Geophys. J. R. astr. Soc. (1986) **86,** 885–892

Curie temperature analyses of Upper Jurassic and Lower Cretaceous pelagic limestones

Bruno Galbrun *Laboratoire de Stratigraphie, UA CNRS 319, Universite Pierre et Marie Curie (Paris VI), 75252 Paris cedex 05, France*

Robert F. Butler *Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA*

Accepted 1986 February 28. Received 1986 February 21; in original form 1985 October 24

Summary. Magnetic extracts were prepared from samples of Upper Jurassic and Lower Cretaceous pelagic limestones from France and Spain. Thermomagnetic analysis of the magnetic extracts using a microbalance required careful monitoring of base weight changes during heating. Heating in argon gas atmosphere induced production of magnetite during heating while slight oxidation occurred during heating in air. The dominant Curie temperature detected by the thermomagnetic analyses was the 585°C Curie temperature of magnetite. The 680°C Curie temperature of haematite was only detected when isothermal remanent magnetism (IRM) data indicated large concentrations of haematite. Even when IRM data indicated its presence, the thermomagnetic analyses did not detect the Neel temperature of goethite. Although thermomagnetic analyses of magnetic extracts provide more direct identification of the dominant, strongly ferromagnetic minerals, IRM acquisition and subsequent thermal demagnetization is a superior technique in detecting high coercivity, weakly ferromagnetic minerals such as goethite and haematite.

Key words: magnetic mineralogy, thermomagnetic analysis, pelagic limestones

1 Introduction

Pelagic limestone sections have been extensively used for palaeomagnetic studies, especially for magnetostratigraphy. Many pelagic limestones have yielded excellent palaeomagnetic records. While it is generally agreed that the primary natural remanent magnetism (NRM) in most pelagic limestones is a post-depositional remanent magnetism (PDRM) acquired by detrital magnetite, the magnetic properties are varied and sometimes complex (Lowrie & Heller 1982). In addition to magnetite, other magnetic minerals including haematite,

goethite, and various iron sulphides have been detected (Lowrie & Alvarez 1975; Heller 1978). Indeed, detailed analysis of palaeomagnetism of a single bed of Cretaceous Scaglia-type pelagic limestone by Channell (1978) revealed anti-parallel components carried by magnetite and haematite. Because of low concentrations of magnetic minerals and difficulty of magnetic extraction, direct studies of the mineralogy of magnetic minerals in pelagic limestones by techniques such as Curie temperature analysis, optical microscopy, X-ray or microprobe analyses are rarely attempted. Two notable exceptions are the studies of Upper Cretaceous Scaglia Rossa limestones by Lowrie & Alvarez (1975) and deep sea sediments by Lovlie, Lowrie & Jacobs (1971). In both studies, the dominant ferromagnetic mineral was found to be magnetite.

Because of the difficulty of preparing representative magnetic extracts from pelagic limestones for more direct mineralogical analyses, less direct but more convenient techniques have generally been used. The most effective technique is a combination of acquisition and subsequent thermal demagnetization of isothermal remanent magnetism (IRM). Magnetite (or titanomagnetite) acquires IRM in magnetizing fields below 300 mT while haematite and goethite display much higher coercivities (Dunlop 1972). Thermal demagnetization of acquired IRM generally reveals a distribution of blocking temperatures below the Curie temperature of the dominant ferromagnetic mineral. In straightforward cases, acquisition and subsequent thermal demagnetization of IRM can be very effective in identifying the dominant ferromagnetic mineral.

Given the widespread application of the IRM technique, it is of interest to determine the correspondence between the IRM results and results of more direct analyses of magnetic extracts, such as Curie temperature determination by strong-field thermomagnetic analysis. We report here results of strong-field thermomagnetic analysis of magnetic extracts from Upper Jurassic and Lower Cretaceous pelagic limestones of France and Spain. IRM analyses were determined for samples from the same stratigraphic horizons as the bulk samples used for magnetic extraction so that direct comparisons between the different techniques are possible.

2 Experimental procedures

2.1 SAMPLE COLLECTION AND MAGNETIC EXTRACTION

Samples were collected from Upper Jurassic and Lower Cretaceous sections in SE France and in Spain. These sections have previously been the subject of magnetostratigraphic study (Galbrun 1984). The facies and localities of the nine samples studied are listed in Table 1.

The samples were crushed and the carbonate matrix was dissolved by placing them in a solution of acetic acid (10 per cent) until the production of CO_2 gas was negligible (2 or 3 weeks). After washing, the residual material was placed in an ultrasonic cleaner for about 10 min. The magnetic extraction was made by slowly circulating the residue and water slurry with a pump through a rubber tube which passed vertically through the pole pieces of a permanent magnet. The extraction took place over 2 or 3 days for each sample until further extraction of magnetic particles became negligible. The resulting separate was then dried. With this technique, significant amounts of paramagnetic and diamagnetic grains are also entrained so that the amounts of magnetic extract (Table 1) are not an accurate measure of the absolute concentration of ferromagnetic minerals. However, amounts of magnetic extract in comparison to original sample weights are similar to those described for deep-sea sediments (Lovlie *et al.* 1971). Although we did not carry out such analysis on a regular basis, comparison of room temperature saturation magnetization of magnetic extracts with

Table 1. Locations, descriptions, weights of bulk samples and magnetic extract fractions.

Sample	Facies type	Location	Sample weight (gm)	Calcium carbonate (%)	Magnetic fraction weight (gm)	Magnetic fraction percent (%)
BE041	Blue-gray micritic limestone	Berrias, Ardeche, France	611	93	.092	.015
BE049			786	98	.137	.017
PI006	Yellowish micritic limestone	Col du Pin, Drome, France	349	98	.331	.095
PI028			441	98	.228	.052
SF052	gray sandy limestone	Sierra de Foncalent, Province of Alicante Spain	534	91	.081	.015
SF203	gray-green marly limestone		821	81	.020	.002
SL022	"Ammonitico-Rosso" limestone	Sierra de Lugar, Province of Murcie, Spain	435	98	.097	.022
SL124	White micritic limestone		339	99	.271	.080
CV014	Black marly limestone	Mont Charvin, Savoie, France	764	87	.135	.018

All samples are of Berriasian age except SL022 (Oxfordian) and SF203 (Valanginian).

that of magnetite standards indicates concentrations of ferromagnetic minerals in the magnetic extracts can vary from as low as 25 per cent to as high as 90 per cent by weight. Given the difference in sediment types (unconsolidated deep sea sediments versus Mesozoic pelagic limestones), a more detailed comparison of the efficiency of the present extraction technique with that of Lovlie *et al.* (1971) does not seem warranted.

2.2 STRONG-FIELD THERMOMAGNETIC EXPERIMENTS

Principles of Curie temperature determination by strong-field thermomagnetic analysis (hereafter referred to as thermomagnetic analysis) using a microbalance have been discussed by Doell & Cox (1967) and Collinson (1983). The apparent increase in weight of the sample by application of a magnetic field is proportional to the magnetic moment (and therefore to the magnetization) of the sample. If the applied magnetic field is of sufficient strength (300 mT for magnetite), the magnetization of the ferromagnetic mineral will be saturated and the apparent weight increase produced by application of the magnetic field will be proportional to the saturation magnetization. Temperature dependence of the apparent weight increase thus reveals the temperature dependence of the saturation magnetization from which the Curie temperature should be clearly indicated. Given the much higher saturation magnetization of magnetite (4.8×10^5 A m^{-1} at 20°C) compared with haematite (2×10^3 A m^{-1} at 20°C), it will obviously be much more difficult to detect haematite than magnetite with thermomagnetic analyses.

The thermomagnetic analyses were performed using a Cahn 2000 recording microbalance interfaced to a microprocessor. Temperature and apparent weight are displayed in real time on an $X-Y$ plotter. The heating and cooling rate (nominally 10°C min^{-1}) as well as the maximum temperature are controlled by the microprocessor which also records the temperature and apparent weight data in memory. In addition, the microprocessor turns the

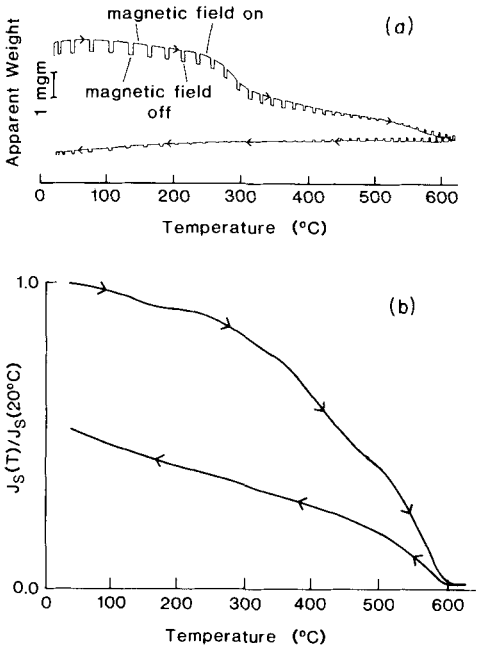

Figure 1. (a) Apparent weight versus temperature during thermomagnetic analysis in air of magnetic extract from sample SF052. Bar at left shows weight scale. Arrows show heating and cooling curve. Example parts of curve with magnetic field on and off are indicated. Negative weight with field on at high temperatures is due to diamagnetism of sample holder. Magnetic field strength was 200 mT. (b) Computer-processed thermomagnetic analysis. Base weight changes have been removed from raw data shown in (a) yielding normalized temperature variation of strong-field magnetization. Arrows indicate heating and cooling curve.

magnet off at prescribed intervals to allow monitoring of the sample base weight. The magnet used is a 10 cm diameter electromagnet equipped with constant gradient pole caps. The thermocouple is embedded in a dummy sample holder 0.5 cm below the sample holder which is suspended from the microbalance by a 0.013 cm diameter platinum wire. Sample holders are constructed of machinable ceramic. Following each experiment, the data file in microprocessor memory is shipped to a computer where the data are reduced to remove base weight changes by linearly interpolating between base weight readings.

With impure magnetic extracts containing clays, there are usually changes in base weight during the heating which can be many times the apparent weight change produced by application of the magnetic field. A typical example of the raw data from the thermomagnetic experiment on a magnetic extract from a pelagic limestone is illustrated in Fig. 1(a). Note that the change in base weight ('magnetic field off' points) between 200 and 350°C during heating is particularly dramatic and is several times the apparent weight change produced by application of the magnetic field. Fig. 1(b) illustrates the reduced data after removal of base weight changes. The dominant Curie temperature at 580–590°C is easily identifiable in the processed data. It is obvious that the base weight must be monitored carefully and changes in the base weight must be removed.

The thermomagnetic experiments were first performed in an atmosphere of argon gas because it was believed this might help to inhibit oxidation of fine-grained iron oxides. Experiments were also performed in vacuum of 10^{-4} torr. However, we found that

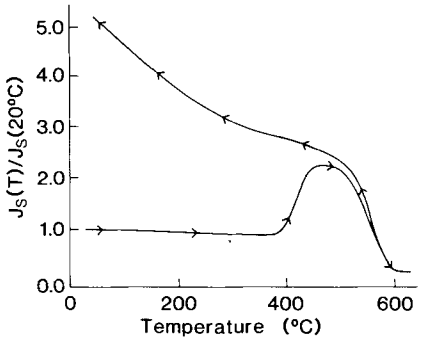

Figure 2. Thermomagnetic behaviour of magnetic extact from sample BE049 heated in 0.5 atm of argon gas. Magnetic field strength was 200 mT.

irreversible chemical changes resulting in production of magnetite were induced by heatings in argon gas and in vacuum. An illustration is given in Fig. 2. The increased magnetization observed during heating from 400 to 500°C is the result of production of magnetite in this temperature interval. Heatings in argon were thus abandoned and samples were heated in air. As shown in Fig. 1(b) and in the following thermomagnetic results, some oxidation did occur during heatings in air as evidenced by the lower magnetization during cooling than during heating.

3 Results

Fig. 3 illustrates the acquisition and subsequent thermal demagnetization of IRM for sample BE049 along with the results of thermomagnetic analysis of the magnetic extract. The IRM saturates in a magnetizing field of 300 mT and displays blocking temperatures distributed below 600°C suggesting that magnetite is the only significant carrier of IRM. The thermomagnetic analysis reveals a single Curie temperature indicating that magnetite is the only significant ferromagnetic mineral in the magnetic extract. Thus, results of all experiments on this sample indicate a straightforward mineralogy in which magnetite is the only significant ferromagnetic mineral. (The Curie temperature indicated by this experiment is apparently slightly in excess of 600°C rather than 585°C as anticipated for magnetite. This is an artefact of an experimental problem with thermocouple calibration which was subsequently remedied. Having expended the magnetic extract for this sample, we were unable to repeat this thermomagnetic analysis.)

In Fig. 4, we illustrate acquisition of IRM by sample PI028 and the thermal demagnetization of that IRM along with results of thermomagnetic analysis of the magnetic extract. The IRM results suggest a mineralogy of magnetic minerals which is more complex than encountered in the previous sample. Rapid acquisition of IRM up to 300 mT followed by increased IRM in higher magnetizing fields indicates the presence of considerable amount of high coercivity mineral(s) in addition to magnetite. Thermal demagnetization suggests the presence of three magnetic minerals. IRM decreases to about 50 per cent of its initial value upon thermal demagnetization to 100°C. Such behaviour is indicative of goethite (Lowrie & Heller 1982). Most of the remaining IRM has blocking temperatures distributed below 600°C as expected for magnetite, but blocking temperatures up to 680°C are observed indicating the presence of haematite. The strong-field thermomagnetic data do show Curie temperatures at both 585°C due to magnetite and at 680°C due to haematite. However,

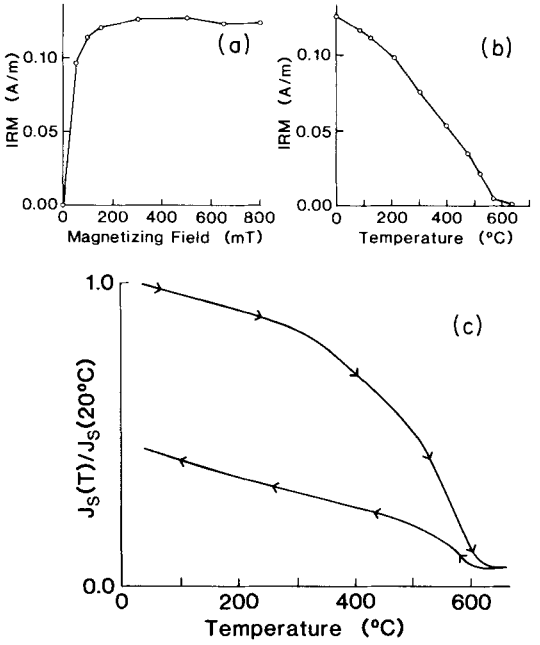

Figure 3. IRM acquisition (a) and thermal demagnetization of IRM (b) for sample BE049 compared with thermomagnetic analysis in air (c) of magnetic extract from the same sample. Magnetic field strength during thermomagnetic experiment was 300 mT.

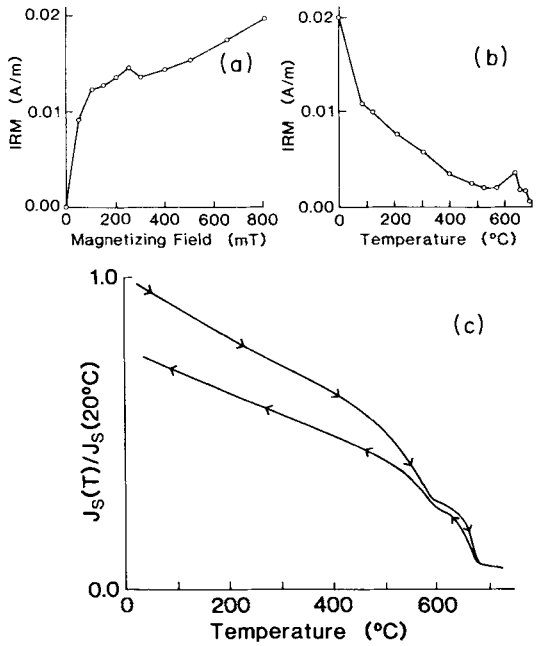

Figure 4. IRM acquisition (a) and thermal demagnetization of IRM (b) for sample PI028 compared with thermomagnetic analysis in air (c) of magnetic extract from same sample. Magnetic field strength in thermomagnetic experiment was 300 mT.

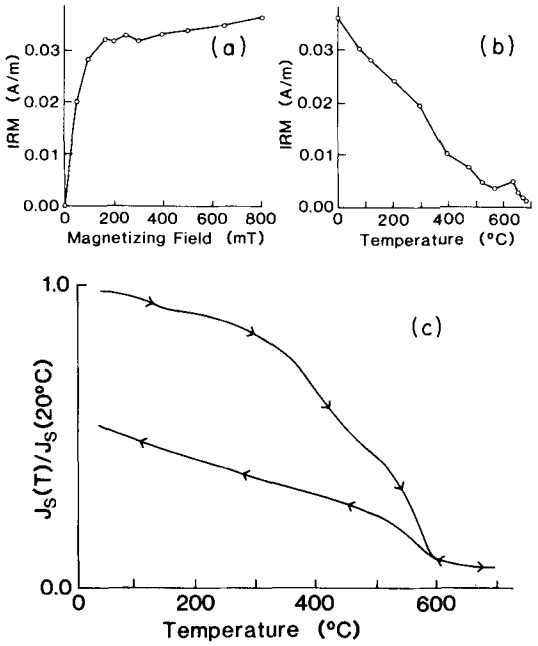

Figure 5. IRM acquisition (a) and thermal demagnetization of IRM (b) for sample SF052 compared with thermomagnetic analysis in air (c) of magnetic extract from same sample. Magnetic field strength in thermomagnetic experiment was 200 mT.

there is no indication of a goethite Neel temperature at 110–120°C (Hedley 1971). This inability to detect the presence of goethite could be either due to goethite not being efficiently extracted or due to the very low saturation magnetization of goethite. It is also possible that some of the haematite detected during the thermomagnetic analysis results from dehydration of goethite during the heating.

A final example is given in Fig. 5 which illustrates IRM results for sample SF052 along with thermomagnetic results on the magnetic extract. Again rapid acquisition of IRM in magnetizing fields up to 300 mT suggests a large proportion of magnetite while the slight increase above 300 mT indicates the presence of a high coercivity mineral. The proportion of this high coercivity mineral in sample SF052 is substantially less than that observed in PI028 (Fig. 4). Thermal demagnetization of IRM reveals blocking temperatures dominantly below the 585°C Curie temperature of magnetite but about 10 per cent of the IRM has blocking temperatures up to 680°C indicating a significant content of haematite. The thermomagnetic results show only the Curie temperature of magnetite. No Curie temperature is detected at 680°C. Failure of the thermomagnetic analysis on the magnetic extract to detect the haematite could again be due either to inefficient extraction of haematite or to the low saturation magnetization of haematite compared to magnetite.

With the exception of sample PI006 which showed Curie temperatures for both magnetite and haematite, all remaining magnetic extracts from samples listed in Table 1 showed only Curie temperatures of magnetite. It is noteworthy that thermomagnetic analysis on the magnetic extracts from the red 'Ammonitico Rosso' limestones did not detect haematite Curie temperatures, even though the magnetic extracts were visibly reddish. Again this is probably due to an inability to extract haematite efficiently (Butler 1982) and also due to the difficulty of detecting it during thermomagnetic analysis because of the low saturation

magnetization of haematite. IRM and thermomagnetic results for the Ammonitico Rosso samples were similar to those of samples from Sierra de Foncalent illustrated in Fig. 5.

4 Conclusions

The dominant, usually exclusive, Curie temperature detected by thermomagnetic analysis of magnetic extracts from these Upper Jurassic and Lower Cretaceous pelagic limestones is that of magnetite. Haematite is only detected when the IRM data suggest that it is present in substantial concentrations. In many samples for which the IRM data indicate significant haematite in addition to magnetite, only the magnetite is detected by thermomagnetic analysis of magnetic extracts. Although IRM data occasionally suggested the presence of goethite, no thermomagnetic analysis of magnetic extracts detected the Neel temperature of goethite. Thus acquisition and subsequent thermal demagnetization of IRM is indeed a very effective technique for determining the mineralogy of ferromagnetic minerals in sedimentary rocks, especially pelagic limestones. Not only does this convenient IRM technique detect the dominant ferromagnetic minerals evident from thermomagnetic analysis of magnetic extracts but it also is far superior in detection of high coercivity, weakly ferromagnetic minerals such as goethite and haematite. In addition to these advantages, the IRM technique does not require the special sample preparation necessary for thermomagnetic analysis.

Acknowledgments

We thank Kris McClellan, Wes Bilodeau, and Steve May for assistance. We are grateful to anonymous reviewers for critical readings of the manuscript. The work was carried out during a 6-month visit by B. Galbrun to Department of Geosciences, University of Arizona. This visit was financed by the French Ministry of External Relations. Funding was also provided by NSF grant EAR 8405360.

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