Efficiency of heavy liquid separation to concentrate magnetic particles

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Accepted 2007 May 7. Received 2007 May 7; in original form 2006 March 31

SUMMARY

Low-temperature rock magnetic measurements have distinct diagnostic value. However, in most bulk marine sediments the concentration of ferrimagnetic and antiferromagnetic minerals is extremely low, so even sensitive instrumentation often responds to the paramagnetic contribution of the silicate matrix in the residual field of the magnetometer. Analysis of magnetic extracts is usually performed to solve the problems raised by low magnetic concentrations. Additionally magnetic extracts can be used for several other analyses, for example electron microscopy or X-ray diffraction. The magnetic extraction technique is generally sufficient for sediments dominated by magnetite. In this study however, we show that high-coercivity components are rather underrepresented in magnetic extracts of sediments with a more complex magnetic mineralogy. We test heavy liquid separation, using hydrophilic sodium polytungstenate solution Na₆[H₂W₁₂O₄₀], to demonstrate the efficiencies of both concentration techniques. Low-temperature cycling of zero-field-cooled, field-cooled and saturation isothermal remanent magnetization acquired at room temperature was performed on dry bulk sediments, magnetic extracts, and heavy liquid separates of clay-rich pelagic sediments originating from the Equatorial Atlantic. The results of the thermomagnetic measurements clarify that magnetic extraction favours components with high spontaneous magnetization, such as magnetite and titanomagnetite. The heavy liquid separation is unbiased with respect to high- and low-coercive minerals, thus it represents the entire magnetic assemblage.

Key words: heavy liquid separation, magnetic extraction, marine sediments, rock magnetism.

1 INTRODUCTION

Rock magnetic investigations of marine sediments aim at unravelling depositional history and diagenetic changes of the magnetic mineralogy for geomagnetic and palaeoceanographic investigations. As a rule in marine sediments, mixed magnetic components occur in very low concentration, down to the ppm range. In addition, the grain size range of such particles spans from a few tens of micrometres down to the nanometres range.

Besides carbonates and silica, clay minerals are the most abundant non-ferrimagnetic components in the sediment, and may interfere with the performance of several non-magnetic mineral identification techniques, for example, microscopy or X-ray diffraction. Additionally, they are important for a proper interpretation of lowtemperature magnetic measurements of the bulk sediment, due to their paramagnetic behaviour. Because of their abundance, clay minerals may induce distinct magnetic moments even in the small residual fields prevailing in the magnetometer. Moreover, at temperatures below 25 K, paramagnetic (clay) minerals start to show collective magnetic behaviour that may give rise to appreciable magnetic moments (e.g. Coey 1988). Therefore, they attenuate diagnostic temperature-dependent transitions of ferrimagnetic and antiferromagnetic phases, such as the Verwey-, 34 K-, and Morin-transition of magnetite, pyrrhotite and hematite, respectively.

The standard tool to enhance the concentration of the magnetic fraction for various analyses is the magnetic extraction. Various extraction protocols exist (e.g. Petersen *et al.* 1986; von Dobeneck 1987; Dekkers 1988; Hounslow & Maher 1999). In some recipes carbonates are dissolved by leaching the bulk sample material in acetic acid (pH 4–5). Magnetic extraction can be easily applied to wet bulk sediments of marine origin which yield a reasonable amount of extracted magnetic material, that subsequently can be analysed, for example, with a sensitive Magnetic Properties Measurement System (MPMS) or in an electron microscope. The extraction duration and careful implementation is crucial for the extraction yield. Nevertheless, the amount of magnetic extract is generally still too low to allow easy mass determination with a (semi-)microbalance. This expounds problems of true quantification, required for budget calculations.

Hounslow & Maher (1996) presented a detailed quantitative study on magnetic extracts from a broad variety of sediment samples. The extraction efficiency was calculated by comparing before- and after-extraction rock magnetic measurements. They conclude that the extraction yield is strongly dependent on the magnetic mineralogy, the morphology of the magnetic particles, and the lithology of the bulk sediment sample. Comparisons of magnetic extract data with the original bulk sediment signal, in order to determine how representative the extract actually is, are not always feasible in practice. Magnetic extraction methods favour (rather strongly) ferrimagnetic mineral phases (mainly (titano-)magnetite, maghemite, pyrrhotite and greigite), being magnetically softer, over magnetically harder antiferromagnetic phases (such as hematite or goethite) (Dekkers 1988; Hounslow & Maher 1999). Extraction efficiencies of over 75 per cent were achieved by Hounslow & Maher (1996) for magnetite dominated sediments, but were rather low for sediments dominated by iron sulphides or high-coercive minerals efficiencies.

In this study, we explored heavy liquid separation on marine dry bulk sediments comprising complex magnetic mineralogies (Franke 2006; Franke *et al.* 2007b.) as an alternative extraction method to achieve a more complete 'magnetic' fraction, consisting of the heavy mineral portion (density $>3.0 \times 10^3$ kg m⁻³). This fraction should include all magnetic mineral phases present in the sample. Hydrophilic sodium polytungstenate solution Na₆[H₂W₁₂O₄₀] was applied, providing the possibility to separate the magnetic fraction in very fine-grained material, particularly in clay-rich samples.

Watery lithium heteropolytungsten solution with a density of 2.85×10^3 kg m⁻³ was advantageously used by Lagroix *et al.* (2004) to separate the magnetic Fe–Ti oxide fraction from the volcanic glass fraction in their tephra samples. This specific Old Crow tephra occurs intercalated in loess deposits at Halfway House in central Alaska. By classical gravity separation for 24 h, they managed to divide the magnetic fraction into the lighter volcanic glass (< 2.85×10^3 kg m⁻³) and the rest of the (coarser grained) magnetic Fe–Ti oxides (> 5.0×10^3 kg m⁻³). The heavy fraction represents between 0.5 and 1.5 per cent of the bulk sample mass. They argue that their light mineral fraction still contains most of the SP particles. The density separation certainly enhanced the possibilities to identify the Fe–Ti oxides in the heavy fraction, but concentrations in the light fraction were still high enough to magnetically identify its composition.

The overwhelming amount of paramagnetic components in marine sediments complicates the separation. Therefore, we use hydrophilic sodium polytungstenate solution with an even higher density of 3.0×10^{-3} kg m⁻³ in our study combined with ultrasonic dispersion and centrifuging techniques to 'purify' the magnetic fraction from the siliceous components in the bulk sediment. The advantage of this non-magnetic separation method is that all magnetic components are extracted regardless of their magnetic moment.

2 SAMPLE MATERIAL

The chosen sample suite includes six specimens from clayrich pelagic sediments of three gravity cores of a west–east profile throughout the Equatorial Atlantic. The gravity cores were recovered from the Ceará Rise (CER; GeoB 1523-1; $3^{\circ}50.8'$ N/41°36.6'W), the equatorial Mid-Atlantic Ridge (MAR; GeoB 4313-2; 4°02.8'N/33°26.3'W) and the Sierra Leone Rise (SLR; GeoB 2910-1; 4°50.7'N/21°03.2'W) during *RV Meteor* cruises M16/2, M29/3 and M38/1. This zone in the Equatorial Atlantic is presently oligotrophic (Funk *et al.* 2004b). The pelagic sediments of all three gravity cores are characterized as clay- and foram-bearing nannofossil oozes. Magnetic particles in these sediments originate from several distinct sources: continental eolian dust (Sahara), fluvial discharge (Amazon River) and submarine weathered ocean ridge basalts (Mid-Atlantic Ridge). Authigenic sources for magnetic particles include the biogenic formation of bacterial magnetosomes and the (inorganic) recrystallization of earlier iron sulphides (Franke 2006). For further details on gravity core localities and general settings see Schulz *et al.* (1991), Henrich *et al.* (1994), Fischer *et al.* (1998), Funk *et al.* (2004a,b) and Reitz *et al.* (2004).

Two discrete samples were processed from each of the three gravity cores, one corresponding to Marine Isotope Stage (MIS) 4, that is, a glacial stage, and the other to MIS 5.5 (Eemian), an interglacial stage. These samples, chosen for the detailed studies, represent typical conditions throughout the gravity cores. In glacial conditions a coarser magnetic inventory is found, while interglacial conditions are characterized by a finer magnetic grain size distribution (Funk *et al.* 2004a,b; Franke 2006; Franke *et al.* 2007b). So, the performance of magnetic separation procedures can be assessed for different compositions formed under contrasting climatic conditions. In the following, we will simply refer to these two time slices as 'glacial' and 'interglacial'.

3 MINERAL CONCENTRATION PROCEDURES

3.1 Magnetic extraction

Magnetic extraction was performed on 10 cm³ of the wet bulk sediment samples using the method of Petersen *et al.* (1986). The extraction run was usually stopped after 8–12 hrs per sample, when no visible gain in material was achieved anymore. The extracted particles were stored in small glass vials filled with ethanol. For MPMS measurements the fluid (containing the magnetic extract) was applied into a gelatine capsule, which was subsequently dried at room temperature, by evaporating the ethanol in air. Since the extracts were stored in ethanol, the application of the wet extract into the delicate gelatine capsules (that dissolve rapidly in water) poses no problems. Mass determination of the magnetic extracts with a semi-microbalance was not possible, since the typical amount of material is beyond the metering precision of a semi-microbalance ($d = 10^{-8}$ kg). Other, more detailed MPMS sample preparation aspects and instrumental settings are outlined in Frederichs *et al.* (2003).

3.2 Heavy liquid separation

Heavy liquid separation was performed on typically 0.8×10^{-3} kg of the freeze-dried bulk sediments (referred to as dry bulk sediment). After weighing, the samples were dispersed in 20 ml hydrophilic sodium polytungstenate solution (Na₆[H₂W₁₂O₄₀]), with a density of exactly 3.0×10^3 kg m⁻³ (manual shaking until no obvious clustering was visible anymore, followed by 10 min of ultrasonic bath agitation). Hereafter, the 50 ml plastic centrifuge vessels with the sediment-fluid suspension, were directly centrifuged for 5 min using a Heraeus Minifuge T at 4000 rps. During this process, the sediment-fluid suspension separates into a floating light sediment fraction (LF) with a density $<3.0 \times 10^3$ kg m⁻³, the so-called fluid mirror (= 3.0×10^3 kg m⁻³) in the middle of the centrifuge tube and a heavy sediment fraction (HF) at the bottom, with a density $> 3.0 \times$ 10³ kg m⁻³. If necessary, the 5 min centrifuge run was repeated without re-homogenizing the sample. The LF on top of the fluid mirror and the fluid mirror itself were separated from the HF using a special 10 ml precision pipette, and both fractions were suction filtered separately after separation. For filtration, cellulose acetate filters with 0.1 μ m pores were applied. Further rock magnetic measurements clearly indicate that the <0.1 μ m fraction was retained in the HF, presumably due to the clustering tendency of these particles (see Section 4). The sediment fractions were dried in air over night at room temperature, removed from the filters, weighed and placed in gelatine capsules for MPMS measurements.

3.3 Extraction efficiency

In Table 1, the mass of the starting material of the dry bulk sediment is given, in comparison with the mass of the light and heavy fractions resulting from the density separation. The heavy mineral fraction for this sample set ranged from 0.022 to 0.04×10^{-4} kg, typically 1.4 per cent of the starting bulk material. The discrepancy between starting material and the sum of light and heavy fractions stems from material remaining on the filters and can be further estimated by weighing the filters before and after the heavy liquid separation. A small fraction of the material is not removable from the filters anymore since it penetrates the filter membrane. The amount of material remaining on the filters is typically ~7.4 per cent and comparable for both density fractions.

The yield of the magnetic extracts for the same sample set using a much higher amount of starting material (10 cm^3 of wet bulk sediment) is much lower, and cannot be meaningfully mass quantified. With the exception of the magnetic extract measurements, all thermomagnetic curves are mass normalized (Table 2) in the following. An additional advantage of the sodium polytungstenate solution as a heavy liquid solution is its non-toxicity. Further, the separates can be flushed or washed extensively during filtration, due to the hydrophilic character of the sodium polytungstenate solution.

The extraction efficiency (Table 1) of both concentration techniques can be quantified by comparing the remanence values of the bulk sediment to the values from the respective residuals. In case of the magnetic extraction, the residuals were recovered from the suspension by simple drying in air. The residuals of the heavy liquid separation are represented by the light fraction. The efficiency for the magnetic extraction technique was calculated by the ratio of the mass specific IRM values (measured at 2.5 T and room temperature) for the bulk sediment (r_{BS}) and the respective residuals (r_{Res}) after the extraction run (see eq. 1). For the heavy liquid separation, the extraction efficiencies were derived by the ratio of the mass specific SIRM (measured at 5 T and 300 K) for the bulk sediment ($r_{\rm BS}$) and the respective light fractions $(r_{\rm LF})$ (see eq. 2). The magnetic extraction efficiencies range from 8 to 76 per cent whereas the efficiencies for the heavy liquid separation show values between 30 and 98 per cent.

$$\text{Efficiency}_{\text{magn.extration}} = 100 \times \left(1 - \frac{r_{\text{Res}}}{r_{\text{BS}}}\right)\%$$
(1)

Efficiency_{heavy.liquid.sep.} =
$$100 \times \left(1 - \frac{r_{\rm LF}}{r_{\rm BS}}\right)\%$$
 (2)

4 THERMOMAGNETIC OBSERVATIONS

4.1 Thermomagnetic measurements

For clarity the various thermomagnetic measurement types performed are summarized in Table 3. Low-temperature zero-fieldcooled (ZFC) and field-cooled (FC) measurements were performed within several weeks after drying the various extracts and separates, using a *Quantum Design XL7 Magnetic Properties Measurement System* (MPMS; noise level $\sim 10^{-11}$ Am²). Low-temperature

lable 1. Masses of starting	material, as well as the separ-	ated light and heavy fractions	, and the material on the niters	tor neavy liquid separation (gi	iven in per cent of the starting ma	terial).
àample	Mass of starting material (g)	Total mass light fraction (per cent)	Total mass heavy fraction (per cent)	Material on filters (per cent)	Magnetic extraction efficiency (per cent)	Heavy liquid separation efficiency (per cent)
GeoB 1523-1, 160 cm	0.85575	95.3	0.6	4.1	10.2	7.79
GeoB 1523-1, 311 cm	0.65728	89.8	1.4	8.6	53.9	45.0
GeoB 4313-2, 130 cm	0.68251	90.7	1.4	7.9	8.1	37.7
GeoB 4313-2, 245 cm	0.79249	89.4	2.8	7.9	75.7	39.6
GeoB 2910-1, 60 cm	0.97421	92.4	0.4	7.2	20.1	30.2
GeoB 2910-1, 141 cm	0.87386	89.7	1.7	8.6	29.7	45.7
The last two columns show	the efficiencies of magnetic e	xtraction and heavy liquid set	paration (for efficiency calcula	tion see Section 3.3).		

Table 2.	Masses of the	dry bulk	sediment,	light a	and heavy	r fraction	samples
used for	thermomagneti	ic measu	rements.				

Sample	Mass dry bulk	Mass light	Mass heavy
	sediment	fraction	fraction
	(g)	(g)	(g)
GeoB 1523-1, 160 cm	0.03153	0.0625	0.0050
GeoB 1523-1, 311 cm	0.02663	0.0609	0.0092
GeoB 4313-2, 130 cm	0.02806	0.0510	0.0096
GeoB 4313-2, 245 cm	0.03429	0.0288	0.0221
GeoB 2910-1, 60 cm	0.02902	0.0491	0.0041

These masses were applied for mass specific normalization. Measurements on dry bulk sediment were performed on identical material with sample masses given in the second column. Note that only a minor portion of the light fraction was used for MPMS measurements.

warming curves (5-300 K) were determined for dry bulk sediments, magnetic extracts, and heavy liquid separates, all monitored in 2 K increments. For the ZFC measurements, the field was applied at 5 K (in case of dry bulk sediments at 10 K) and switched off before warming back to 300 K, whereas for the FC measurements, the field was applied at 300 K throughout cooling and switched off before warming back to 300 K. Where appropriate, the first derivatives of both ZFC and FC remanences versus temperature were calculated (with a 6 K running average) in order to better visualize changes of the magnetic state during sample warming.

To test for the presence of high-coercivity components (specifically goethite) in the samples (see Section 4.3), dedicated heating experiments were performed. First of all, a portion of pristine dry bulk sediment samples was heated in air up to 340°C and subsequently cooled in zero-field back to room temperature. Afterwards, the same procedure for low-temperature ZFC and FC runs in the MPMS was performed. The original pristine and the heated bulk sediment samples were weighed before performing the low-temperature measurements; therefore, mass-normalized curves are directly comparable.

For identification of the high-coercivity component(s), additional high-temperature field cycling was performed on the dry bulk sediment samples, applying a 7 T field at room temperature. The samples were run in-field (FH) from 300 to 400 K (heating) and back to 300 K (cooling), followed by a zero-field (ZFH) cycle within the same temperature range. All high-temperature measurements using the MPMS were also monitored in 2 K increments. FH curves are corrected for the paramagnetic contribution of the sample. This was done by measuring the magnetic moment in fields between 4 and 7 T at room temperature, assuming linear behaviour between these fields. This assumption is reasonable because at room temperature paramagnetism is linear with field up to hundreds of Tesla. Goethite on the other hand is not entirely saturated in such fields (e.g. Rochette *et al.* 2005). However, the deviation of the in-field magnetization from linearity is small. Room temperature saturation isothermal remanent magnetization (RT-SIRM) measurements were performed on dry bulk sediments, magnetic extracts, and heavy liquid separates. A 5 T field was applied at RT, subsequently the sample was cycled from 300 to 5 K (cooling) and back to 300 K (warming) in zero-field, monitored in 2 K increments.

4.2 Low-temperature ZFC and FC results of dry bulk sediments

For all dry bulk sediment measurements, the low-temperature warming curves of ZFC and FC remanence did not show any pronounced remanence transitions (Fig. 1). A rapid decrease in ZFC and FC remanence between 10 and 40 K (corresponding to the local minimum in the respective first derivative curves) was observed for all six samples. A similar phenomenon was observed in partially oxidized magnetite of synthetic (Özdemir *et al.* 1993) as well as natural origin (Smirnov & Tarduno 2000). In the latter, co-existing ultrafinegrained superparamagnetic (SP) material is argued to occur. Passier & Dekkers (2002) discussed the possibilities of magnetic interaction, surface effects in very fine grains, or the presence of surface layers around coarser magnetic particles as other possible explanations for such behaviour.

The most important observation of all dry bulk sediment experiments was the remarkable discrepancy between corresponding ZFC and FC curves. These divergences are maximum at 10 K and disappear towards room temperature in our samples, as described also by Smirnov & Tarduno (2000). Divergences are generally larger in glacial samples (Figs 1a, c and e) than in interglacial samples (Figs 1b, d and f).

4.3 Heating experiments of dry bulk sediments

The hypothesis of the presence of goethite was tested by the heating experiments outlined in Section 4.1. The discrepancy between ZFC and FC curves decreased dramatically after heating. For most of the samples, ZFC and FC curves merge at temperatures >40–60 K (compare Fig. 1 with Fig. 2). Through its transformation to hematite, goethite is chemically removed from the sediment by heating to 340° C. Therefore, the low-temperature ZFC-FC divergence and its substantial decrease after the heating to 340° C is interpreted as being related to goethite.

Further high-temperature remanence measurements (see Section 4.1) were performed to confirm this interpretation and check for the possibility of thin maghemitized surface layers of magnetite grains (van Velzen & Zijderveld 1992, 1995; van Velzen & Dekkers 1999a,b). All ZFH and FH curves and their first derivatives (Figs 3 and 4) show a drop at 390 K (\sim 117°C), indicating the Néel point of goethite (e.g. Hedley 1971; Dekkers 1989). The original non-smoothed raw data (not shown here) confirms a clear decreasing trend of the curve around that temperature. Due to instrumental

Table 3. Summary of all thermomagnetic measurements performed on bulk sediments, magnetic extracts, light and heavy fractions.

	ZFC	FC	RT-SIRM	FH	ZFH
Applied field (T)	5	5	5	7	7
Temperature range (K)	5 (10) to 300	5 (10) to 300	300 to 5	300 to 400	300 to 400
Temperature increment (K)	5	5	5	2	2
Cooling/warming rates (K/min)	2	2	2	2	2

The numbers in brackets give the starting temperature for the bulk sediment samples. ZFC = zero-field-cooled remanence, FC = field cooled remanence, FH = field-heated magnetization, ZFH zero-field-heated remanence, RT-SIRM = room-temperature saturation isothermal remanent magnetization.



Figure 1. Low-temperature ZFC and FC remanent magnetization curves for six dry bulk sediment samples (solid line = ZFC, dashed line = FC) along an Equatorial Atlantic west–east profile (from top to bottom). Glacial samples are shown on the left (scaled to a maximum value of 28×10^{-3} Am² kg⁻¹) and interglacial samples are shown on the right (scaled to a maximum value of 12×10^{-3} Am² kg⁻¹), for instrumental settings see Table 3. The first derivatives are given in grey, filled symbols for ZFC and open symbols for FC.

restrictions the maximum temperature available is 400 K, but the characteristic drop just below this temperature is not caused by an instrumental setting and varies slightly in temperature for each sample. During cooling of the ZFH curves (Fig. 3) no new remanence should be acquired by the samples, due to the lack of an inducing field. The minor remanence acquisition in some of the ZFH cooling curves is caused by a small remaining field (in the order of \sim 150 μ T), which is still present after the quenching of the MPMS magnet (Kosterov et al. 2006). The FH heating curves show a characteristic Hopkinson peak at 360 K (~87°C, e.g. Heller 1978) for most of the samples (Figs 4c-f weakly expressed in Fig. 4a). This feature is even more prominent in the first derivative curves of the FH of samples from GeoB 4313-2 (Figs 4c and d). Note that the intensities of the samples increase after heating above the Néel point of goethite. This is a further indication that indeed most likely some goethite is present in these samples.

4.4 Low-temperature ZFC and FC results of magnetic extracts

Due to the low amount of magnetic extract, the curves (both ZFC and FC) have been simply normalized to the ZFC value at 5 K.

The ZFC and FC curves depict a slightly broadened Verwey transition at \sim 110 K for the samples from the westernmost and the central equatorial sediment cores (GeoB 1523-1 and GeoB 4313-2; Figs 5a–d). No Verwey transition was observed for GeoB 2910-1, the easternmost site (Figs 5e and f). The shift to lower transition temperatures is indicative of non-stoichiometric slightly oxidized magnetite (Özdemir *et al.* 1993; Kosterov 2003).

The evident discrepancy between ZFC and FC warming curves in the dry bulk sediments was not observed in the magnetic extract data (compare Fig. 1 with Fig. 5). ZFC and FC warming curves of the magnetic extracts diverge only between 5 and 30 K. They are more or less merged at temperatures from \sim 110 K up to room temperature (see also Smirnov & Tarduno 2000). The substantially reduced ZFC-FC divergence in the magnetic extracts as compared to the bulk material would comply with the (near) absence of goethite in the magnetic extracts, because magnetic separation is biased towards strongly magnetic low-coercivity material.

4.5 Low-temperature ZFC and FC results of heavy liquid separates

Low-temperature warming curves of ZFC and FC remanence of the separated heavy fraction are overall an order of magnitude higher



Figure 2. Low-temperature ZFC and FC remanent magnetization curves for six pristine dry bulk sediment samples (solid line = ZFC, dashed line = FC) from west to east (from top to bottom) in comparison with the cross symbols, which refer to dry bulk sediments previously heated to 340° C; cross symbols for ZFC warming, x-symbols for FC warming curves. Samples from the glacial stage are shown on the left, samples from the interglacial stage are shown on the right (for scaling compare Fig. 1). For instrumental settings see Table 3. Note the very slight offset at ~300 K of the heated bulk sediment set of curves, which is assumed to originate from an instrumental offset and is disregarded here. All curves are normalized to their respective sample mass (Table 2).

in intensity than those of the dry bulk sediments (Fig. 6). The ZFC and FC warming behaviour of the light fractions does not show any characteristic features and is, therefore, not shown here. The heavy fractions show a very distinct steep slope between 5 and 40 K, corresponding to the sharp change of slope in the respective first derivatives. This might be due to the presence of an ultrafine-grained superparamagnetic (SP) phase (Özdemir *et al.* 1993; Smirnov & Tarduno 2000). The Verwey transition at ~110 K was exclusively detected in the westernmost samples of core GeoB 1523-1 (Figs 6a and b), it is weakly expressed in the first derivatives of the corresponding ZFC and FC curves.

The discrepancy between ZFC and FC curves mentioned earlier, which is interpreted to be caused by the presence of goethite, is much more prominent in the heavy fractions than in the magnetic extracts (compare Figs 5 with Fig. 6). However, the discrepancy is less strong than that in the dry bulk sediment samples (compare Fig. 1 with Fig. 5). Therefore, the high-coercivity fraction is partly successfully extracted during the heavy liquid separation. This presence of the high-coercivity component might also be the reason for the blurring of the Verwey transition earlier detected in the Mid Atlantic Ridge samples. The heavy liquid separation is not biased towards magnetite in comparison to titanomagnetite or goethite, thus the curves of the heavy fraction represent better the entire magnetic assemblage.

4.6 RT-SIRM cycling results

4.6.1 Dry bulk sediments compared with heavy liquid separates

Fig. 7 shows the RT-SIRM curves of the bulk sediment (BS) samples compared to the heavy (HF) and light fraction (LF) derived from heavy liquid separation. During cooling, the remanence of all dry bulk sediments ('BS' curves in Fig. 7) increases gradually from 300 K down to 10 K. The increase is distinctly enhanced below 10 K for most of the samples. On warming, the curves duplicate the corresponding cooling curves back to \sim 150 K. Above 150 K the warming



Figure 3. High-temperature cycling of the dry bulk sediments in zero-field (ZFH, solid line), for instrumental settings see Table 3. Grey shaded areas mark the sharp drop in remanence at 390–395 K. Filled symbols show the first derivative of the ZFH heating curve. Note that the ZFH cycle was performed after the FH cycle (compare Fig. 4). All curves are normalized to their respective sample mass (Table 2). The magnetic non-goethite amount are established by linear extrapolation (dashed lines, after Dekkers 1989) of the decay curve from temperatures above the bending point (vertical bold arrows).

curves are below the cooling curves. No specific magnetic transitions were noted in the dry bulk sediment measurements.

The remarkable increase in remanence occurring in the very low temperature range between 10 and 5 K can also be observed in the room temperature SIRM curves of the light fraction (LF; Figs 7a–f). Therefore, it is most likely due to low-temperature magnetic ordering of paramagnetic (clay-)minerals (Coey 1988). Because the residual field of the MPMS is very low, this lowtemperature ordering of the clay minerals in zero-field could be caused by the SIRM residing in magnetic mineral phases. This could magnetically couple to, for example, clay mineral coatings or ferrihydrite in the direct vicinity of the magnetic particles. Transmission electron microscopic (TEM) investigations of the samples support the presence of such mineral phases (Franke 2006; Franke *et al.*

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2007b). This would also suggest that the LF still contains part of the very fine-grained SP fraction.

Usually the shape of the LF curves is quite similar to that of the dry bulk sediment curves (Fig. 7; compare LF and BS). Generally, they show a less steep slope towards lower temperatures and a weaker total intensity. No specific magnetic transitions are detected in the LF. This seems reasonable, because the heavy magnetic minerals are present in the HF (and of course in the dry bulk sediments), whereas the LF should be dominated by the lighter non-magnetic mineral fraction, such as clays, silicates, carbonates, etc.

If the separation would be 100 per cent successful, the LF would not carry any magnetic remanence and, therefore, would show a purely paramagnetic low-temperature curve. In practice, the



Figure 4. High-temperature cycling of induced magnetization of pristine dry bulk sediments (FH, solid line) for instrumental settings see Table 3. The FH magnetization curves are corrected for the paramagnetic contribution. According to the Curie-Weiss-Law, the paramagnetic contribution is linear with the inverse of the absolute temperature. It was calculated from field-dependent measurements of the dry bulk sediments between 4 and 7 T at room temperature (not shown here). Open symbols show the first derivatives of the FH heating curves. Grey shaded areas indicate the position of the Hopkinson peak in FH heating curves between 370 and 380 K in samples from core GeoB 4313-2. Cooling curves of the FH measurements show an increase in induced magnetization at room temperature, except for sample GeoB 1523-1, 160 cm. All curves are normalized to their respective sample mass (Table 2).

separation is 30–97 per cent efficient. Therefore, we see the signal of a minor antiferromagnetic component in the LF, possibly mingled with a lesser ferrimagnetic contribution.

The RT-SIRM curves of the HF (Fig. 7) show characteristic lowtemperature curves for (titano-)magnetite (Özdemir *et al.* 2002; Kosterov 2003; Lagroix *et al.* 2004; Özdemir & Dunlop 2003; Garming *et al.* 2007), although we realize that RT-SIRM behaviour of (titano-)magnetites is not really well covered in the literature. Comparison of our HF curves with the titanomagnetite results from Özdemir & Dunlop (2003), Lagroix *et al.* (2004) and the RT-SIRM curves of Engelmann *et al.* (personal communication, 2006) from synthetic Fe-Ti oxide phases of various well defined Ti-content (Lattard *et al.* 2005) confirm the presence of (slightly oxidized) magnetite, various titanomagnetite, and titanohematite components in our samples. The occurrence of various Ti-Fe oxides is expressed by several minor changes of the cooling curve slope between 240 and 180 K (Figs 8a–f). The undulations in the cooling curves above \sim 210 K should document the low-temperature magnetic ordering of titanohematite, induced by the room temperature remanent magnetization of the intergrown titanomagnetite phase (Garming *et al.* 2007). The undulations detected on cooling below 210 K can be explained as magnetoelastical domain wall pinning postulated for this temperature range by Özdemir & Dunlop (2003).



Figure 5. Low-temperature ZFC and FC remanence warming curves for magnetic extracts of all six samples from the west to east profile (from top to bottom). Lines refer to the ZFC and FC warming curves of the magnetic extract (solid line = ZFC, dashed line = FC), for instrumental settings see Table 3. Curves are normalized to the magnitude of the respective ZFC value at 5 K (given for each individual panel). Grey squares refer to the first derivatives of the remanence curves (filled symbols = slope of ZFC, open symbols = slope of FC). All ZFC and FC curves have the same ordinate scale.

4.6.2 Magnetic extracts compared with heavy liquid separates

Fig. 8 shows the RT-SIRM curves of the magnetic extracts compared to the HF. For the sake of comparison, all curves were normalized to their value at 300 K. The RT-SIRM curves of the magnetic extracts (ME) clearly show ferrimagnetism-dominated curves, typically of magnetite (Özdemir et al. 2002; Kosterov 2003). The cooling and warming ME curves are more or less reversible in the temperature range between 5 and 110 K. The relative changes of the remanence loss (derived from the absolute values) during the complete cooling-warming-cycle are only subtle. Generally samples from the westernmost sediment core (CER; Figs 8a and b) show remanence losses of ~ 9 per cent, the samples from the Mid-Atlantic Ridge site (Figs 8c and d) result in \sim 8 per cent remanence loss and the easternmost samples (SLR; Figs 8e and f) have the largest remanence losses of ~ 13 per cent. The smooth increase with decreasing temperature in the HF curves, caused by the high-coercivity component, is not present in the magnetic extract curves. Comparing the

differences between 125 and 105 K for both types of curves (ME and HF) shows that this drop in remanence – which is closely related to the presence of magnetite – is two times larger in the magnetic extracts relative to the HF curves.

All cooling branches of the RT-SIRM curves (Fig. 8) of the HF show this continuous increase with decreasing temperature if one compares the initial value at 300 K and the value at 5 K. Vice versa, the reversed trend is observed in the RT-SIRM warming branches of the HF curves. This effect is attributed to the goethite component discussed before (Lowrie & Heller 1982; Dekkers 1989). The general shapes of the RT-SIRM curves of the HF were already briefly described before.

The RT-SIRM cycles of the interglacial HF samples of the cores GeoB 4313-2 and GeoB 2910-1 (Figs 8d and f) rather demonstrate curves characteristic for very Ti-rich oxide phases (Engelmann *et al.* personal communication, 2006) showing a reversing remanence behaviour during cooling and warming between 110 and 5 K. This is also expressed in the remanence loss behaviour of the HF



Figure 6. Low-temperature ZFC and FC remanence warming curves for the heavy fractions of the heavy liquid separates of the six samples from the west to east profile (from top to bottom). Lines refer to the ZFC and FC warming curves of the heavy fraction (solid line = ZFC, dashed line = FC), for instrumental setting see Table 3. Grey triangles refer to the first derivative of the respective remanence curves (filled symbols = slope of ZFC, open symbols = slope of FC). All curves are normalized to their respective sample mass (Table 2).

samples (calculated from the respective initial and final absolute values): the westernmost sediment core GeoB 1523-1 shows a remanence loss of ~15 per cent (Fig. 8b) for the interglacial sample, comparable to the remanence loss of ~12 per cent for the interglacial samples from the Mid Atlantic Ridge (GeoB 4313-2; Fig. 8d) and the easternmost core (GeoB 2910-1; Fig. 8f). In contrast, the glacial samples of cores GeoB 1523-1 (Fig. 8a), GeoB 4313-2 (Fig. 8c), and GeoB 2910-1 (Fig. 8e) have the largest remanence loss of 25–35 per cent. This corresponds with findings of Özdemir *et al.* (2002), who describe an increasing remanence loss for stoichiometric magnetite of increasing grain size.

5 DISCUSSION

The expression of the Verwey transition in the ZFC and FC curves in the magnetic extracts can be totally suppressed by oxidation/maghemitization of z = 0.3 (e.g. Özdemir *et al.* 1993) or by a fairly low Ti-content of $x \ge 0.04$ in magnetite (e.g. Kakol *et al.* 1994). The Ti-content is expressed by the characteristic shape of the RT-SIRM curves of the HF from GeoB 4313-2 and GeoB 2910-1 as earlier discussed in Section 4.6. SEM observations, using element dispersive spectroscopy (Goldstein *et al.* 1992), confirm the differ-

ent Ti-content in the magnetic mineral assemblage of these sediments (Franke 2006; Franke *et al.* 2007b). In addition, accessory Ti-rich titanohematite particles have been identified with electron backscatter diffraction techniques (Franke *et al.* 2007a).

The magnetic extracts do not contain much of the high-coercivity component. Therefore, they mainly express the low-temperature behaviour of the low-coercivity fraction in the magnetic assembly. ZFC and FC warming curves of the interglacial samples have a slightly steeper slope than those of the glacial samples. This indicates a finer magnetic grain size of the low-coercivity fraction, which concurs with other magnetic grain size observations in the dry bulk sediment measurements.

In the heavy liquid extraction procedure high-coercivity components, such as goethite, were successfully extracted and contribute distinctly to the characteristics of the magnetic signal. In particular the RT-SIRM curves offer additional mineralogical and grain size information, which was not detected by the low-temperature SIRM curves. Therefore, low-temperature measurements on marine sediments using the heavy fraction might result in more detailed curves of more complete and quantitative samples. Comparison of the results from the glacial and interglacial samples showed that the HF distinguished between their coarser and finer magnetic



Figure 7. Zero-field cycles of room temperature SIRM curves for the pristine dry bulk sediment samples (BS; filled dots), heavy fractions (HF; black triangles), and light fractions (LF; open diamonds) originating from the heavy liquid separation for the six samples from the west to east profile (from top to bottom). Samples from the glacial stage are shown on the left, samples from the interglacial stage are shown on the right. The BS and LF curves refer to the respective left ordinate axes, HF curves to the respective right ordinate axes. All curves are normalized to their respective sample mass (Table 2).



Figure 8. Comparisons of the zero-field cycles of RT-SIRM for the heavy fractions (HF; black triangles) and the magnetic extracts (ME; open squares) of the six samples from the west to east profile (from top to bottom). ME curves are clearly dominated by the soft component magnetite, where as the HF curves show a steeper slope due to the high coercivity component goethite. Further detailed transitions in the temperature range between 240 and 180 K corresponding to the various present Fe-Ti phases. All ME and HF curves are normalized to the value of the respective ZFC curve at 300 K as weight normalization was not meaningful in case of the ME samples. The magnetically coarser samples from the glacial stage are shown in the left column and the magnetically finer samples from the interglacial stage are shown in the right column.

inventory and also showed a clear west–east trend in dependence of the Ti-content. Funk *et al.* (2004a) described the magnetic grain sizes of MIS 4 (glacial) as much coarser than those of MIS 5.5 (interglacial). This concurs with the reasoning that the (enhanced) presence of SP material is coupled to an increased discrepancy of ZFC and FC curves for the interglacial samples. Another reasonable explanation of these ZFC and FC curve discrepancies was found in the temperature-dependent behaviour of goethite (Smirnov & Tarduno 2000). In this study, we are dealing with natural samples of obviously complex compositions and grain size distributions and, therefore, our RT-SIRM curves reflect the features of all present components in a non-trivial manner. The absence in the HF measurements of the ferrimagnetic ordering of paramagnetic material at very low temperatures confirms the success in separating the diaand paramagnetic fraction from the ferrimagnetic and antiferromagnetic fractions.

When comparing both extraction methods, the magnetic extract (nearly) exclusively represents the soft magnetic components of the dry bulk sediment. Within the range of soft magnetic components, magnetite has the highest spontaneous magnetization and is, therefore, preferably extracted by methods such as described by Petersen *et al.* (1986) or Dekkers (1988). Additionally, the magnetic extraction leads generally to extracts that are relatively coarsergrained than the starting bulk sediment.

The extraction efficiencies presented in Table 1 show that the yield of the extraction is strongly dependent on the lithology of the starting material (particularly of its clay-mineral content), the prevailing magnetic mineral assemblage, and its grain size distribution. Quantification by performing before- and after-extraction magnetic measurements is, therefore, strongly influenced by the proportion of low- to high-coercive magnetic components in the resulting concentrate. Even if the concentration of goethite in a sample is much higher than that of (titano-)magnetite, the magnetization still is mainly carried by the low-coercive mineral fraction. Therefore, the extraction efficiency of the heavy liquid separation can be regarded as an 'absolute' efficiency because both coercivity fractions are equally extracted from the bulk sediment sample. The efficiency for the magnetic extraction technique is rather a 'maximum' efficiency, since it prefers the low-coercive fraction. This has to be kept in mind when comparing the results of both concentration techniques.

Any sample concentration technique can potentially alter the original material. For marine sediments from suboxic or anoxic environments, this could actually cause undesired oxidation of iron sulphide mineral phases (e.g. greigite or pyrite). If the samples are suspended in a sediment slurry, the suspension should be deoxygenized by purging with an inert gas. This can be achieved by performing the upgrading in a closed cycle under argon atmosphere and the usage of ethanol instead of water as suspension medium.

Non-toxic sodium polytungstenate solution Na₆[H₂W₁₂O₄₀] does not react with the sample material and causes no additional oxidation. Its hydrophilic character allows to disperse the relatively clay-rich homogenized dry bulk sediment reasonably well without usage of any additional peptiser. No chemical leaching had to be used, so the risk of alteration or even dissolution, particularly of the magnetic nanoparticles can be disregarded. The combination of heavy liquid separation, mechanical and ultrasonic agitation, and centrifuging accelerates the gravity separation method and leads to generally better results for marine sediment samples, avoiding clustering problems due to high clay content. The light fraction always serves as a control measure for the success of the separation. Alternatively, as shown in Lagroix et al. (2004), the specific density of the heavy liquid can be easily adjusted so that slightly different magnetic fractions can be separated. In case of presence of paramagnetic heavy minerals, such as barite or siderite, these minerals are evidently included in the heavy fraction and have to be taken into account during low-temperature measurements (Frederichs et al. 2003).

The magnetic results for the heavy liquid separates presented here, confirm that the heavy fraction represents the complete magnetic inventory to a reasonable extent. Using this technique, a much larger amount of magnetic material is available for measurements, which can be sufficiently quantified. The success of the separation is generally dependent on the grain size distribution of the magnetic inventory. Especially components such as ultrafine SP material remain difficult to extract completely. (1) Magnetic extracts are not always representative of the magnetic inventory in bulk sediments. Soft ferrimagnetic material is overrepresented in the extract. Vice versa, much more weakly magnetic (antiferromagnetic) material, is underrepresented. This has to be kept in mind during interpretation of the mineral magnetic data, for example, low-temperature remanence curves.

(2) Heavy liquid separation (with sodium polytungstenate solution) is a useful tool to achieve a more complete 'magnetic' extract. It is as straightforward as magnetic extraction, both methods do not demand much experimental time. Heavy liquid separation allows the quantification of the resulting heavy and light mineral fractions and leads to larger yields of 'magnetic' extracts in particular for clay-rich material. Applied to fine-grained unconsolidated marine sediments, the combination of a hydrophilic heavy liquid (polytungstenate) dispersion with ultrasonic waves and subsequent centrifuging was very successful in separating the lighter dia- and paramagnetic mineral fraction from the heavy ferrimagnetic fraction. In sediments with appreciable non-ferrimagnetic heavy minerals, these will be included in the heavy liquid separate as well.

(3) Comparison of the glacial and interglacial samples showed that the heavy liquid extraction improves in quality with increasing magnetic grain size. However, even very fine material is still reasonably well extracted.

(4) The RT-SIRM curves turned out to be the most indicative measurements for our marine sediment samples. Due to the variable Ti-content of the magnetite particles these curves are more diagnostic in comparison to LT-ZFC and FC warming curves. Nevertheless, we recommend a combination of both remanence measurements for the sake of completeness and understanding of the low-temperature rock magnetic analysis.

ACKNOWLEDGMENTS

The authors would like to thank Mark Hounslow and France Lagroix for their helpful reviews. The heavy liquid separation was performed at facilities of the Marine Geochemistry section, University of Bremen, we would like to thank particularly Michael Schweizer and Natascha Riedinger for their assistance. TC-Tungsten Compounds Enterprises provided advice and heavy liquid solution for test runs. We also owe thanks to the members of the Marine Geophysics section (University of Bremen) and the Palaeomagnetic Laboratory (Utrecht University) for their support and advice. Financial support of CF was provided by the DFG through the European Graduate College EUROPROX, (Universities of Bremen and Utrecht) and by NWO through the VMSG, Vening Meinesz Research School of Geodynamics (Utrecht University). This investigation is also associated to the Research Center Ocean Margins (RCOM publication no. 0504) at the University of Bremen.

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