

Low-temperature partial magnetic self-reversal in marine sediments by magnetostatic interaction of titanomagnetite and titanohematite intergrowths

J. F. L. Garming,^{1,2} T. von Dobeneck,^{1,3} C. Franke^{1,4} and U. Bleil¹

¹Department of Geosciences, University of Bremen, Germany. E-mail: linda.garming@tno.nl

²TNO Geological Survey of the Netherlands, Utrecht, The Netherlands

³Research Center Ocean Margins, University of Bremen, Germany

⁴Paleomagnetic Laboratory 'Fort Hoofddijk', Utrecht University, The Netherlands

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SUMMARY

With various low-temperature experiments performed on magnetic mineral extracts of marine sedimentary deposits from the Argentine continental slope near the Rio de la Plata estuary, a so far unreported style of partial magnetic self-reversal has been detected. In these sediments the sulphate–methane transition (SMT) zone is situated at depths between 4 and 8 m, where reductive diagenesis severely alters the magnetic mineral assemblage. Throughout the sediment column magnetite and ilmenite are present together with titanomagnetite and titanohematite of varying compositions. In the SMT zone (titano–)magnetite only occurs as inclusions in a siliceous matrix and as intergrowths with lamellar ilmenite and titanium-rich titanohematite, originating from high temperature deuteric oxidation within the volcanic host rocks. These abundant structures were visualized by scanning electron microscopy and analysed by energy dispersive spectroscopy. Warming of field-cooled and zero-field-cooled low-temperature saturation remanence displays magnetic phase transitions of titanium-rich titanohematite below 50 K and the Verwey transition of magnetite. A prominent irreversible decline characterizes zero-field cooling of room temperature saturation remanence. It typically sets out at ~210 K and is most clearly developed in the lower part of the SMT zone, where low-temperature hysteresis measurements identified ~210 K as the blocking temperature range of a titanohematite phase with a Curie temperature of around 240 K. The mechanism responsible for the marked loss of remanence is, therefore, sought in partial magnetic self-reversal by magnetostatic interaction of (titano–)magnetite and titanohematite. When titanohematite becomes ferrimagnetic upon cooling, its spontaneous magnetic moments order antiparallel to the (titano–)magnetite remanence causing an drastic initial decrease of global magnetization. The loss of remanence during subsequent further cooling appears to result from two combined effects (1) magnetic interaction between the two phases by which the (titano–)magnetite domain structure is substantially modified and (2) low-temperature demagnetization of (titano–)magnetite due to decreasing magnetocrystalline anisotropy. The depletion of titanomagnetite and superior preservation of titanohematite is characteristic for strongly reducing sedimentary environments. Typical residuals of magnetic mineral assemblages derived from basaltic volcanics will be intergrowths of titanohematite lamellae with titanomagnetite relics. Low-temperature remanence cycling is, therefore, proposed as a diagnostic method to magnetically characterize such alteration (palaeo-)environments.

Key words: diagenesis, low-temperature, magnetic interaction, marine sediments, self-reversal, titanohematite, titanomagnetite.

1 INTRODUCTION

Sediments from the Argentine continental slope off the Rio de la Plata estuary have recently been analysed in detail for geochemical

and rock magnetic characteristics by Riedinger *et al.* (2005) and Garming *et al.* (2005), respectively. The principal source of their detrital magnetic mineral fraction is the drainage area of the Rio de la Plata tributaries in the Mesozoic flood basalts of the Paraná Basin

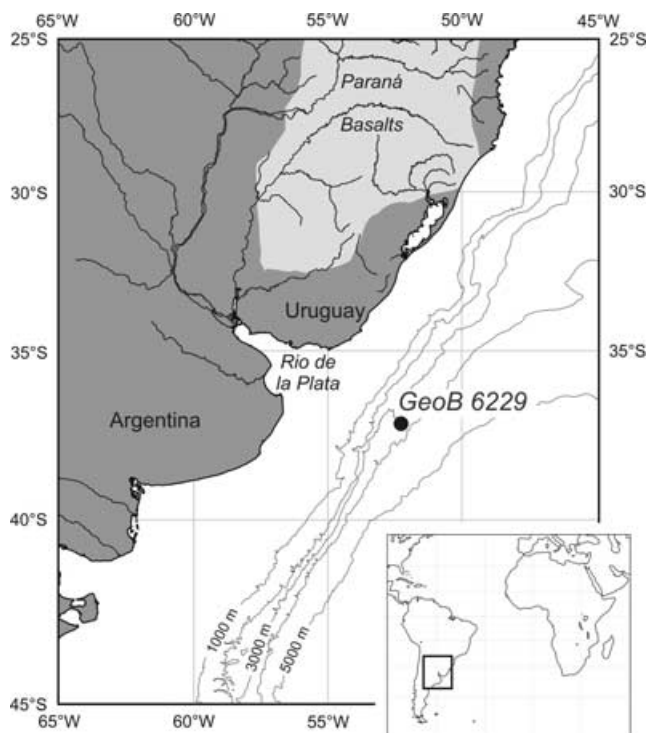


Figure 1. Location of core GeoB 6229 at the South American continental margin off the Rio de la Plata estuary. Light grey shading schematically outlines the Mesozoic flood basalts of the Paraná Basin (Peate *et al.* 1992). Isobaths at 1000 m intervals are according to GEBCO.

(Fig. 1). Main carriers of natural remanent magnetization of these basalts are magnetite and low Ti bearing, slightly maghemitized titanomagnetite (Kosterov *et al.* 1998; Tamrat & Ernesto 1999).

At gravity core location GeoB 6229 (37°12.4'S/52°39.0'W, 3446 m water depth; Schulz *et al.* 2001) suboxic conditions are established close to the sediment surface and anaerobic oxidation of methane (AOM) is observed in a few metres sediment depth (Riedinger *et al.* 2005; Fig. 2). In this distinct redox zonation the magnetic iron oxide mineral inventory undergoes a two-stage diagenetic alteration. At the iron redox boundary in the uppermost metre, about one quarter of the bulk ferrimagnetic mineral content has been dissolved resulting in a significant coarsening of magnetic grain size and diminishing of bulk coercivities (Garming *et al.* 2005). Such reductive diagenesis in the suboxic zone is a common and frequently studied phenomenon in organic-rich marine sediments (e.g. Karlin & Levi 1983; Canfield & Berner 1987; Karlin 1990a,b; Funk *et al.* 2004a,b). In contrast, the diagenetic processes in the more intensely reducing environment of the sulphate–methane transition (SMT) zone surrounding the AOM have been scarcely investigated so far.

In the present example, only a small fraction (<10 per cent) of the primary (titano-)magnetite escaped dissolution being protected either as inclusions in a siliceous matrix or as relic intergrowths with high titanium content and well-preserved titanohematite lamellae (Garming *et al.* 2005). A greater stability of Ti bearing oxides relative to pure Fe oxides (e.g. Karlin 1990b; Emiroglu *et al.* 2004) can be plausibly explained by the fact that every Ti^{4+} substitution in Fe oxides lowers twofold the number of Fe^{3+} cations acting as electron acceptors under anaerobic conditions. In case of substantial Ti^{4+} substitution, the remaining iron is almost entirely in the

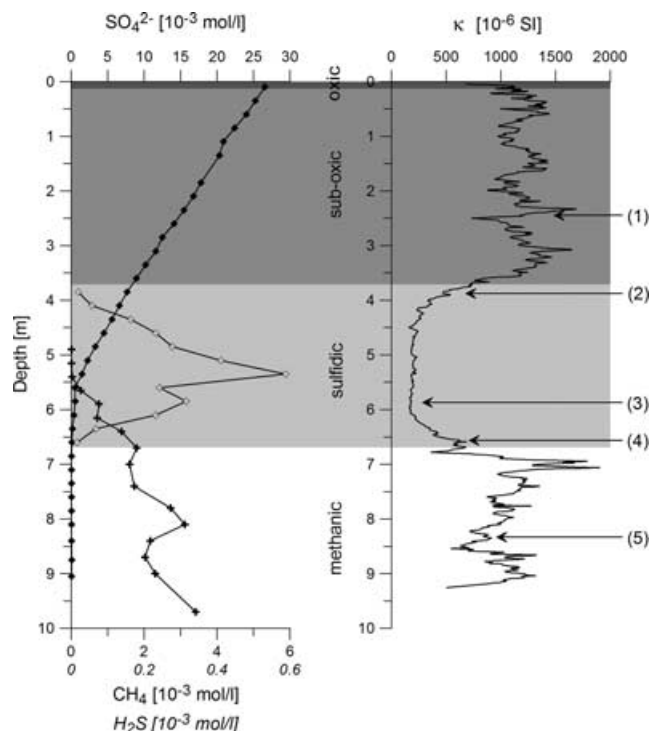


Figure 2. Core GeoB 6229 depth profiles of pore water sulphate (solid diamonds), methane (crosses) and sulphide (open diamonds) concentrations measured directly after core recovery and low field magnetic susceptibility κ . Arrows indicate sample positions for low-temperature studies. Redrawn after Riedinger *et al.* (2005) and Garming *et al.* (2005).

reduced ferrous (Fe^{2+}) state, rendering the mineral less reactive and vulnerable to reductive dissolution.

Titanohematite $\text{Fe}_{2-y}\text{Ti}_y\text{O}_3$ with composition of $0 \leq y \leq 0.5$ is essentially antiferromagnetic with a weak parasitic ferromagnetism, like hematite. In the range $0.5 < y < 1$, titanohematites are ferromagnetic. For compositions $y > 0.7$, the Curie temperature T_c is below room temperature (Ishikawa & Akimoto 1957).

To demonstrate the compositional changes of the magnetic mineral fraction during progressive sub and anoxic diagenesis, various low-temperature experiments have been performed on magnetic mineral extracts. The results are discussed here together with findings of scanning electron microscopic (SEM) analyses and energy dispersive spectroscopy (EDS).

2 SAMPLES AND MEASUREMENTS

The magnetic extraction technique of Petersen *et al.* (1986) was applied to obtain magnetic separates for five samples from key positions within the vertical redox zonation of gravity core GeoB 6229 (Fig. 2): (1) the suboxic zone below the iron redox boundary (2.45 m depth); (2) the transitional interval from suboxic to sulphidic conditions in the SMT zone (3.85 m depth); (3) the sulphidic SMT zone (5.85 m depth); (4) the transitional interval between the SMT zone and methanogenic zone (6.55 m depth) and (5) the methanogenic zone (8.35 m depth). After extraction the samples were not further purified in order to minimize the risk of losing material. Microscopic analysis has shown that still a significant fraction of paramagnetic material was present in the extracts (Garming *et al.* 2005).

For low-temperature measurements with a Quantum Design Magnetic Property Measurement System (MPMS XL-7) accurately

weighed amounts of these extracts were fixed with vacuum grease in small gelatine capsules. Susceptibility was determined from 5 to 300 K in 5 K steps applying a 110 Hz field of 0.4 mT amplitude. Saturation isothermal remanent magnetization (SIRM) experiments comprised thermal demagnetization to room temperature of a low-temperature (LT) 5 T SIRM acquired at 5 K after zero-field-cooling (ZFC) as well as after field-cooling (FC), and cycling of a 5 T room temperature (RT, 300 K) SIRM down to 5 K and back in zero field. For sample (4) hysteresis loops were determined with peak fields of 2 T at 18 selected temperatures between 275 and 160 K as well as a more detailed low-temperature cycling of 5 T RT-SIRM to different returning temperatures.

SEM observations were performed on polished sections with a *FEI XL30 SFE* at 15 kV and 1.5 nm beam size. Element spectra were (semi-)quantified from EDS spot analyses using the '*EDAX PhiRhoZ Quantification*' software version 3.4.

3 RESULTS

3.1 Low-temperature susceptibilities

Variations of in-phase susceptibility (Fig. 3) exhibit generally similar characteristics for all five samples between 5 and 300 K. Increasing gradients above ~30 K and inflections in slope at around 60 K could hint at the presence of ilmenite (Nagata & Akimoto 1956) and high Ti content ($\gamma > \sim 0.8$) titanohematite (Ishikawa *et al.* 1985). Low Ti content titanomagnetite likely contributes to this effect (Moskowitz *et al.* 1998). A steep rise in susceptibilities above 90 K and a maximum at about 130 K reflect reduced coercivities towards and at the Verwey transition T_V and the isotropic point T_I of magnetite (Dunlop & Özdemir 1997). A third broad

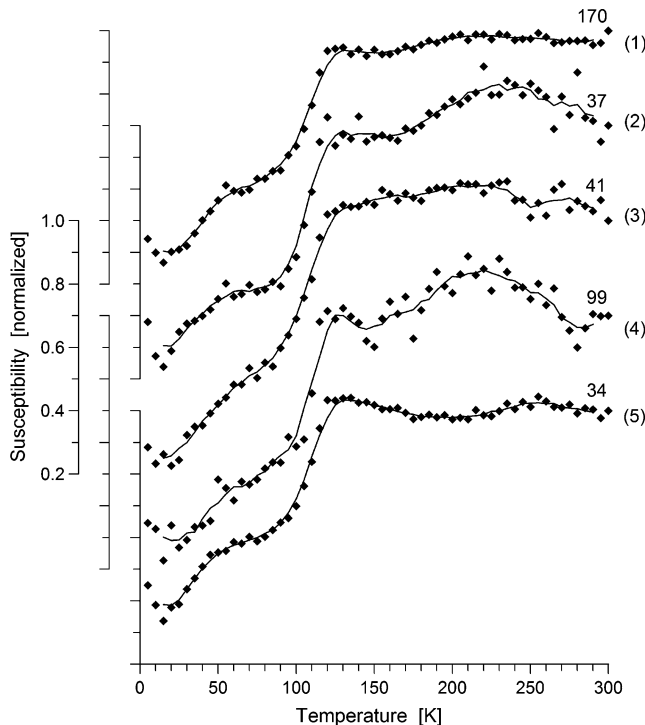


Figure 3. Magnetic in-phase susceptibility measured between 5 and 300 K applying a 110 Hz field of 0.4 mT amplitude. Solid lines represent smoothed 5 point averages. Respective sample code (see Fig. 2) and susceptibility at 300 K (in $10^{-6} \text{ m}^3 \text{ kg}^{-1}$) used as normalizer are indicated.

maximum around 220–230 K is most clearly developed for samples (2)–(4) from the sulphidic SMT zone and its transitional margins to the suboxic and methanic domains. In the suboxic sediment (1) this feature is faint, in the methanic zone (5) it seems to be shifted to higher temperatures (~255 K). A similar though much more clearly developed peak at 210 K in in-phase susceptibility measurements of the central Alaskan Old Crow tephra has been attributed to the transition of a titanium-rich titanohematite phase (TH83) from the ferrimagnetic to the paramagnetic state (Lagroix *et al.* 2004a).

3.2 Low-temperature SIRM experiments

Results of FC- and ZFC-SIRM (5 K, 5 T) zero-field warming are shown in Fig. 4. Samples (2)–(4) from the SMT zone acquired 21–26 per cent more remanence by FC than by ZFC, while the difference is noticeably smaller for sample (1) from the suboxic (14 per cent) and sample (5) from the methanic (8 per cent) zones, possibly indicating a coarser grained magnetic mineral assemblage. All samples lose ~90 per cent of their initial 5 K remanence upon warming to 300 K. According to magnetic phase relations in the ilmenite–hematite solid solution series (Brown *et al.* 1993; Harrison & Redfern 2001) and experimental results obtained on synthetic materials (Ishikawa *et al.* 1985), ilmenite and Ti-rich titanohematite should substantially contribute to the large remanence loss between 5 and about 50 K. The Verwey

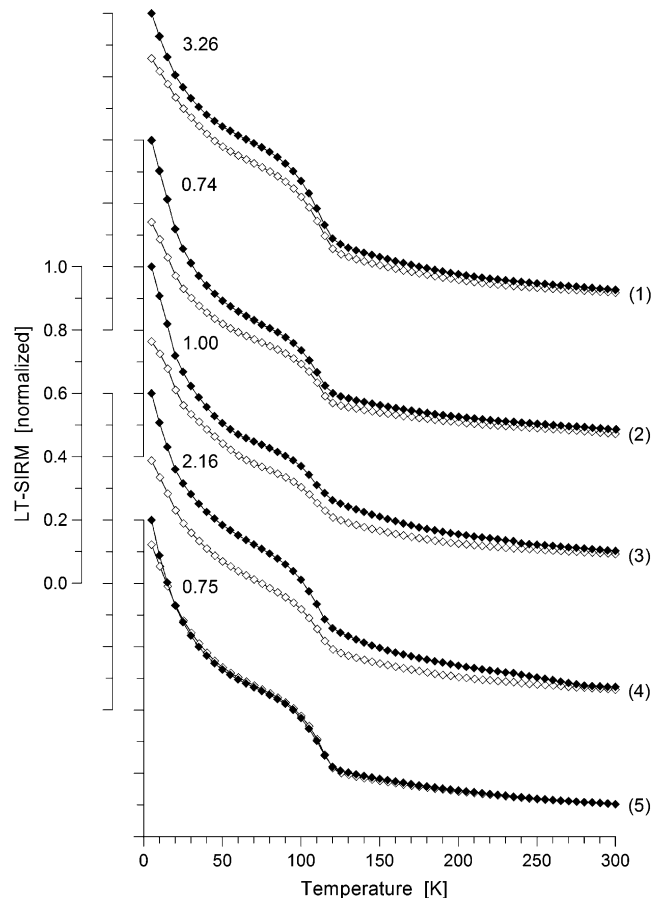


Figure 4. Thermal demagnetization between 5 and 300 K of 5 T SIRM acquired at 5 K after zero-field-cooling (open symbols) and 5 T field-cooling (solid symbols). Respective sample code (see Fig. 2) and 5 K FC-SIRM (in $\text{A m}^2 \text{ kg}^{-1}$) used as normalizer are indicated.

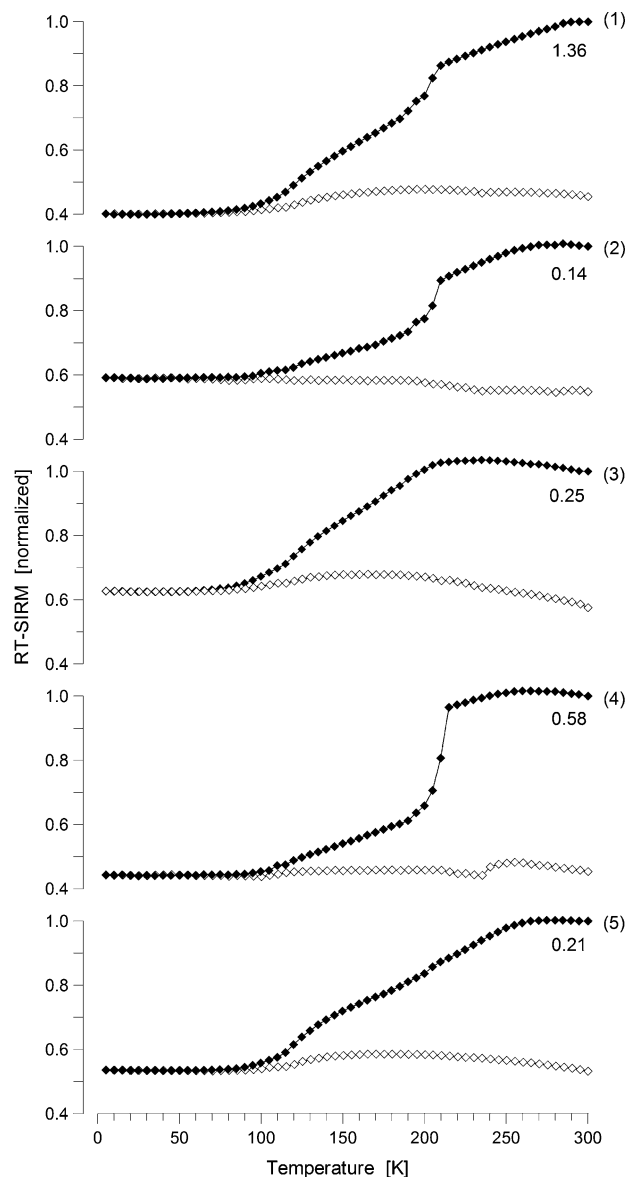


Figure 5. Zero-field-cooling (300–5 K, solid symbols) and warming (5–300 K, open symbols) of 5 T room temperature (300 K) SIRM. Sample code (see Fig. 2) and 300 K saturation magnetization (in $\text{A m}^2 \text{kg}^{-1}$) used as normalizer are indicated.

transition ($T_V \approx 120$ K) is broadened, indicating partially oxidized and/or slightly Ti substituted magnetite (Özdemir *et al.* 1993). Unlike susceptibility (Fig. 3), FC- and ZFC-SIRM warming curves and their first derivatives (not shown) display no particular features in the 220–255 K interval.

Although zero-field cooling of RT-SIRM (300 K, 5 T) also reveals marked slope changes around the Verwey transition for all samples (Fig. 5), a more prominent remanence loss already occurs at higher temperatures. It is most clearly developed in the samples (2) and (4) from the SMT transitional zones, where abrupt breaks in slopes are observed at 210 and 215 K, respectively. Suboxic sample (1) shows a similar kink, whereas the remanence loss of the SMT zone sample (3) extends over a much wider temperature range below 210 K. For methanic zone sample (5) the decline of RT-SIRM already starts at about 260 K and only a faint undulation in gradient is seen around 210 K. Overall, these results are fully consistent with the susceptibility data, indicating the presence of Ti-rich titanohematite

phases. At 5 K between 40 and 60 per cent of the initial RT-SIRM remains. Upon warming it is reversible up to ~ 50 K and shows only a very limited recovery passing through T_V . Above 235 K, the remanence slightly increases in case of sample (4), an effect which is restricted to very minor changes in slope or is missing in the other samples.

3.3 Low-temperature hysteresis properties

For transition zone sample (4) the temperature dependence of hysteresis properties has been determined between 160 and 275 K at peak fields of 2 T. As examples, slope corrected hysteresis loops are shown in Fig. 6 for four temperatures (160, 210, 230 and 275 K). Saturation magnetization (σ_s), saturation remanent magnetization (σ_{rs}), coercive field (B_c) and domain state index (σ_{rs}/σ_s) were quantified from these data. Saturation magnetization (Fig. 7a) increases linearly by $0.007 \text{ A m}^2 \text{kg}^{-1}$ per Kelvin, when cooling from 275 to 245 K, and from 230 to 160 K, respectively. In correspondence to the previous findings (Figs 3–5), the abrupt 8 per cent shift between 245 and 230 K suggests that a new magnetic phase is ordering. A continuous increase with cooling is also observed for saturation remanence (Fig. 7b). The σ_{rs}/σ_s ratio (Fig. 7d) indicates grain sizes at the multidomain to pseudo-single-domain boundary, slightly fining towards lower temperatures. Comparable to the coercive field B_c (Fig. 7c), it reaches a minimum at 230 K. B_c changes at a higher rate (~ 0.03 mT per Kelvin) below 210 K than above 245 K (~ 0.002 mT per Kelvin).

3.4 Electron microscope analyses

SEM examination and EDS analyses of polished sections revealed the presence of a variety of iron titanium oxide minerals both from the titanomagnetite and the titanohematite solid solution series. According to the EDS analyses, titanohematite lamellae (Fig. 8), have compositions ranging from almost pure ilmenite (Fig. 8a) to approximately $0.85\text{FeTiO}_3\text{-}0.15\text{Fe}_2\text{O}_3$ ($y = 0.85$, TH85, Fig. 8b) and also lower titanium contents. Franke *et al.* (2007) have studied the titanomagnetite/titanohematite intergrowths using the electron backscatter diffraction (EBSD) technique which clearly discriminates cubic versus rhombohedral Fe–Ti oxide structures.

Some of the composition estimates for relic titanomagnetite intergrowths (Fig. 8b) suggest relatively high Ti contents (up to approximately TM40). Most likely these analyses are biased by adjacent or underlying Ti-rich titanohematite lamellae. Likewise, a contamination of titanohematite analyses by titanomagnetite intergrowths cannot be excluded. Almost pure magnetite is positively documented in the low-temperature susceptibility and SIRM records (Figs 3–5). Garming *et al.* (2005) showed evidence of its presence as inclusions in a siliceous matrix. No hematite has been identified.

4 DISCUSSION

The results of this study and of Garming *et al.* (2005) show that the iron oxide mineral inventory of continental slope sediments off the Rio de la Plata estuary mainly consists of magnetite and ilmenite, titanomagnetite and titanohematite of variable compositions. Garming *et al.* (2005) additionally identified the secondary mineral pyrite in the sulphidic zone surrounding the SMT by high-temperature magnetic analyses.

At room temperature solely magnetite and, for the compositional range identified, titanomagnetite carry the remanent magnetization. In the sulphidic zone, they are either present as inclusions in a siliceous matrix (Garming *et al.* 2005) or intergrown with

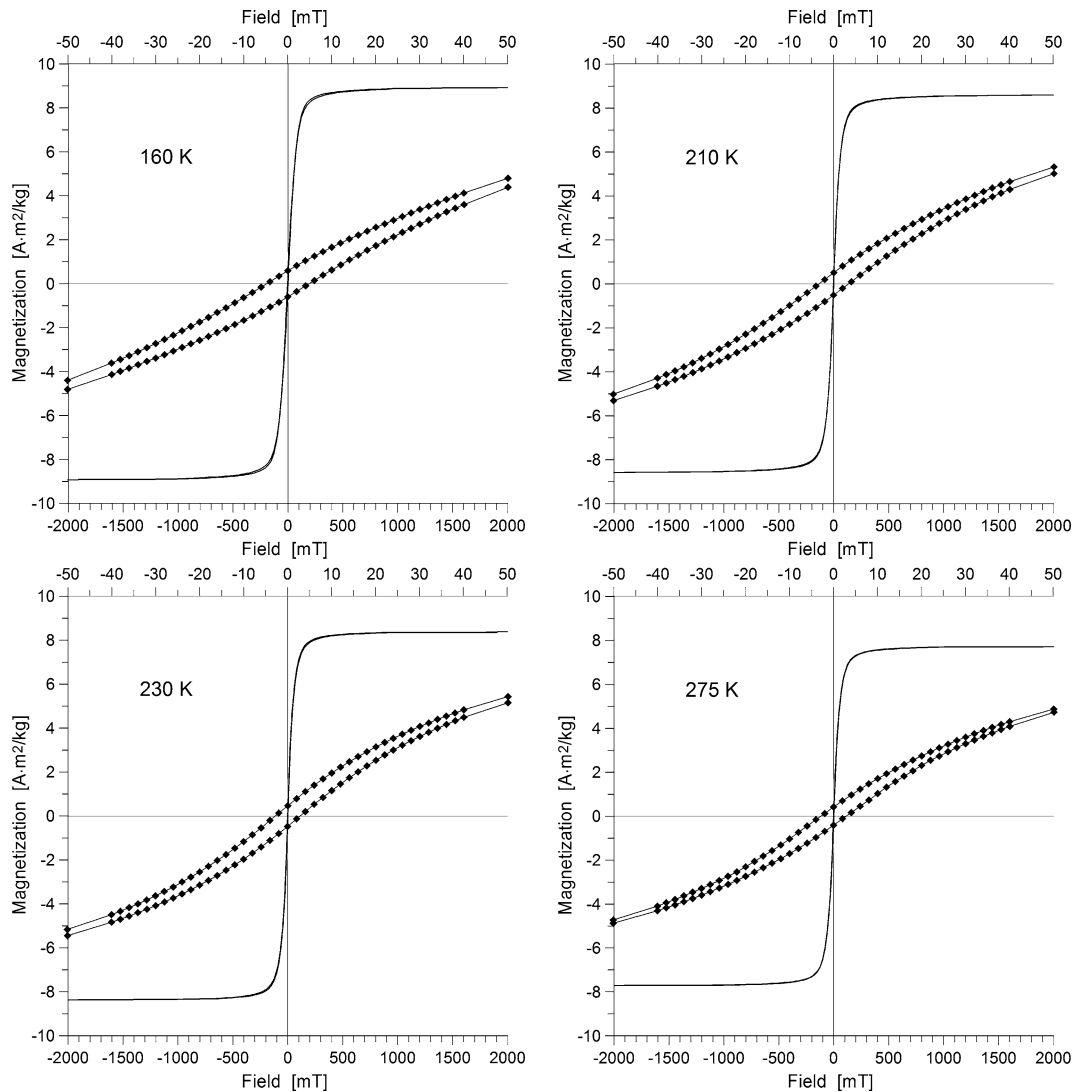


Figure 6. Slope corrected hysteresis loops to 2 T for sample (4) at temperatures of 160, 210, 230 and 275 K. The enlarged sections around the origin refer to upper-field scales.

titanohematite lamellae (Fig. 8). The intergrowths, originating from high-temperature deuteric oxidation in the basaltic host rock, consist of Ti-poor titanomagnetite to pure magnetite and Ti-rich titanohematite to pure ilmenite. At room temperature, the coercivity B_c is remarkably low (Fig. 7c) and the domain state index σ_{rs}/σ_s indicates near multidomain behaviour (Fig. 7d). SEM observations (Fig. 8) typically show (titano-)magnetite of only a few micron, falling within the PSD grain size range. Their likely interaction should explain the observed low coercivities (Davis & Evans 1976 and references therein) and apparent MD behaviour.

According to the EDS analyses, titanohematite lamellae have approximate compositions of TH85 ($y = 0.85$), but higher and lower Ti contents were observed as well. TH85, paramagnetic at room temperature, becomes ferrimagnetic below about 200 K (Nagata & Akimoto 1956) and exhibits weak hysteretic behaviour (Brown *et al.* 1993). With further increasing Ti concentration the Curie temperature of titanohematite decreases almost linearly down to 55 K for pure ilmenite (Nagata & Akimoto 1956). According to thermodynamic calculations (Ghiorso 1997), which have been experimentally verified for TH70 (Lagroix *et al.* 2004b), such a linear trend is only a rough approximation and Curie temperatures are actually

somewhat higher. Compositions of $y \geq 0.88$ are strictly superparamagnetic below T_c (Ishikawa 1962). Compositions of $0.79 \leq y \leq 1$ show antiferromagnetic spin glass properties at very low temperatures allowing for a considerable parasitic remanent magnetization (Ishikawa *et al.* 1985; Brown *et al.* 1993). Yet, such a FC remanence is almost entirely lost upon warming to about 50 K and leaves no trace at the Curie temperature transition (Ishikawa *et al.* 1985). The steep decrease of ZFC and FC remanences between 5 and 50 K of all our samples (Fig. 4) should mainly be due to this effect, which would also explain the absence of any further decline around T_c . Some caution with these interpretations may be recommended as the ilmenite–hematite magnetic phase diagram at the high Ti end is perhaps not yet fully understood at very low temperatures.

Low-temperature hysteresis measurements of sample 4 (Fig. 7) indicate a Curie temperature of about 240 K which would correspond to TH80 assuming a linear correlation between T_c and Ti content (Nagata & Akimoto 1956). The composition of approximately TH85 obtained from EDS analysis of titanohematite lamellae (Fig. 8b) reasonably complies with the T_c estimate if a slightly concave shaped relationship applies as suggested by the above cited studies.

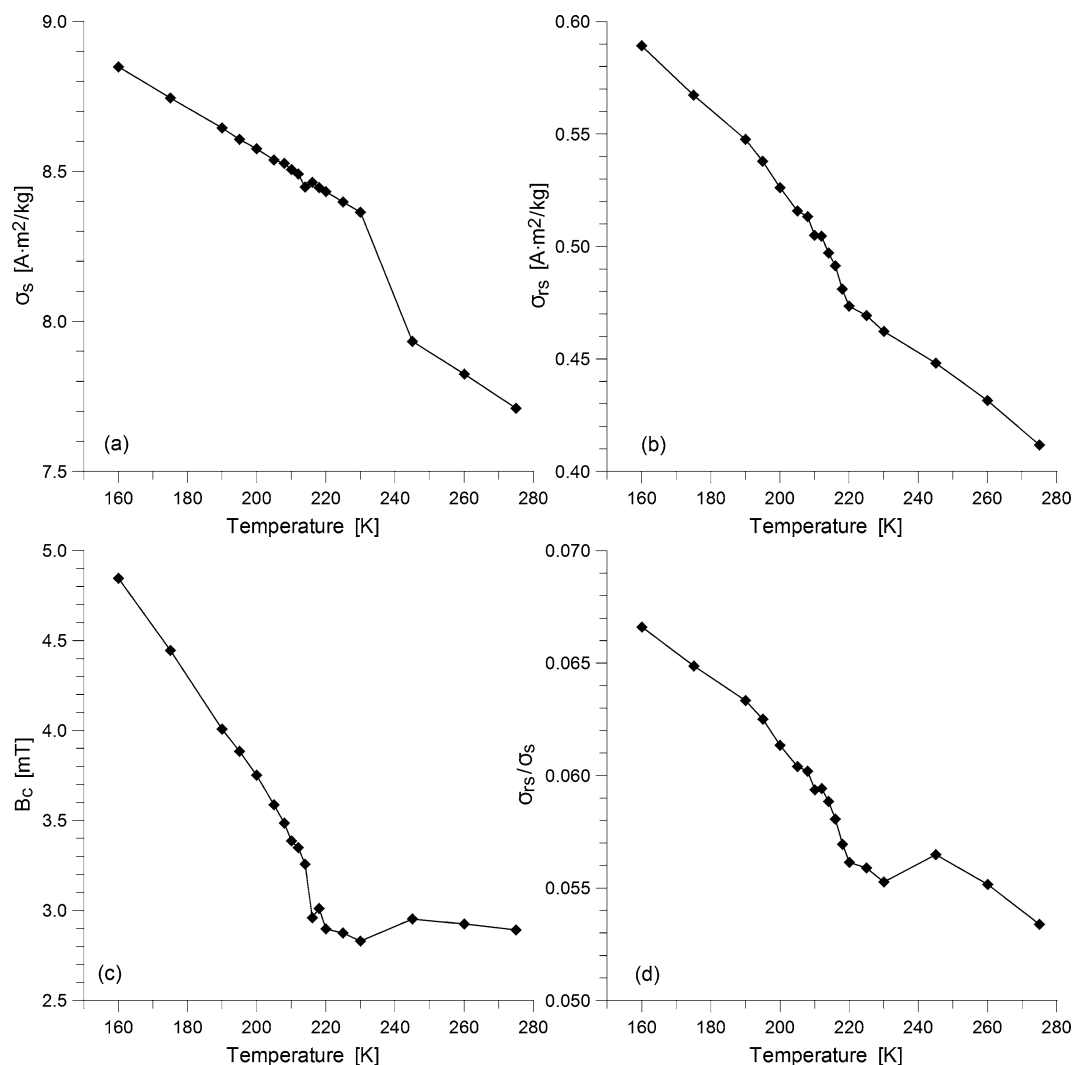


Figure 7. Results of hysteresis measurements for sample (4). Low-temperature dependence of (a) saturation magnetization σ_s , (b) saturation remanence σ_{rs} , (c) coercive field B_c and (d) domain state index σ_{rs}/σ_s .

The hysteresis parameters document a gradual transition from a paramagnetic to a superparamagnetic and finally to a stable ferrimagnetic state. B_c and σ_{rs}/σ_s minima between 230 and 210 K (Figs 7c and d) substantiate that titanohematite is predominantly superparamagnetic in this range. This is also in agreement with a relative susceptibility maximum around this temperature (Fig. 3). A stable ferrimagnetic state is attained around 190 K.

The most prominent feature in cycling the room temperature SIRM to 5 K and back is a drastic decline between ~ 210 K (~ 250 K for sample 5) and the Verwey transition (Fig. 5). To obtain further insight into the processes involved, additional low-temperature cycling experiments have been performed at higher resolution (1 K steps) on sample 4 (Fig. 9). A RT-SIRM was consecutively cycled in zero-field between 300 K and return temperatures from 200 to 100 K in 20 K steps. Before each cycle, a new RT-SIRM has been imparted in a 5 T field. These experiments were performed about one year after the initial measurement (Fig. 5) and there are some indications for a slight alteration (oxidation?) of the sample during storage. However, the characteristic features appear well preserved.

The general morphology of the cooling and warming branches is basically identical in all cases (Fig. 9). A small, but systematically increasing shift of each consecutive starting SIRM is observed.

While the cooling branches coincide quite well (after correcting for this effect), the warming branches show significant offsets reflecting largely irreversible remanence losses between the different returning temperatures. Noteworthy is the very sharp decrease between about 210 and 180 K which takes place in two steps, a fact that had not been identified at the lower resolution (5 K steps) of the initial RT-SIRM cycle.

What causes the marked RT-SIRM variations during low-temperature cycling? Major parts should result from low-temperature demagnetization due to decreasing magnetocrystalline anisotropy of magnetite (Dunlop 2003). The RT-SIRM cycles of samples 3 and 5 (Fig. 5) may be completely explained by this effect. On the other hand, the sharp drop below about 210 K observed for samples 1 and 2 and most clearly developed in sample 4 need additional justification. Four hypotheses are considered:

- (1) A (yet unknown) phase transition other than Curie temperatures in one of the magnetic mineral components present.
- (2) Self-reversal within titanohematite by exchange coupling of two phases with $T_c > 0^\circ\text{C}$ and $T_c < 0^\circ\text{C}$, respectively.
- (3) Inverse magnetostatic coupling of (titano-)magnetite ($T_c > 0^\circ\text{C}$) and Ti-rich titanohematite ($T_c < 0^\circ\text{C}$).

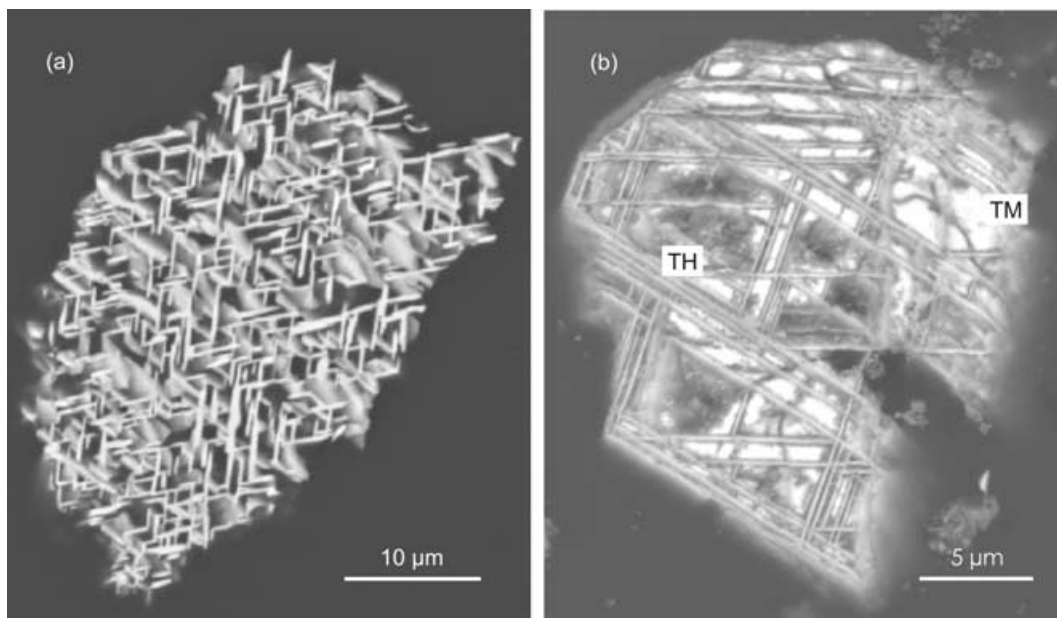


Figure 8. SEM micrographs showing (a) almost pure ilmenite lamellae and (b) intergrown titanohematite lamellae (TH) and titanomagnetite (TM).

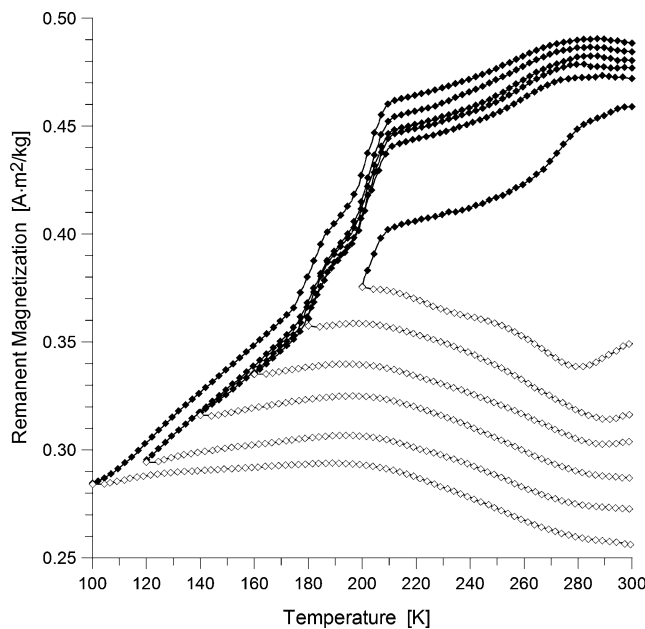


Figure 9. Sample (4): consecutive zero-field-cooling of 5 T room temperature (300 K) SIRM (solid symbols) to 200, 180, 160, 140, 120 and 100 K. A new RT-SIRM was imparted after each warming cycle (open symbols).

(4) Reorganization of (titano-)magnetite ($T_c > 0^\circ\text{C}$) domain structure due to magnetostatic interaction with a gradually stabilizing titanohematite ($T_c < 0^\circ\text{C}$) phase.

The only known magnetic phase transition in the relevant temperature range is the Morin transition of hematite (Morin 1950) at around 260 K (Dunlop & Özdemir 1997). Hematite has not been found in the electron microscopic analyses and is also not indicated by any of the magnetic measurements.

Self-reversal by exchange coupling acting between crystallographically different, coexisting titanohematite phases was repeatedly observed in volcanic rocks of dacitic to andesitic composition

(e.g. Nagata *et al.* 1953; Heller *et al.* 1986; Kennedy & Osborne 1987) and has been discussed and modelled in various studies (e.g. Uyeda 1958; Hoffman 1975; Prévot *et al.* 2001). According to Westcott-Lewis & Parry (1971), it is an intrinsic property of titanohematites with compositions of $0.51 \leq y \leq 0.73$. This range is atypical for basalts, however. Explaining our findings by titanohematite exchange coupling self-reversal would be a so far not yet reported low-temperature analogue to the well-established observations above room temperature. A true analogue, however, would also require full reversibility upon thermal cycling (e.g. Bina *et al.* 1999) which is in contrast to our data (Figs 5 and 9).

The ‘magnetostatic coupling’ hypothesis postulates an inverse interaction between intergrown Ti-poor titanomagnetites and Ti-rich titanohematites. SEM observations and EDS analyses have clearly identified both phases in our samples. The low-temperature dependence of susceptibility (Fig. 3) and zero-field warming of FC and ZFC LT-SIRM (Fig. 4) provide further evidence that magnetite and Ti-rich ($y \geq 0.8$) titanohematite are abundant magnetic minerals. Magnetostatic coupling assumes that the TH phases are magnetized in the magnetic field of adjacent TM phases carrying a room temperature remanent magnetization. Within the lamellar intergrowth structure of TM and TH, an antiparallel magnetization of the TH phase would be the obvious configuration according to geometric and energetic principles, resulting in a systematic reduction of the global magnetization. Magnetostatic interaction of two physically decoupled magnetic phases is one of Néel’s (1951) classic self-reversal concepts. Dunlop & Özdemir (1997) stated that no undisputed natural example for this mechanism has been demonstrated. However, more recently Krása *et al.* (2005) presented convincing evidence for its quite common occurrence in basaltic rocks. The first problem with this hypothetical model arises from the fact that the drop in RT-SIRM upon cooling below the TH Curie temperature is considerably larger than the increase of TH saturation magnetization and remanence (Figs 7a and b), which should define upper bounds to any inverse magnetization. Moreover, the absence of a notable recovery of remanence at around T_c of the TH phase during subsequent warming (Figs 5 and 9) creates an equally serious conflict.

These two problems are solved by a 'domain reorganization' hypothesis, in which the newly ordering TH phase plays both an 'antipodal' and a 'catalytic' role in reducing the global magnetization of both intergrown phases. During the initial superparamagnetic state of the TH phase (below ~240 K for sample 4; Figs 7c and d), its low and instable magnetization has little influence on the TM remanence. The abrupt drop in RT-SIRM starts, when the TH phase cools into its blocking temperature range (below 210 K for sample 4; Figs 7c and d). In the temperature interval to about 180 K the 'antipodal' effect, that is, partial self-reversal predominates, whereas low-temperature demagnetization of (titano-)magnetite due to decreasing magnetocrystalline anisotropy is still of subordinate importance (Dunlop 2003). From 180 to around 100 K it should be largely responsible for the continuous decrease in remanence, however. In addition, the gradually stabilizing and self-organizing TH phase sets out to enhance irreversible domain reorganization of the TM remanence structure (Figs 5 and 9). As titanohematite coercivity grows faster than titanomagnetite coercivity upon further cooling (Fig. 7d), this process may proceed all the way down to the Verwey transition, where the initial remanence of the intergrown (titano-)magnetite is mostly destroyed (Fig. 5). The remaining stable 40–60 per cent of RT-SIRM apparently resides in an independent (titano-)magnetite phase included in a silicate matrix.

5 CONCLUSIONS

Higher stability of titanium rich versus titanium poor iron oxides in strongly reducing sedimentary environments leads to significant changes of the primary magnetic mineral inventory. In the marine deposits off the Rio de la Plata estuary these processes have been encountered in the magnetically depleted SMT zone. As documented by electron microscopy and strongly supported by low-temperature magnetic analyses, a major component of the residual iron oxides are intergrowths of Ti-rich titanohematite lamellae with relic (titano-)magnetite.

The most conspicuous finding in low-temperature cycling experiments is a marked drop in room temperature saturation remanences below about 210 K, which does not reverse upon warming. Saturation hysteresis loops recorded in the surrounding temperature interval show that a new magnetic phase develops at around 240 K, corresponding to the Curie temperature of titanohematite with an approximate composition of $\text{Fe}_{1.15}\text{Ti}_{0.85}\text{O}_3$, and subsequently stabilizes at about 210 K. It is characterized by a higher magnetic stability and grain size index compared to the carrier of RT-SIRM, (titano-)magnetite.

To explain the decline in RT-SIRM between about 210 K and the Verwey transition different hypothesis are discussed. There is little supporting evidence for a self-reversal mechanism due to exchange interaction between crystallographically different regions within titanohematite. Instead, magnetostatic interaction between intergrown Ti-poor titanomagnetite and Ti-rich titanohematite is a much more plausible concept. When titanohematite becomes ferri-magnetic upon cooling through ~240 K, its spontaneous magnetic moments order antiparallel to the (titano-)magnetite remanence causing an drastic initial decrease of global magnetization, a partial magnetic self-reversal. The subsequent loss of remanence during further cooling results from domain structure reorganization within the (titano-)magnetite phase due to diminishing magnetocrystalline anisotropy and the magnetic interaction between the two Fe–Ti oxide phases.

The partial self-reversal documented here would hardly be detectable in the host rocks. The magnetization of the Mesozoic

flood basalts of the Paraná Basin is entirely dominated by (titano-)magnetite and most likely would mask the weak contribution of reverse magnetostatic titanohematite-titanomagnetite interactions. Due to the diagenetic depletion of titanomagnetite and superior preservation of titanohematite in the sediments analysed, the phenomenon is unusually highlighted. Low-temperature remanence cycling is, therefore, proposed as a diagnostic method to identify residual magnetic mineral inventories which have suffered pervasive diagenesis, and to characterize respective (palaeo-)environments.

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