependent measurements have been made on IRM acquired at liquid nitrogen temperature. Typical results obtained from the different limestone facies types will be described in the following sections.

Marl-Rich Limestones. Figure 2 presents rockmagnetic data of a marl-rich limestone sample. During AF demagnetization of NRM (Fig. 2a) in fields up to

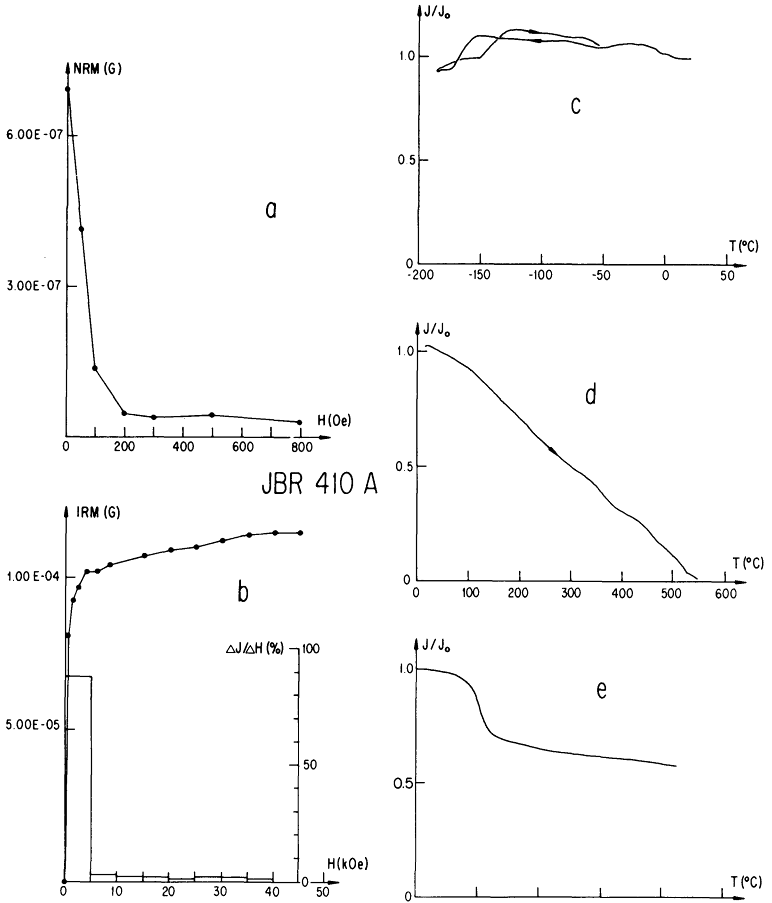

Fig. 2a–e. NRM and IRM characteristics of a marl-rich limestone sample (JBR 410A) containing magnetite. **a** AF-demagnetization of NRM intensity. **b** IRM acquisition at $T = 0°$ C and resulting coercivity spectrum. **c** Cyclical behaviour of room temperature IRM during low temperature treatment. **d** Continuous thermal demagnetization of IRM during heating. **e** Behaviour of low temperature IRM (given at $T = -196°$ C) on re-warming to room temperature

800 Oe a large soft component is removed by a peak field of 200 Oe. Above this field amplitude a small, but stable component remains. Only minor directional changes of NRM are observed during AF cleaning.

IRM acquired in fields up to 45 kOe (Fig. 2b) increases rapidly up to 4 kOe. Above 4 kOe the curve has a very low gradient and seems to saturate at the highest field amplitudes available. According to Dunlop (1972) this type of curve represents magnetite as the main carrier of IRM with a small additional contribution to the IRM by a high coercivity mineral which usually is suggested to be hematite. As we will see later, it is probable that the high coercivity part of IRM is carried by goethite.

During cooling (Fig. 2c) the IRM intensity increases very slightly until −150° C where about 15% of the magnetization are lost upon further cooling. On re-warming to room temperature the original magnetization is fully recovered showing a sharp increase in intensity which starts around −150° C. The observed thermal hysteresis is caused by the large sample size (volume: 11.4 cm^3). The observed low temperature transition can be attributed to the K_1 zero-transition of almost pure magnetite and agrees with the interpretation of the IRM acquisition curve in which most of the magnetization is acquired below 4 kOe due to the presence of magnetite. The reversibility of the cooling and re-warming cycle as well as the high percentage of magnetization which is not affected by the low temperature treatment may indicate that the magnetite grain size is very small and the IRM is essentially carried by single and pseudosingle domain grains of magnetite (Merrill, 1970).

The same conclusions can be drawn from Figure 2e where the IRM—acquired at liquid nitrogen temperature—of another marl-rich limestone has been plotted as a function of temperature on re-warming to room temperature. Again part of the magnetite magnetization is lost during the K_1 transition at around −150° C. Upon further warming the intensity of magnetization decreases slightly. As the experiment was done in zero field and as the room temperature IRM does not change during cooling (Fig. 2c), the decrease can be attributed mainly to a change from the ferrimagnetic to the superparamagnetic state of a small percentage of magnetite particles contained in the sample. Therefore this experiment confirms that the grain size distribution covers mainly single domain grains, the magnetization of which is not affected by the low temperature treatment, pseudosingle domain grains, which reversibly show the transition effect, and even superparamagnetic grains at room temperature. Subsequent heating of IRM to high temperatures (Fig. 2d) yields an uppermost blocking temperature $T_{b\max} \cong 550°$ C which again can be interpreted as being due to almost pure magnetite. The low and high temperature curves of IRM do not allow the positive identification of the high coercivity magnetic mineral.

Micritic Limestones. Typical data for a micritic pure limestone sample are given in Figure 3. NRM is almost stable against alternating demagnetizing fields up to 800 Oe (Fig. 3a), but the demagnetization curve is zigzagged between 50 Oe and 300 Oe. These intensity fluctuations which are not accompanied by directional variations of the remanence vector, arise from a strong temperature dependence of magnetization (cf. Fig. 3c and d) rather than from spurious magnetization processes during cleaning. Therefore during the various steps of IRM acquisition all the samples were kept at constant temperature $T = 0°$ C (ice water) to avoid irregularly shaped magnetization curves.

As demonstrated in Figure 3b, the sample acquires only a very small IRM component in DC fields below 10 kOe which possibly may reside in a negligible amount of magnetite present in the sample. Most of the magnetization is acquired at fields higher than 15 kOe and saturation is not reached even at $H =$ 45 kOe. The coercivity spectrum of IRM therefore is dominated by high field components.

The low temperature curve of IRM (Fig. 3c) shows a very peculiar intensity

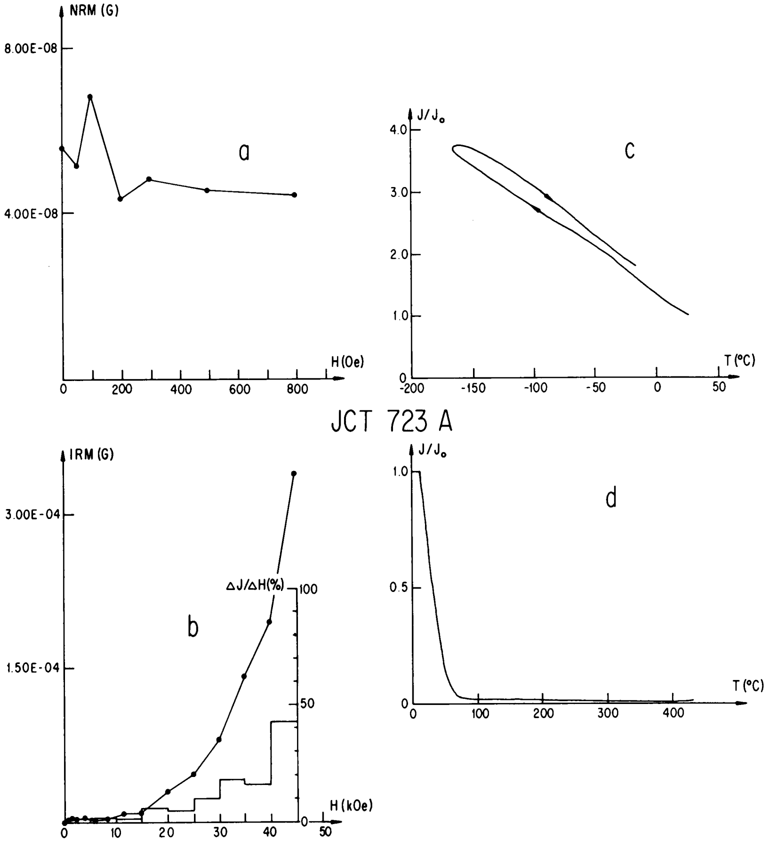

Fig. 3a–d. NRM and IRM characteristics of a micritic, pure limestone sample (JCT 723 A) containing goethite. For the significance of Figure 3a–d see Figure 2a–d

increase during cooling which is reversible on re-warming to room temperature except that again thermal hysteresis is observed. As IRM is acquired at $T = 0°$ C and measured in zero field during low temperature treatment, the drastic intensity change (amounting to about 3% per °C) must be due to a strong temperature dependence of spontaneous magnetization. Subsequent heating of IRM (Fig. 3d) shows a maximum blocking temperature $T_{b\max} \cong 70°$ C. Above this temperature essentially no remanent magnetization is left.

The high stability during AF cleaning, the extremely high coercivity spectrum of IRM and the low maximum blocking temperature suggest that goethite, the α-form of iron oxyhydroxyde (FeO OH) is the most important ferromagnetic mineral in the micritic limestones. It should be mentioned that a few micritic limestones have been found which possess maximum blocking temperatures as high as $T_{b\max} \cong 610°$ C. They may correspond to the presence of hematite which formed by oxydation from a pre-existing goethite.

Limestones With Reduced Clay-Content. The facies change from marls and marl-rich limestones to pure micritic limestones, which causes a reduction in NRM intensity (Fig. 1), occurs rather gradually. Figure 4 shows the characteristics of the rockmagnetic parameters investigated in a sample originating from this zone of facies transition. As in the previous example of a marl-rich limestone a high percentage of NRM is removed without directional change by AF cleaning up to 300 Oe (Fig. 4a). The remaining component is stable even in a peak field of 3000 Oe. Again intensity fluctuations are observed during the cleaning procedure which are due to the temperature sensitivity of goethite present in the sample. The IRM acquisition curve (Fig. 4b) reveals a significant amount

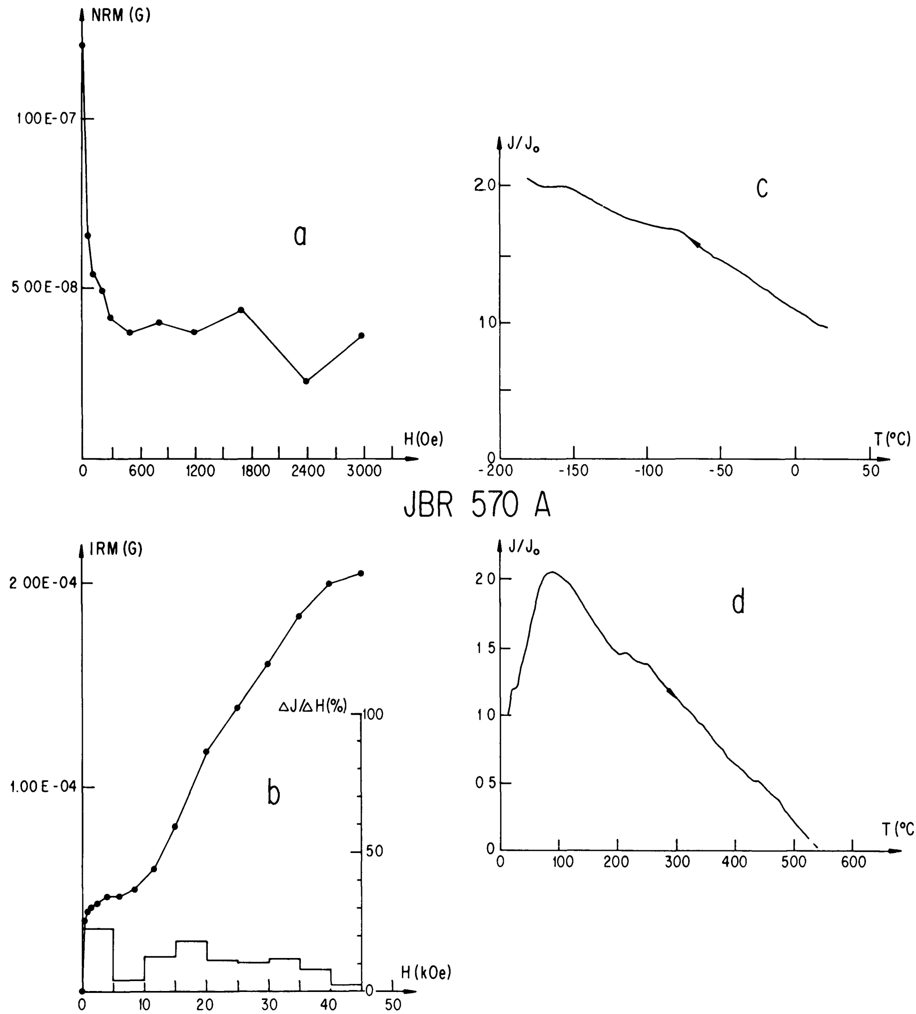

Fig. 4a–d. NRM and IRM characteristics of a limestone sample (JBR 570A) containing both magnetite and goethite. For the significance of Figure 4a–d see Figure 2a–d

of magnetite, indicated by the sharp initial increase and subsequent saturation of magnetization up to 4 kOe. Again between 10 kOe and 15 kOe IRM starts to increase. Saturation is not observed, although the curve gradient flattens off at the highest fields available. Corresponding to these observations the coercivity spectrum of IRM has two peaks, one being situated between 0 kOe and 5 kOe and the other sitting on top of a widely distributed spectrum at 15 kOe to 30 kOe. This broad spectrum probably indicates a large range of grain sizes of goethite and may arise from different degree of crystallization of this mineral.

The presence of goethite is recognized in the increase of IRM intensity during cooling in zero field (Fig. 4c), whereas the magnetite low temperature transition is only vaguely indicated by a flexure in the IRM(T) curve just below $-150°$ C. Before heating (Fig. 4d) the sample was first given an IRM in a field of 45 kOe, and then given an IRM in a 10 kOe field in the antiparallel direction. Thus the maximum blocking temperatures of goethite and magnetite could easily be separated (Fig. 4d). Magnetite has a $T_{b\max} \cong 550°$ C which is very near to that of pure magnetite and the maximum blocking temperature of goethite can be determined to be $T_{b\max} \cong 90°$ C.

Bafflestones. The third main type of limestone facies are the bafflestones. Their rockmagnetic parameters are very similar to those of the micritic limestones. The ferromagnetic mineralogy is dominated by goethite, occasionally hematite and minor amounts of magnetite. The NRM intensity (and direction) often does not change during AF cleaning as shown by the sample of Figure 5a. In the course of IRM acquisition only a high coercivity phase is detected in this sample (Fig. 5b). The strong reversible change of IRM intensity during low temperature treatment indicates the presence of goethite only (Fig. 5c), and low temperature transitions due to magnetite or hematite have not been found. During heating (Fig. 5d) we recognize that 70% of the magnetization is carried by goethite whose maximum blocking temperature lies around $T_{b\max} \cong 90°$ C. The rest of remanence is due to hematite with $T_{b\max} \cong 635°$ C. The Morin transition is not found during low temperature treatment, because either the hematite grain size is too small or the transition is suppressed due to the presence of impurity ions in hematite.

2.2. Thermal Treatment of Goethite

It has been demonstrated by Dunlop (1972) that a remanence coercivity spectrum can be derived from IRM acquisition curves simply by plotting the increment ΔJ of isothermal remanence in intervals ΔH of a certain width of the applied field H. Dunlop also showed how changes of the coercivity spectra obtained during heating can be interpreted in terms of changes in the ferromagnetic mineralogy. This technique has been applied to a bafflestone sample which initially contained goethite as the only ferromagnetic mineral. The coercivity spectra (increment $\Delta H = 5$ kOe, $\Delta H = 1$ kOe for $H \leqq 5$ kOe) obtained after heating to stepwise increased maximum temperatures are given in Figure 6. The

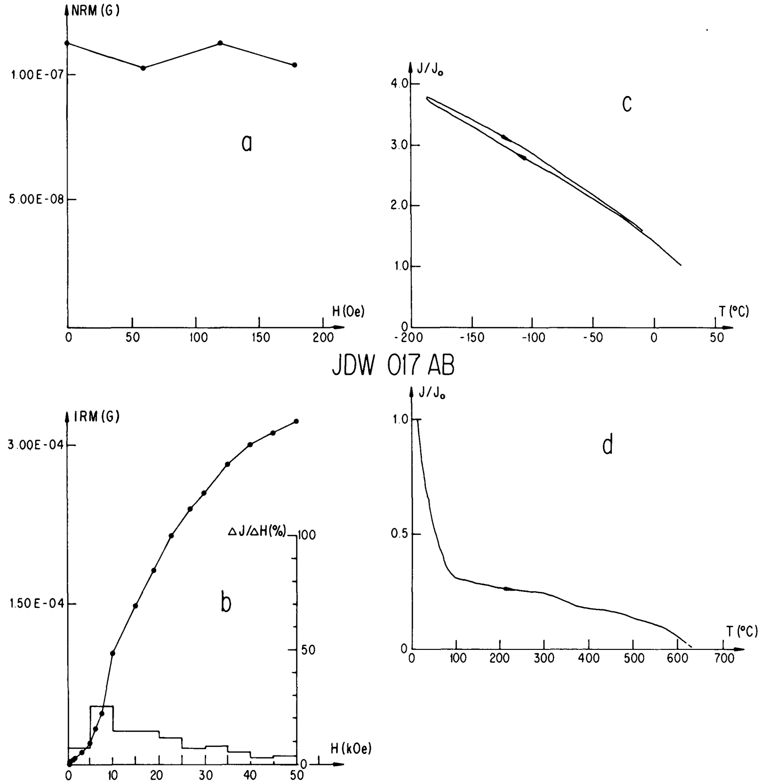

Fig. 5a–d. NRM and IRM characteristics of a bafflestone sample (JDW 017 AB) containing goethite and hematite. For the significance of Figure 5a–d see Figure 2a–d

IRM intensity decay during each heating cycle (heating rate always $dT/dt = 10°$ C/min) has been measured continuously and plotted in Figure 7. After having attained the maximum heating temperature the sample always was allowed to immediately cool down to room temperature again.

Before heating ($T = 0°$ C) we observe a broad coercivity spectrum which has a maximum between 5 kOe and 20 kOe (Fig. 6a). The maximum blocking temperature is about 60° C (Fig. 7a). After heating to $T_{\max} = 90°$ C the shape of the coercivity spectrum as well as the maximum blocking temperature change very little (Figs. 6b and 7b), but the intensity of magnetization is increased by about 50% of the initial IRM produced by $H = 50$ kOe. The intensity increase possibly is caused by grain size growth of very small (superparamagnetic?) goethite particles dispersed throughout the sample and/or by advancing crystallization of poorly crystalline material due to modest heat treatment. Heating to $T_{\max} = 225°$ C does not affect the magnetic properties of the sample essentially; also its colour remains white. After heating to $T_{\max} = 310°$ C major changes occur. They are due to dehydration and decomposition of goethite which starts

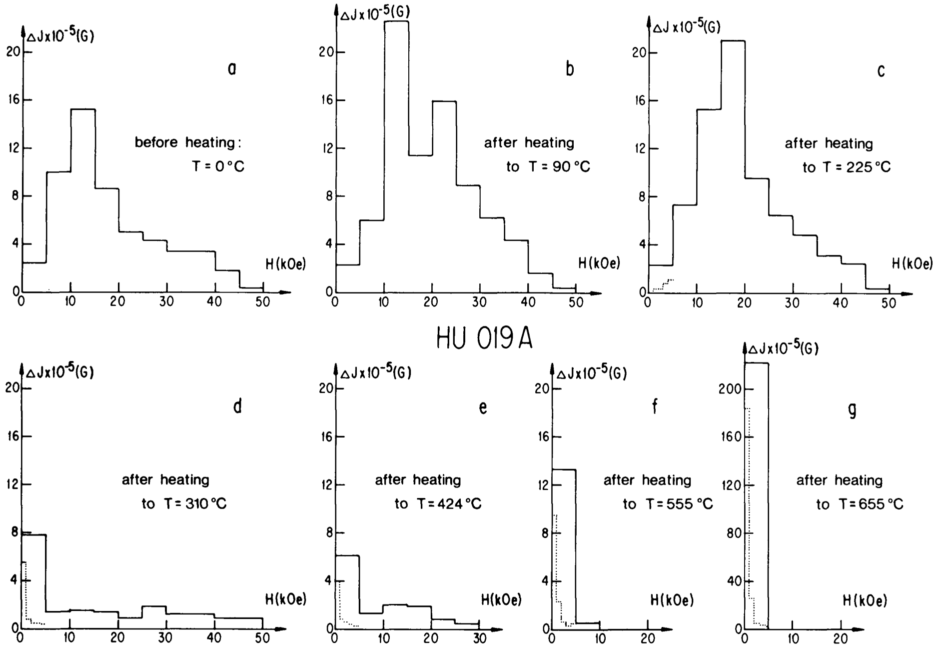

Fig. 6a–g. Coercivity spectra of IRM of a goethite containing bafflestone sample (HU 019 A) obtained after heating to stepwise increased maximum temperature. Note change of scale in Figure 6g

arround 290° C (Hedley, 1968). The colour of the limestone begins to redden. The reddish colour is observed only in the bafflestones which before heating obviously contain finely dispersed iron-hydroxides. These are converted during heating to very fine grained hematite which causes the colour change. Thus the suggestion made by Lowrie and Alvarez (1977) that hematite formed by dehydration of goethite in the Scaglia Rossa limestones from Italy, is supported by the observed colour changes. The former coercivity spectrum breaks down having a well developed maximum now at fields $H < 5$ kOe, but fields 5 kOe $< H <$ 50 kOe still contribute about half of the IRM (Fig. 6d). The finer ΔH increments (dotted lines in Fig. 6d–g) show the beginning development of a magnetic mineral phase having a coercivity $H_{\mathrm{cr}} \leqq 1$ kOe. The IRM intensity is reduced by a factor 5 and therefore, although the sample appears reddish, hematite does not seem to contribute very much to the remanence probably because its grain size is very small. Upon further heating we see a kink in the IRM decay curve around 70° C (Fig. 7d) which indicates that some goethite still has survived, but the main part of IRM is associated with higher blocking temperatures. Heating to $T_{\max} = 424°$ C does not reach the maximum blocking temperature of this IRM, but it turns out that after this heating cycle the IRM intensity decreases even further. The colour of the limestone still is red and the subsequent IRM acquicisiton curve saturates at $H = 30$ kOe (Fig. 6e). Thus the coercivity spectrum begins to shorten. The magnetization component which has a coercivity $H_{\mathrm{cr}} \leqq 1$ kOe shows a very slight decrease. Subsequent

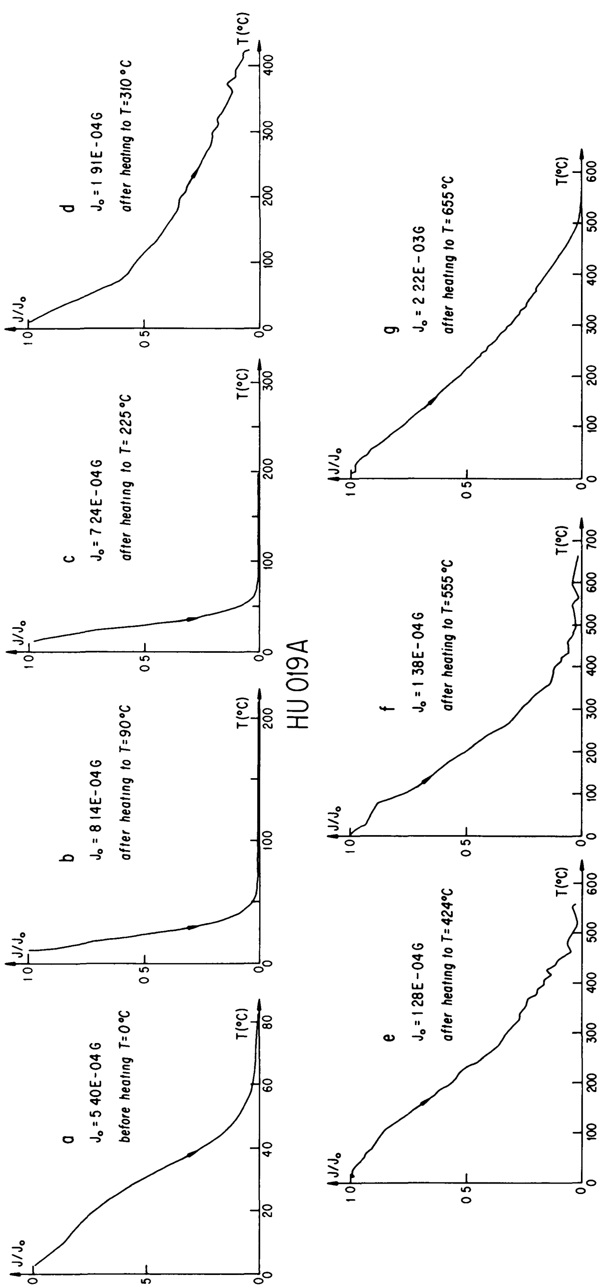

Fig. 7a–g. Continuous thermal demagnetization of IRM up to stepwise increased maximum temperature. J_0 denotes initial IRM intensity before each heating cycle

heating (Fig. 7e) does not show signs of goethite magnetization components, but the uppermost blocking temperatures seem to be reached around 500° C. This heating cycle up to $T_{max} = 555°$ C restricts the coercivity spectrum to $0 < H_{cr} \leq 10$ kOe with a definitely increased low coercivity component (Fig. 6f) which now carries the main portion of IRM. The colour of the sample becomes grey with some small patches on the surface still being red. After heating to $T_{\max} = 665°$ C another drastic change of the magnetic properties becomes evident. There is no further colour change, but the IRM intensity has increased by a factor 20 (Fig. 6g; ordinate with enlarged scale!); nearly 100% of the magnetization are held by a magnetic phase which has a coercivity $H_{cr} \leqq 2$ kOe. The maximum blocking temperature is found to be $T_{b_{\max}} \cong 540°$ C (Fig. 7g).

It is evident from these experiments that not only hematite is formed by thermal destruction of goethite. At temperatures below 300° C goethite is the only ferromagnetic mineral present in the limestone sample. Figures 6d and e and 7d and e show that between 300° C and 450° C probably hematite is forming and partly contributing to the IRM, as the component with $10 < H_{cr} \leqq 20$ kOe increases and at least part of the high coercivity component of IRM is due to a magnetically hard mineral with blocking temperatures well above 100° C. The carrier of the low coercivity component formed within this temperature range cannot be positively identified from the measurements. Because heating to 424° C reduces the intensity of this component slightly, possibly maghemite was formed after heating to 310° C and is going to be destroyed upon further heating. Its formation during oxidation of goethite was also noted by Kelly (1956). But it cannot be excluded alternatively that possibly magnetite is responsible for this portion of IRM. Heating to temperatures $> 500°$ C causes magnetite to constitute. Evidence for magnetite comes from the intensity increase of the low coercivity component by one to two orders of magnitude, from the coercivity spectrum reduction to $H_{cr} \leqq 2$ kOe, from the maximum blocking temperature being about $T_{b_{\max}} = 540°$ C and from a faint indication of a low temperature transition at $-150°$ C during low temperature treatment. The formation of magnetite at these relatively low temperatures (beginning around 550° C) is unusual (cf. Dunlop, 1972), but it is probably due to the large amount of organic compounds contained in the bafflestones which decompose upon heating and create reducing conditions in the sample at higher temperature.

3. Non-Magnetic Identification of Ore Minerals

3.1. Ore Microscopy

Ore microscopic studies reveal the presence of several opaque minerals whose occurrence depends on the facies type of the limestones. No ore mineral—especially no magnetite—could be identified in the Oxfordian marl-rich limestones. In the micritic limestones weakly reflecting, grey goethite has been observed. The grains predominantly have idiomorphic to hypidiomorphic (cubic!) shape (Fig. 8b) and it seems that they have replaced pyrite which also is found at places in this part of the section. These goethite grains range in size between 10 μm and 1000 μm. Small brightly reflecting patches within the larger goethite grains and red internal reflections along the grain margins indicate that they have been partly altered to hematite. The bafflestones contain very irregularly shaped (Fig. 8a) goethite grains of various size (10 μm to 100 μm) which often

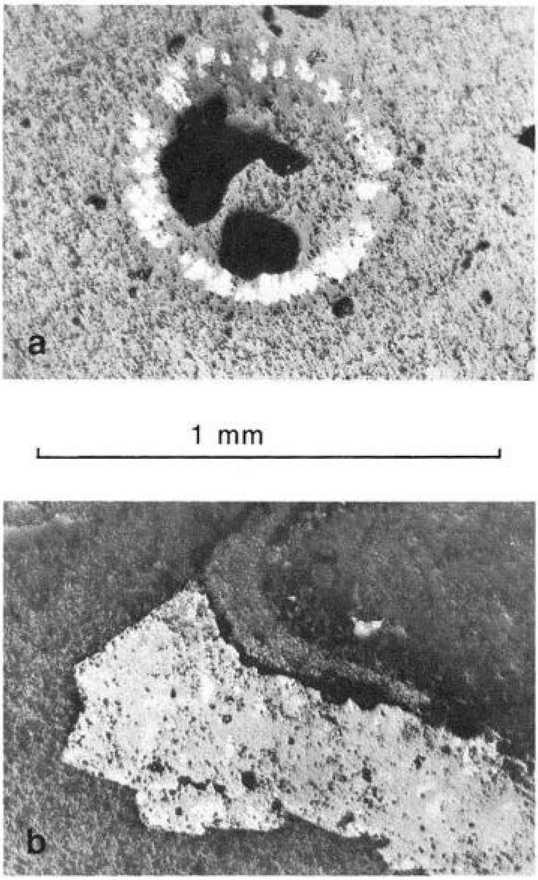

Fig. 8. a Irregularly shaped goethite, probably concentrated around a fossil relict. Bafflestone sample (HU 018 D).
b Regularly shaped goethite (grey) which has replaced pyrite. The brighter patches within goethite indicate oxidation. Micritic limestone sample (JBH 085 AA)

seem to be oxydized to hematite more strongly than in the micritic limestones. Usually these goethites occur in the close neighbourhood of fossil fragments.

3.2. Electron Microprobe and X-Ray Analysis

Table 1 gives the results of microprobe analysis. No other cations such as Ni, Cr, Mn, Al, Ca, Mg have been detected. The iron contents of pyrite and "idiomorphic" goethite are very near to stoichiometry for pure FeS_2, and FeO OH, respectively, whereas the iron content of the irregularly shaped goethite is slightly reduced. All the goethites contain a small amount of silica up to 2 wt% for single point analyses. Sulphur is absent in the "idiomorphic" goethite suggesting a thorough oxidation of pyrite which probably preceeded this type of goethite.

Heavy mineral extracts taken from a marl-rich limestone and two bafflestone samples yielded useful X-ray powder photographs only for the bafflestones.

Table 1. Microprobe analysis of ore minerals. Elements analyzed: Fe, Si, S; *N* denotes number of analyses

Limestone facies, mineral	*N*	Fe wt%	Si wt%	S wt%
Micritic limestone, 'idiomorphic' goethite	33	63.14 ± 1.11	1.65 ± 0.40	–
Micritic limestone, irregular goethite	4	58.77 ± 1.86	1.76 ± 0.08	–
Bafflestone, irregular goethite	30	58.27 ± 2.49	1.70 ± 0.19	–
Bafflestone, pyrite	9	46.40 ± 0.37	0.04 ± 0.03	52.16 ± 1.29

Table 2. Lattice constants of orthorhombic goethite (α – FeOOH)

Sample	a (Å)	b (Å)	c (Å)	Camera	*T* (°C)
HU 003	4.618 ± 0.002	9.969 ± 0.003	3.020 ± 0.001	Jago	20
JDW 027	4.618 ± 0.004	9.971 ± 0.005	3.019 ± 0.001	Jago	20
JDW 027	4.610 ± 0.007	9.967 ± 0.011	3.019 ± 0.002	Simon	20
JDW 027	4.601 ± 0.005	9.959 ± 0.006	3.017 ± 0.002	Simon	–150

These photographs obtained with a Guinier focussing camera (Jagodzinski type) using Si as internal standard, again showed goethite as the only ferromagnetic mineral to be identified. Broad diffraction lines indicate poor crystallization of the material. The lattice constants are given in Table 2. The table also includes lattice parameters of goethite which have been measured with another Guinier camera (Simon type) at room temperature as well as at low temperature (– 150° C) in order to find out if there is a correlation between cell constants and magnetic properties of goethite during low temperature treatment. The data given in Table 2 agree closely with the values published by Sampson (1969) on synthetic goethite and indicate a trend to slightly reduced lattice constants at low temperature.

4. Discussion

4.1. Physical Properties of Goethite

Goethite is known to be antiferromagnetic with a weak ferromagnetism superimposed (Strangway et al., 1968; Forsyth et al., 1968). Hedley (1971) suggested that the ferromagnetism is due to spin imbalance between the antiferromagnetic sublattices caused either by vacancies or faults in the crystal structure or by impurity ions entering the lattice.

The extreme stability of NRM against alternating demagnetizing fields up to 3000 Oe (Fig. 5) as well as the spectra of very high coercivity of IRM observed in the goethite containing limestones support Hedley's idea that the ferromagnetic magnetization shares the strong antiferromagnetic anisotropy. The maximum blocking temperatures range between 55° C and 95° C. If we assume that the maximum blocking temperatures coincide with the corresponding Néel-temperatures, then these relatively low temperatures point to poorly crystallized material (Hedley, 1971). This is in agreement with the X-ray examination where broad diffraction lines have been observed. We have noted a small amount of Si in our goethites (Table 1). Therefore the goethite ferromagnetism could be caused by imbalance due to Si impurities, but it is not clear how Si enters the lattice non-randomly. We see on the other hand in Table 1 a higher Fe-content (63.1 wt%) which is near to stoichiometry of the pure mineral, in the "idiomorphic" goethite compared to a slightly reduced iron content (58.5 wt%) in the irregular goethite. The NRM and IRM intensities of sediments containing "idiomorphic" goethite generally are reduced by a factor 5 compared to the limestones with irregular goethite, which may imply that vacancies play a rôle in the stronger magnetization of the irregular goethites.

It is difficult to encounter the mechanism which causes the observed ferromagnetism in the goethite because of uncertainties about the degree of crystallization and oxidation state of the material which in small clusters may be altered to hematite. The trend to a lattice contraction at low temperature may account for the strong temperature dependence of spontaneous magnetization (increase of IRM with decreasing temperature in zero field), but a quantitative explanation cannot be given before a better knowledge of the chemical and structural properties of these goethites has been achieved.

4.2. Magnetization Process

We have described in the previous chapters that mainly two phases – magnetite and goethite – dominate the ferromagnetic mineralogy of the limestones. The processes by which these minerals acquired their NRM, are different.

The marls and marl-rich limestones have been deposited during times of increased influx of mud suspensions (v. Freyberg, 1966). Rockmagnetic studies revealed the presence of single- to pseudo-single domain magnetite in these sediments. As the grainsize of magnetite is very small, optical identification and separation methods failed. The fine grainsize on the other hand allowed magnetite to be carried within the mud suspensions and to be aligned during or shortly after deposition so that a detrital remanence (DRM) has been acquired by the magnetite. The mean NRM direction of the marls and marl-rich limestones (Table 3, Malm $\alpha+\beta$) confirms a detrital, synsedimentary origin of natural remanence, because the resulting virtual geomagnetic pole position (VGP: $=68°$ Lat.N; 130° Long.E) has been found to coincide closely with the European Late Triassic palaeopole (cf. Heller, 1977; Fig. 8). The same close agreement has been observed between Late Triassic and Jurassic palaeopoles in North America (Steiner and Helsley, 1972).

When swells became active in the sedimentation basin, the influx of clastic material stopped to a large extent. Consequently magnetite is of little importance for the magnetic properties of the pure, micritic limestones and the bafflestones.

There are at least two time periods when goethite acquired the natural remanence. From ore microscopic observations we have recognized two goethite

Table 3. Mean directions of stable remanence and virtual geomagnetic pole positions (VGP) derived from the Late Jurassic limestones of Southern Germany (site Lat.N: 49°, Long.E: 11°)

Malm Subdivision	Number of samples	Direction of NRM			VGP position	
		D	I	α_{95}	Lat.N	Long.E
δ	125	13	62	5	79	124
γ	48	31	51	8	62	122
$\alpha+\beta$	79	23	53	5	68	130

types. The first type occurring mainly in the micritic limestones has pseudoidiomorphic shape which suggests formation by alteration from pre-existing pyrite. For the timing of this oxidation process which produces a chemical remanent magnetization (CRM), we may use the same arguments as for the magnetite DRM. The micritic limestones have the same stable mean direction (Table 3; part of Malm β and Malm γ) as the marls and marl-rich limestones. On this basis we conclude that the alteration must have taken place soon after deposition of these sediments and that this CRM may also be of Jurassic age. This on the other hand implies that the redox potential of the sediments changed early during diagenesis into more oxigenated conditions.

The other goethite type found predominantly in the bafflestones is irregularly shaped. Apparently it did not form by alteration from pyrite. But still a Jurassic NRM direction could be expected since goethite could precipitate from iron solutions under certain redox conditions (Schellmann, 1959; Stumm and Morgan, 1970) perhaps dependent on the oxidation of organic matter a lot of which has been available in the bafflestones, and it may form irregularly shaped crystals in the neighbourhood of fossil relicts. But we have noted (Table 3; Malm δ) that the stable mean direction of the bafflestones differs significantly from that of the older members of the limestone sequence. This NRM is aligned very near to a Lower Tertiary European field direction and has been interpreted previously to reflect apparent polar wander setting in with the beginning of the middle Lower Kimmeridgian. This interpretation required a sudden and rapid polar movement starting between Malm γ and Malm δ. In view of the rock magnetic information for these bafflestones this interpretation must be revised.

The NRM of the bafflestones probably has a post-sedimentary, secondary origin, possibly connected to Karst formation and red soil development which started during the Lower Cretaceous and reached its climax during the Eocene and Miocene (Birzer, 1939). During this process goethite, if it existed, and other iron minerals were dissolved, and iron-hydroxide (re)-precipitated from iron solutions which penetrated the bafflestones from the land surface. Such an interpretation would easily solve the problems invoked in the introduction.

We can place a lower limit to the age of NRM of the limestones. We have taken samples from an outcrop situated near to the main fault which separates the limestone basin from the Bohemian massif. The steeply dipping limestone layers are overturned here and a magnetization direction which coin-

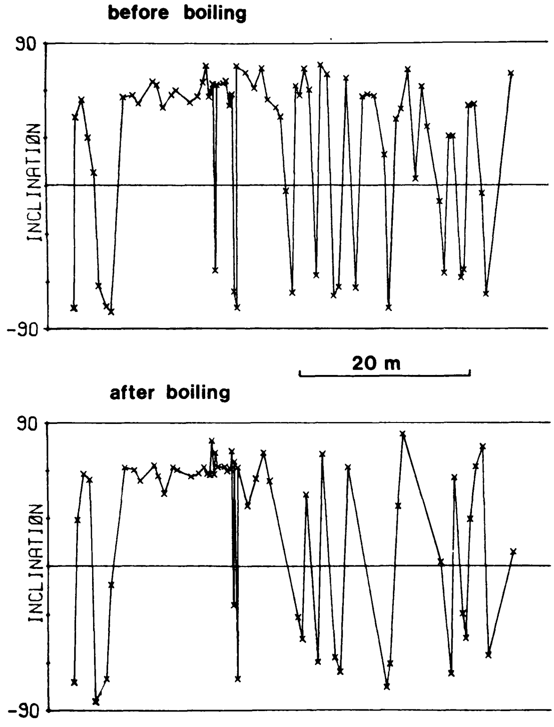

Fig. 9. Inclination of NRM of the Swabian bafflestone section before and after boiling in water

cides with the NRM directions measured elsewhere, can only be obtained by repositioning to the original horizontal position. As the faulting took place certainly before Upper Miocene (Bauberger and Cramer, 1961), the age of NRM must be older than Upper Miocene.

During the period of Karstification the upper parts of the limestones have been eroded and iron contained in the sediments was dissolved when the groundwater level was lowered down (Birzer, 1939). The iron solutions which led to iron ore deposits on the Eocene land surface, also penetrated the underlying limestones where precipitation and, as we see in polished sections, concentration of goethite took place preferentially in the neighbourhood of fossil relicts the remaining organic material of which supported the crystal growth of ironhydroxides. Recipitation and crystal growth of goethite does not necessarily occur contemporaneously throughout a limestone bed, as they depend on factors like porosity, content of organic substances, water content etc. which may vary locally.

This explains readily the observed occurrence of specimens with different NRM polarity within the same sample in the bafflestones. Normal and reversed samples may be found within the same limestone bed at different places, since the goethite crystals may have grown out of the superparamagnetic into the ferromagnetic state at different times in palaeofields of different polarity. The observed polarity sequence then no longer can be attributed to a Jurassic field reversal sequence, but reflects undatable field reversals of probably Lower Tertiary age. It should be mentioned that the apparent polarity profile is not changed by thermal demagnetization which was carried out by boiling in water. After boiling at 100° C the goethite component of NRM has been removed due to the low maximum blocking temperatures, but where a stable NRM component still was present after boiling, the direction of NRM remained unchanged (Fig. 9). This component is due to hematite the magnetization direction of which is controlled by that of goethite. Thus we find magnetic evidence that hematite has been formed by dehydration and oxidation of goethite.

In the Swabian section the Malm δ bafflestones are intercalated with marls and marl-rich limestones which like the Oxfordian facies equivalents always carry a normal magnetization direction. Whereas the bafflestones themselves have been magnetized during the Tertiary, this normal magnetization of Malm δ marls carrying a synsedimentary DRM probably indicates that the period of normal polarity of the geomagnetic field lasted during the Lower Kimmeridgian, too. Following this argument, we may conclude that the younger portion of the Jurassic quiet zone (Larson and Hilde, 1975) comprises both the Oxfordian and the Lower Kimmeridgian.

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