Diagenesis and remanence acquisition in the Lower Pliocene Trubi marls at Punta di Maiata (southern Sicily): palaeomagnetic and rock magnetic observations

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Abstract: Three new profiles (LCM, PMD and CMD) through the lower Cochiti polarity zone enable comparison of the effects of weathering and diagenesis on the magnetic properties of the Early Pliocene Trubi marls. These marls have been well dated, by means of astronomical calibration, and are of particular interest in terms of polarity zonation and regional tectonics. The freshest exposures (LCM profile) carry a remanence associated with pyrrhotite, which is particularly enhanced in some grey layers. This is the first time that occurence of pyrrhotite as the main remanence carrier in the Trubi marls is documented (SD magnetite was previously recognised as the fundamental ferromagnetic phase). The mean ChRM direction from the LCM record does not show the expected 30-35° clockwise rotation found in other studies, and does not record the normal Cochiti interval either (i. e. is reverse throughout the sampled interval), suggesting a relatively late origin for the NRM. Standard rock magnetic techniques are used to investigate the nature of the magnetization in the three laterally equivalent profiles at Punta di Maiata. The actual data set seems to be better explained by a complex diagenetic history involving a multistage redox history that invokes a 'late' anoxia event. The previously postulated iron migration model (van Hoof et al. 1993) was put forward for the 'suboxic situation' and does not take into account the presence of magnetic sulfides, which are clearly demonstrated in the zone under study. The 'extended diagenetic model' inferred here proposes a pathway that accounts for most of the new observations. The salient feature is the postulated existence of a diagenetic phase that has altered the original NRM in some areas (dissolution of magnetite) resulting in a later stage acquisition of chemical remanence that does not date to the timing of deposition of the sediments. The extension and the detailed mechanisms by which such a process has taken part deserve further research. Nonetheless, the present investigation accounts for previously unrecognised features in the Trubi marls from Sicily and outlines how intricate the nature of the mechanisms contributing to the blocking of remanence in sediments can be.

The natural remanent magnetization (NRM) of undeformed sedimentary rocks is a composite of detrital input, compaction, a variety of diagenetic processes (often biologically mediated), lithification and fluid migrations during any of these phases. Each of these processes can give rise to authigenic growth of secondary magnetic phases, or to partial or even complete dissolution of the original detrital grains or even of secondary authigenic grains formed during earlier phases. Deformation may then even further complicate the picture and exposure to weathering may occur after any of these phases. The present investigation involves an interdisciplinary analysis of the impact of the diagenetic and weathering processes on the paleomagnetic record of the Early Pliocene Trubi marls in Sicily in an attempt to better understand the NRM acquisition processes. These deposits are particularly interesting as they show rhythmic sedimentation patterns that have enabled precise dating using astronomical precession and eccentricity cycles (Hilgen 1991, Lourens et al. 1996). Consequently, several studies have already been undertaken to understand their stratigraphic, palaeomagnetic and tectonic significance (e.g. Hilgen & Langereis 1988, Zachariasse et al. 1989, Langereis & Hilgen 1991). These previous studies will be summarised and then the results of the rock-magnetic, geochemical and petrographic observation studies of the new profiles will be outlined. The implications of these findings for the nature of remanence acquisition in these beds will then be discussed at both a local and global scale.

The Trubi marls from Sicily

The open-marine marls of the Trubi Formation in Sicily comprise a cyclically bedded marly-calcareous biogenic sequence that usually conformably overlies non-marine argillaceous sands, known as the Arrenazzolo member that was formed at the end of the Miocene. The boundary between these units, in the Capo Rossello section, has been informally defined as the stratotype for the Miocene/Pliocene boundary and the base of the Zanclean Stage (Cita & Gartner 1973) although it has been proposed that this stratotype boundary should be defined in the nearby Eraclea Minoa section (Hilgen & Langereis, 1993). Formal decision from the International Commission on Stratigraphy has not yet been taken. The Trubi Formation is overlain by the Narbone Formation that consists of marly clays, locally interbedded with sapropelitic layers. In this area of southern Sicily, a series of exposures (Eraclea Minoa, Punta di Maiata, Punta Grande and Punta Piccola) constitute the well-known Rossello composite (Hilgen 1987, Hilgen & Langereis 1989) which contains 119 small-scale sedimentary cycles averaging about one meter thickness (95 cycles in the Trubi Marls and 24 cycles in the Narbone Formation). In the Trubi, each cycle consists of distinct grey-whitel-beige-white2 (G-W1-B-W2) coloured layers (Hilgen 1987). The carbonate content varies from 60 to 85%, with the lowest values in the grey and beige layers. This cyclicity continues into the overlying Narbone Formation where sapropelitic layers are sometimes intercalated into, or substitute, the grey-coloured layers of the carbonate cycle. This quatripartite rhythmic bedding has been

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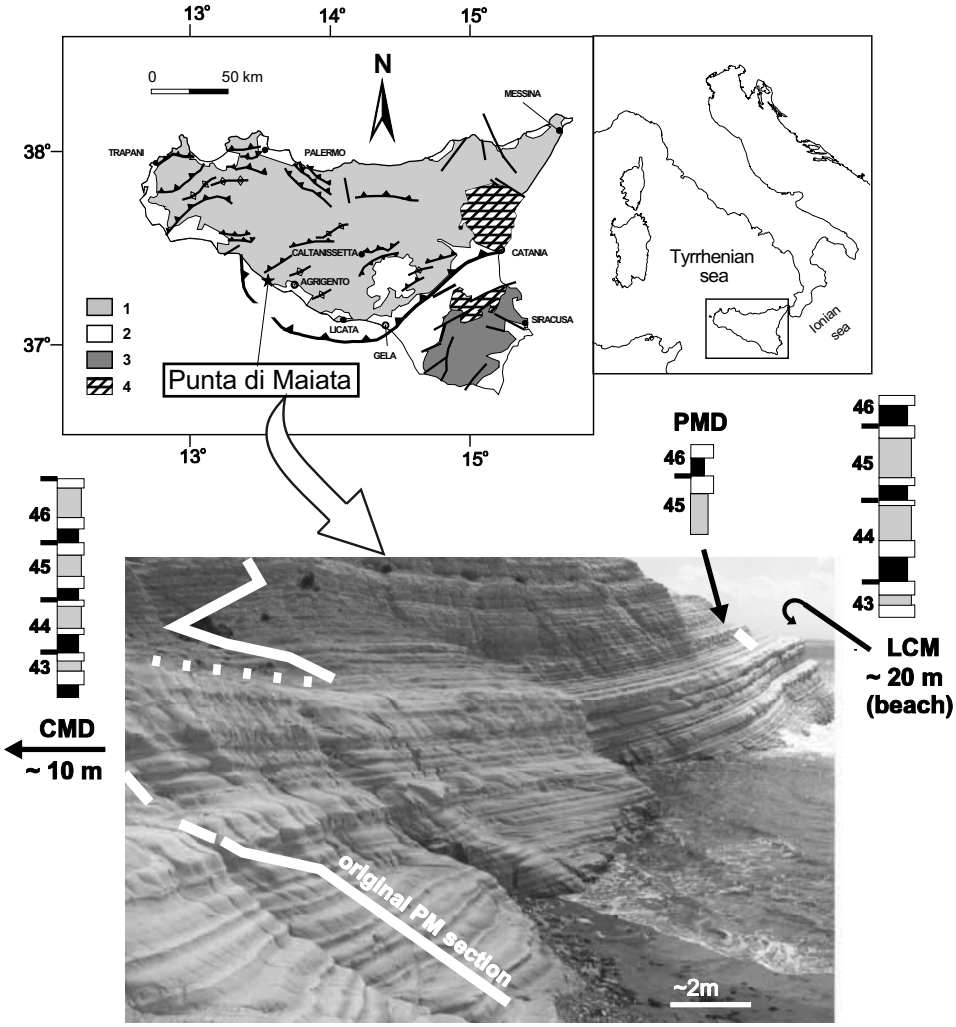

Fig. 1. Schematic geological map of Sicily with the location of the Punta di Maiata and a picture of the outcrop with the different studied sections. Key of map: 1=Pre middle Pliocene rocks; 2= middle Pliocene to recent sediments; 3= Mesozoic volcanic rocks; 4=Pliocene and Pleistocene volcanic rocks. In the lithological columns, white denotes the white layers; black the grey layers and shaded the beige layers of the individual numbered cycles.

correlated to the astronomical precessional cycle, and larger scale cyclicity in the form of recurrence of relatively thick and/or indurated intervals has been related to the eccentricity cycle with periods of about 100 and 400 ka (Hilgen 1991, Lourens et al. 1996). The rhythmites are interpreted as representing changes in the dilution of terrigenous material and in carbonate production in the surface waters controlled by periodical fluctuations in the precipitation and runoff related to orbital forcing (Hilgen 1987, De Visser et al. 1989). The grey layers are interpreted as being deposited under anoxic conditions while suboxic to oxic conditions prevailed during deposition of the white and beige layers. Although most of the exposures along the coast are dippping gently to the N-NE, the Trubi marls have been thrust and folded into a series of southwesterly directed thrust slices facilitated by the Messinian evaporites which acted as a décollement level (Roure et al. 1990, Catalano et al., 1995). At Punta di Maiata, the flatlying coast exposures belong to a footwall syncline of which the overturned limb outcrops some 200-300 m inland. The internal structure in the hinge zone appears complicated and its lateral expression is unknown. The overthrusting hangingwall of this structure is formed by a highly deformed thickened sequence of Messinian evaporites. There are also many microstructures, such as penetrative planes and small-scale faults in this area.

Previous Palaeomagnetic and Rock Magnetic Studies

A detailed magnetostratigraphy, with a resolution averaging 5 to 10 ka, has been established by Hilgen & Langereis (1988), Zachariasse et al. (1989) and Langereis & Hilgen (1991). The section, the Rossello composite section, ranges from below the Thvera Subchron into the Matuyama Chron (4.86-2.45 Ma) and includes the Zanclean neostratotype and the Miocene-Pliocene boundary. The original magnetostratigraphy at Punta di Maiata (Langereis & Hilgen 1991, Hilgen 1991) was established on the western side of the Cape, extending from the beach up to the cliff (Fig. 1). Van Hoof (1993) studied 10 polarity transitions in great

detail (temporal resolution < 1 ka). These were from the lower Thvera to the upper Cochiti (in the Gilbert Chron), the Gilbert-Gauss reversal and the upper Kaena (in the Gauss chron). Nine reversal records are located in the Trubi Formation. Three were studied in the original sections constituting the Rossello composite (the lower and upper Thvera, at Eraclea Minoa, and the upper Cochiti at Punta di Maiata). The six remaining polarity transitions were studied at Capo Bianco, west of Eraclea Minoa. The Punta di Maiata section comprises 65 m stratigraphically (cycles 22 to 80 of the Rossello composite) and ranges from the upper part of the Sidufjall subchron to the lowermost part of the Gauss chron. These include the Nunivak and Cochiti subchronozones, the lower limit of the latter occurring within cycle 45 (Langereis & Hilgen, 1991). Van Velzen & Zijderveld (1990) found a characteristic remanent magnetization (ChRM) in the Trubi marls carried by single domain (SD) magnetite. Scheepers & Langereis (1993) reported that these ChRM directions showed a consistent clockwise rotation of approximately 34° (30.7°, 50.4°, α_{95} = 2.6 Normal; 218.3°, -40.2°, α_{95} = 2.2 Reversed). They took this as support for the primary nature of the ChRM since this rotation is widespread within the Caltanissetta basin and is related to a two-phase Pliocene rotation in the Tyrrenian arc (Scheepers & Langereis 1993, Scheepers 1994). However, some directional behaviour along the reversal boundaries has been found to be very complex. For example, the lower Cochiti reversal at the Capo Bianco exposure is not a simple transition from reverse (R) to normal (N) polarities but involves a complex transition proceeded and followed by a R-N-R and a N-R-N "excursions" respectively (van Hoof, 1993). To explain such behaviour, Van Hoof (1993) postulated that magnetite could form at different times at different levels in the sediment because of early diagenetic diffusion of Fe from the anoxic grey layers into suboxic/oxic zones where secondary magnetite would then form, resulting in delayed remanence acquisition (van Hoof & Langereis, 1991). Weathering effects have also been considered to have changed the remanent properties.

Van Velzen & Zijderveld (1995) showed that samples from the grey and beige layers (Eraclea Minoa) had a remanence carried by single-domain (SD) magnetite that exhibit unusual high coercivities thought to have originated by surface oxidation at low temperatures, i. e. weathering. These high coercivities were attributed to stresses induced by the high gradient in the degree of oxidation between the surface and core of the grains. Heating the samples to ~150°C was considered to release the stresses and hence the high coercivities, as well as changes in other magnetic parameters (decrease of total IRM and ARM, and increase of bulk susceptibility). This model would suggest that such secondary magnetisations could be reduced or eliminated after heating to some 100-150ºC, after which alternating field (AF) demagnetization could more efficiently isolate the pre-weathering component.

The new profiles

Three new sampling profiles have been made through the lower Cochiti transition interval at Punta di Maiata (Fig. 1). The zero-level for each record was arbitrarily defined at a distinct boundary between two layers and the exact stratigraphic position of the individual standard specimens (22 mm height) were determined taking into account the drilling orientation and the attitude of the bedding plane. The mean resolution of a few millimetres implies a time-resolution of ±<100 years. Stepwise thermal demagnetization was performed on one specimen from each core, thus providing a resolution of about 3.5 cm (i. e. < 1 ka). The additional specimens were used for rock-magnetic experiments, petrographic observations and/or geochemical analysis. Profile LCM was in outcrops at the sea level on the eastern side of the Cape where the rocks appear fresher (i.e., blueish layers were sampled below a few centimeters of greyish surface materials) and dip at 14° towards 65°N. Sampling commenced in cycle 43 white1, up to top of cycle 46 grey, totalling 310 cm of section (87 core samples). This profile was extended 8 cycles upwards to cycle 54 grey, by collecting pairs of samples in almost all grey and beige layers. Profile PMD was right at the edge of the pronounced cape where the rocks dip 12° towards 90°N and had grey-white1-beige-white2 colour. It comprises 11 pairs of samples (each pairs some 8 cm apart) from cycle 45 white1 to cycle 46 white1, now recognised as typical of weathering. Additional samples were taken from the underlying cycle 45 grey and the beige and grey layers of cycles 43 and 44. As logistic problems prevented detailed sampling of this profile, the CMD profile has been taken as typical of the weathered properties. The third profile (CMD) was on the western side of the cape, in the cliff section, and about 10-15 m west of the original magnetostratigraphic profile (Fig. 1). This record spanned 295 cm of section from the middle part of cycle 43 grey up to the middle part of cycle 46 beige (139 cores). The strata dip at 20° to 95°N but included a subtle oblique-to-bedding boundary that delimits two distinct weathering profiles. The upper part of the record, above cycle 45 white1, displays the characteristic grey-whitel-beige-white2 colours, but below this level, the cycles tend to be more homogeneously greyish and the different layers are more difficult to recognize. A few meters laterally from this CMD profile, cycles 45 and above display only the homogeneous greyish surface colouring. Samples were collected at a few centimeters depth to ensure there were no substantial change in the colouring. This profile was originally chosen as representative of the most "weathered" setting and similar to that of the original magnetostratigraphic study and our PMD profile. (It was only after the first paleomagnetic analyses were available that it was realized up to which extent the subtle variations in the colour were affecting the magnetic signature along this record).

Magnetic Properties of the Three New Profiles

A variety of rock magnetic properties were investigated in the LCM and PMD profiles in addition to the standard low-field susceptibility and natural remanence (NRM) measurements for all three profiles. These properties included the isothermal remanence (IRM) imparted at 1.5 T, the anhysteretic remanence (ARM) imparted in a 100 mT AF field with a 0.034 mT DC bias field. The back field coercivity, B_{cr}, was measured by a stepwise increase in the DC field strength required to decrease the saturation remanence to zero. The Curie temperatures were obtained with a modified horizontal balance (Mullender et al., 1993). Unless otherwise stated, the intensity is the initial value of the intensity of natural remanence (NRM), i.e. before demagnetisation. The ARM/IRM ratio is commonly used as an indicator of the quantity of fine (single domain and pseudo single domain) ferrimagnetic grains present (Hunt et al. 1995), while the back-field coercivity, B_{cr}, is present, is independent of the presence of paramagentic minerals and the contration of ferromagnetic minerals. Assuming only one ferromagnetic mineral to be present, it can therefore be used as a partial discriminant between different types of ferromagnetic minerals.

The LCM profile

Thermal demagnetization (Fig. 2) showed generally two-components, with a small viscous component removed at 100°C. The low temperature component, removed by 200-400°C, had a present-day direction and was generally small or absent (Fig. 2d & 2h). The ChRM direction was usually removed completely below 360-390°C, although some samples remained blocked until higher temperatures (Fig. 2b & 2e) but was accompanied by an increase of bulk susceptibility and the presence of suspected spurious components. As discussed later, the ChRM appears to be predominantly carried by pyrrhotite. The linearity of the ChRM components was sometimes poor, probably reflecting the low intensity and chemical instability, but the mean direction of the better defined directions (mean angular deviation < 10) (48 of 111 samples) was statistically the same as for all of the samples (Fig. 3a) and so the total number has been take to calculate the mean ChRM direction as entirely reversed, 180.7, -37.3°, (α_{95} = 5.1°).

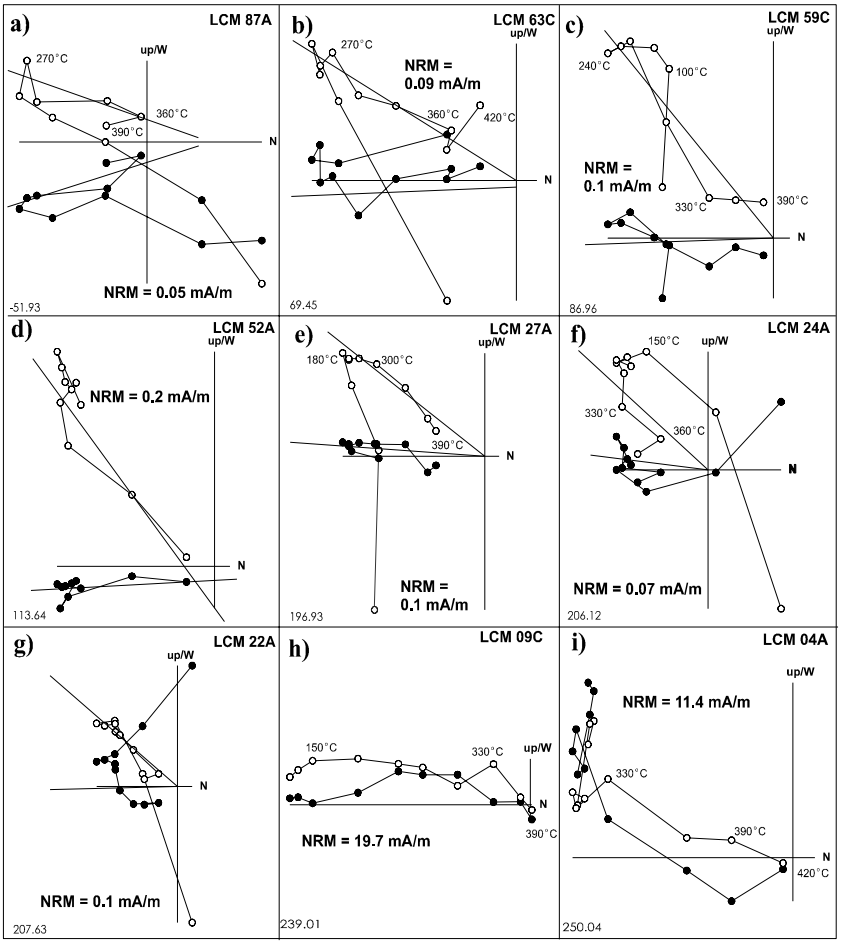

Fig. 2. Bedding-corrected orthogonal projections of stepwise thermal demagnetization of selected samples from the LCM record. Steps of 100, 150, 200, 240, 270, 300, 330, 360, 390, (420) °C were used. Open (closed) circles denote projections on the vertical (horizontal) plane. The stratigraphic position of each sample is indicated in the lower left corner. Note the high NRM intensity in samples LCM.04A (i) and LCM.09C (h) that belong to cycle 46 grey.

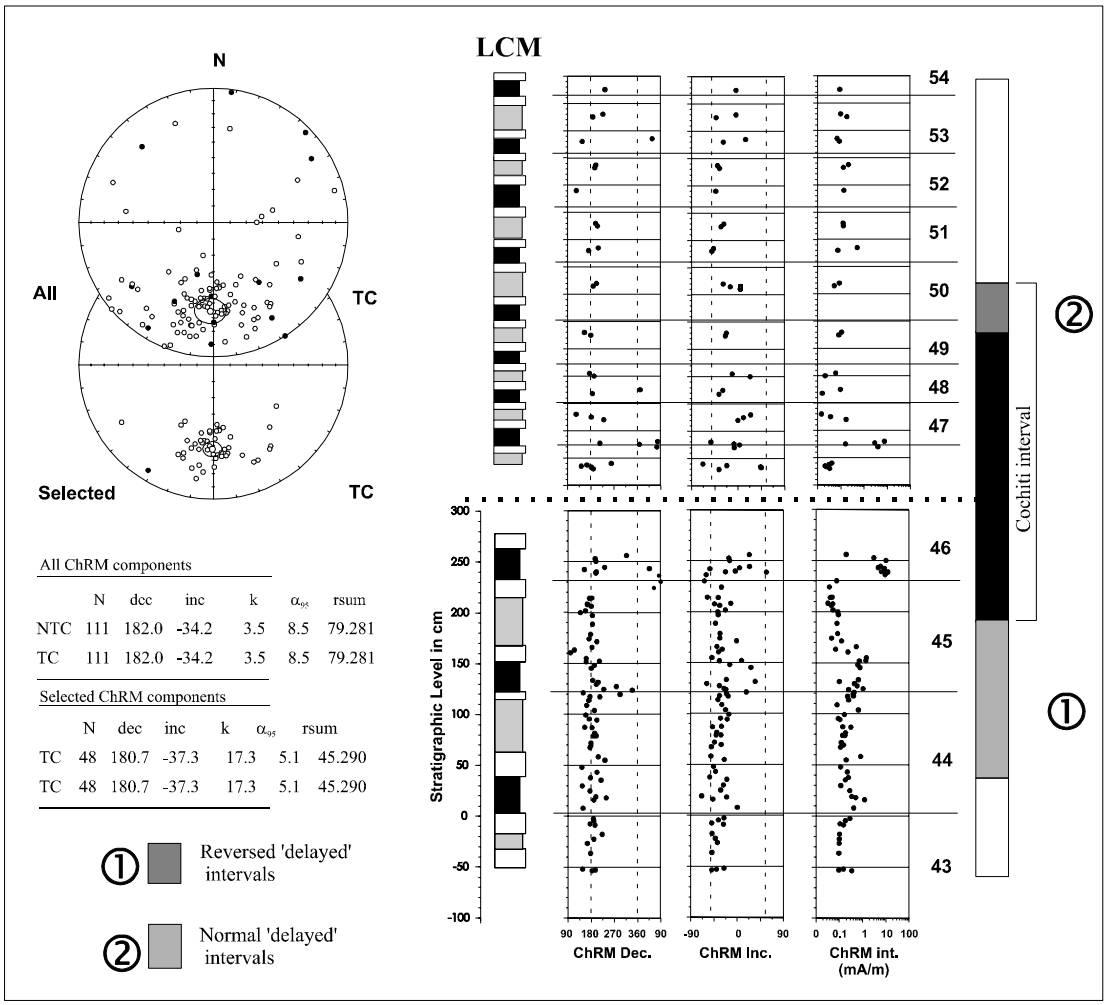

Fig. 3. Paleomagnetic data for the LCM record. (a) Equal-area projection of all and a selection of the best ChRM components after bedding correction. In inset table: N = number of samples, dec = declination, inc = inclination, k = precission parameter, α_{95} = radius of the 95% confidence cone about the mean direction, NTC= before bedding tilt correction, TC = after bedding tilt correction. (b) ChRM declination, inclination and intensity record showing that no clear record of the normal Cochiti interval exists at the LCM track (see text). The expected location of this interval and the zones where intervals holding ´delayed´magnetisations were found in previous studies (van Hoof 1993) are shown. Note the relative higher ChRM intensities in the grey layers of cycles 46 and 47 that correspond also to scattered ChRM directions.

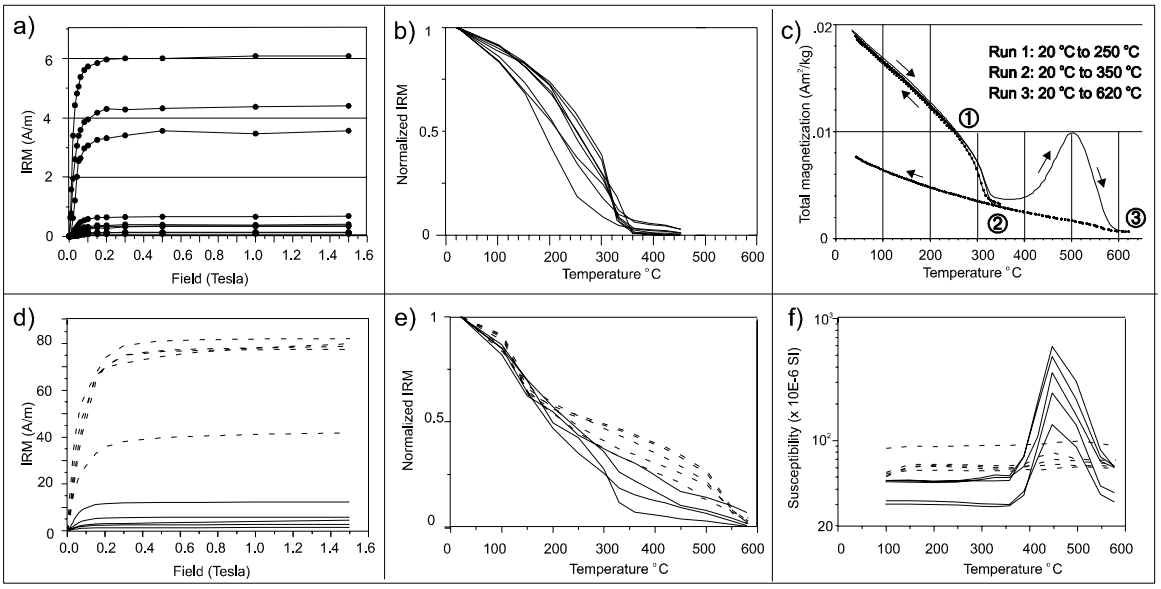

Fig. 4. (a) Isothermal remanent magnetization (IRM) acquisition curves from different lithologies at the LCM record. (b) Stepwise thermal demagnetization of the saturation IRM. (c) Incremental thermomagnetic runs on a sample from the grey layer of cycle 46. (d) IRM acquisition curves from samples from the CMD record. Dashed (continuous) curves are from the upper (lower) domain as defined in Fig. 5b. (e) Stepwise thermal demagnetization of the saturation IRM for the samples from the CMD record. (f) Low-field susceptibility measured at room temperature during thermal demagnetization of the CMD samples.

Generally IRM was attained in field around 0.2 T (Fig. 4a), indicating that a low-coercivity mineral carried the IRM. The blocking temperatures, around 330°C (Fig. 4b), were identical to the Curie temperature, for which the heating and cooling curves were fully reversible up to 350°C (Fig. 4c). This indicates that pyrrhotite is the fundamental carrier of remanence, since other magnetic iron sulfides, such as greigite, usually break down before reaching the Curie point and do not have reversible Curie point curves (Roberts 1995). The intensities of remanence (NRM, IRM and ARM) were all "enhanced" in cycle 46-grey (Figure 5a), being one to two orders of magnitude higher at this level. The ARM/IRM ratio (Fig. 5a), commonly used as an indicator of proxy the presence of fine (single domain and pseudo single domain) ferrimagnetic grains (Hunt et al. 1995), was mostly around 0.02, although the grey layers, particularly cycle 46-grey, were generally lower (c.0.008). The back-field coercivity, B_{cr}, was generally between 50 and 80 mT, although somewhat lower (20 mT) in the upper part (cycle 46-grey). As magnetite is not prominent, these changes in B_{cr} are likely to indicate differences in either the grain-size or the type of iron sulfide. Dekkers (1988) reported coercivities for natural pyrrhotite in the <5 to 250 mm grain-size range that vary from 66 to 6 mT respectively. In the magnetically "enhanced" cycle 46-grey level, relatively large crystals of iron-sulfide were observed (Fig. 6) and their selective presence might explain some of the variation in the observed B_{cr} values.

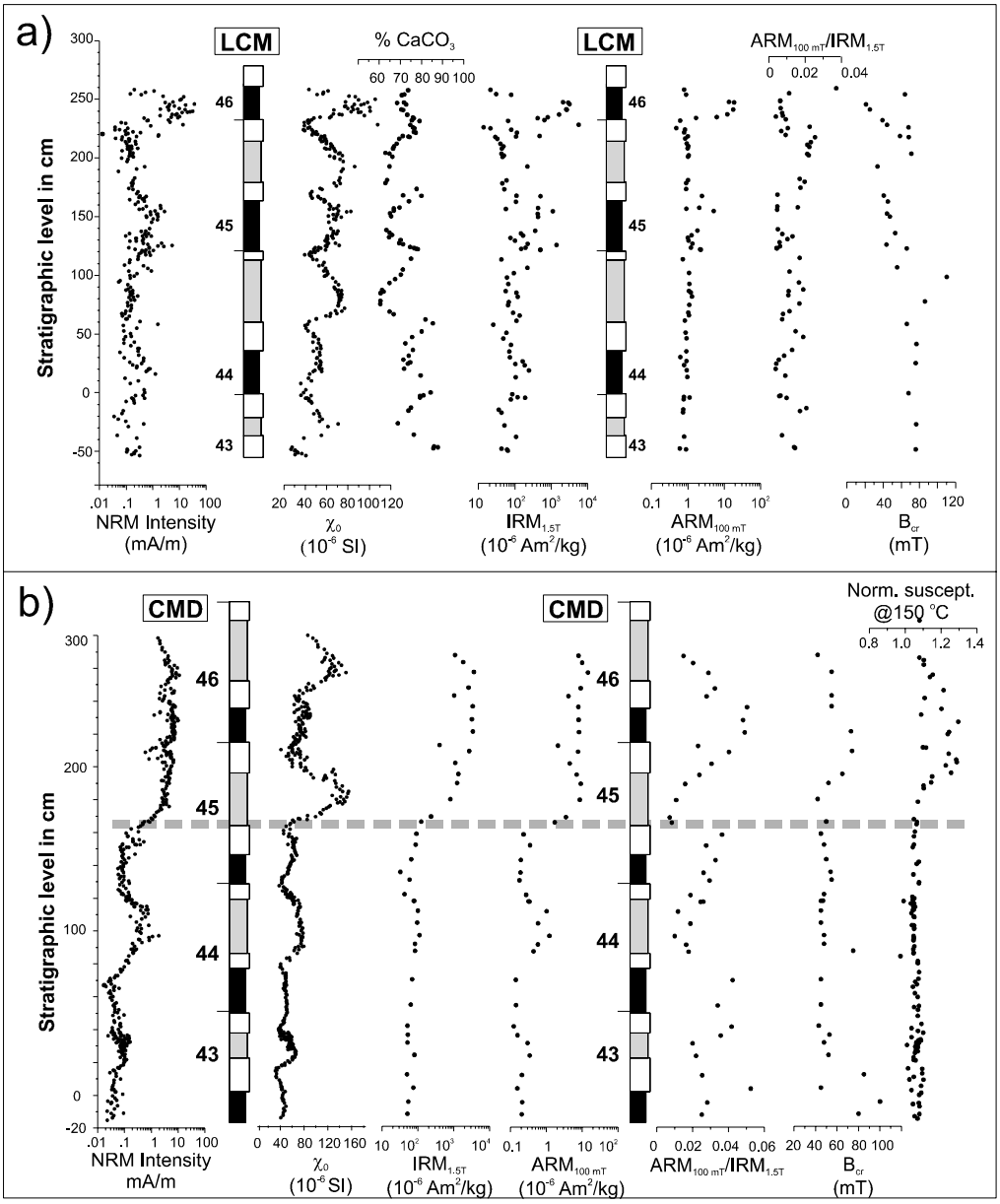

Fig. 5. Rock-magnetic parameters for the LCM (a) and CMD (b) profiles. The $CaCO_3$ content for the LCM record is included. NRM: natural remanent magnetization; χ_0: low-field susceptibility, $IRM_{1.5T}$: isothermal remanent magnetization acquired at 1.5 T; ARM_{100mT}: anhysteretic remanent magnetization acquired at 100 mT peak field and 34 μT DC bias field, B_{cr}: coercivity of remanence. The normalized χ_0 at 150 °C as a proxy wheathering parameter (see text) is shown for the CMD profile. The boundary between the two subdomains in the CMD profile as described in the text is shown by a horizontal dashed line.

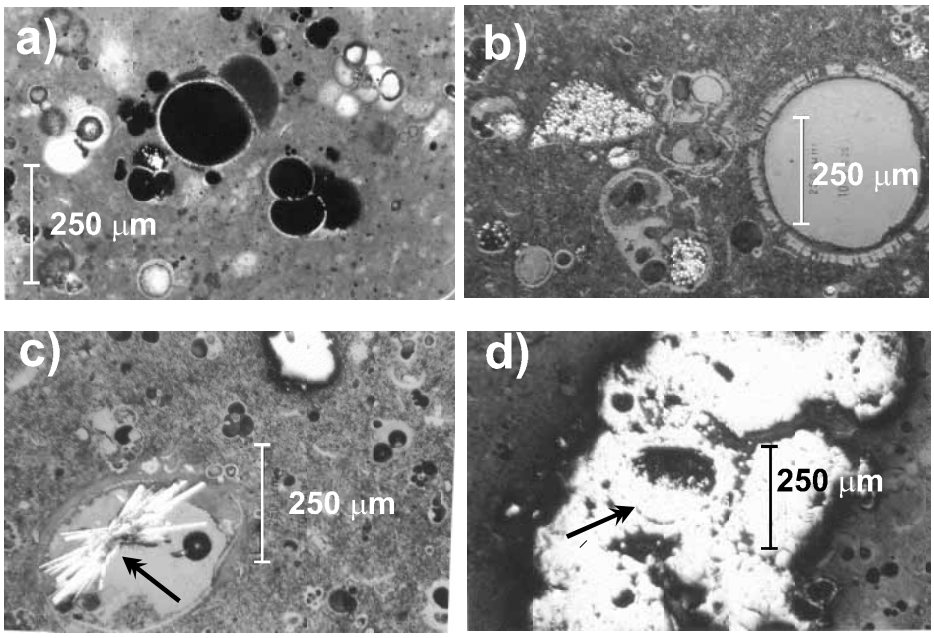

Fig. 6. Optical microscope images from LCM samples (a) Refracted light micrograph illustrating the presence of microforaminifera shells that are filled by opaque minerals (framboidal pyrite). (b) Reflected light micrograph showing the framboidal pyrite (bright) that fills microfossil shells. (c) Reflected light micrograph showing (indicated by arrow) peculiar acicular agregates (likely to be pyrrhotite) in a sample from the grey layer from cycle 46 (G46) which is characterized by "enhanced" magnetic properties. Smaller and similar grains were observed dispersed in the rock matrix. (d) Reflected light micrograph of a massive irregular iron sulfide grain in another sample from G46. Note the microforamminifera shell ghost indicated by the arrow.

The PMD profile

Thermal demagnetisation (Fig. 7a) revealed that two components were present, in addition to a small laboratory component, removed at 100-150°C. The first component was removed between 250-300°C and had a present-day Earth's magnetic field direction. The higher temperature component, taken to be the characteristic remanence (ChRM) had a maximum unblocking temperature of 580°C, suggesting that it was caried by magnetite. The ChRM had both normal and reversed polarity (Fig. 7b) although it was predominantly normal. The normal polarity directions were rotated clockwise by 30° and the fewer reversed directions were rotated in the same sense, but by a greater angle, c.51° but was imprecisely defined (α_{95} = 18.5°) and appear to have been more affected by the presence of some present-day field components - as also observed by Sheepers et al. (1993) in the composite Rossello section. The transition from normal to reverse occurs between the top of cycle 45 grey and the boundary between cycle 45 white1\beige and is interpreted as the lower Cochiti reversal. This reversal was placed by van Hoof (1993) in the upper part of cycle 45 beige in the Capo Bianco section since this layer had reverse polarities in its central part (the normal polarities above and below interpreted as delayed remanences). No detailed rock magnetic studies were made of samples from this profile.

The CMD profile

The two zones, above and below cycle 45-white1, had different characteristics. The lower zone ChRM component was generally removed at temperatures below 350°C (Fig. 8a, b & c) and the polarity was reversed. Somewhat higher blocking temperatures were found in the "mixed" category (Fig. 9a). In the upper zone (above cycle 45-white1), the maximum unblocking temperatures were up to 580°C, typical of magnetite (Fig. 8d, e & f) and the polarity was entirely normal, i.e. the boundary between the two zones coincides with the polarity transition, i.e. in cycle 45-white1 (Fig. 9a). Both the normal and reversed mean ChRM directions showed clockwise rotations (Fig. 9b), 25° and 20° respectively.

The different remanences (NRM, IRM and ARM for the CMD record (Fig 5b), delineate the two domains with distinct characteristics. The upper domain, above cycle 45-white1, presents relatively high remanences that are one to two orders of magnitude higher than those in the lower domain (Fig. 5b, note the logarithmic scale). Departing relative higher intensities in cycle 44 beige and to a lesser extent in cycle 43 beige, are observed in the lower domain. The NRM intensifies from the upper domain (~10 mA/m) are similar to the ones commonly observed in previous studies in the Trubi marls. Therefore, the relatively low NRM intensifies (below 1 mA/m) observed in the lower domain of the CMD profile (and in most of the LCM profile), represents a situation reported only occasionally (i. e. at the Punta Grande section located east of Punta di Maiata, Langereis & Hilgen 1993).

IRM acquisition experiments up to 1.5 T on samples from the two defined domains at the CMD record, and the subsequent thermal demagnetization of the imparted IRM, clearly show noticeable differences. (Fig. 4d & 4e). All samples practically reach saturation below 0.2-0.3 T, although in some cases a progressive small increase in intensifies can be observed at higher fields. As pointed out before, samples from the upper domain acquire higher saturation IRMs (Fig. 4d). The thermal

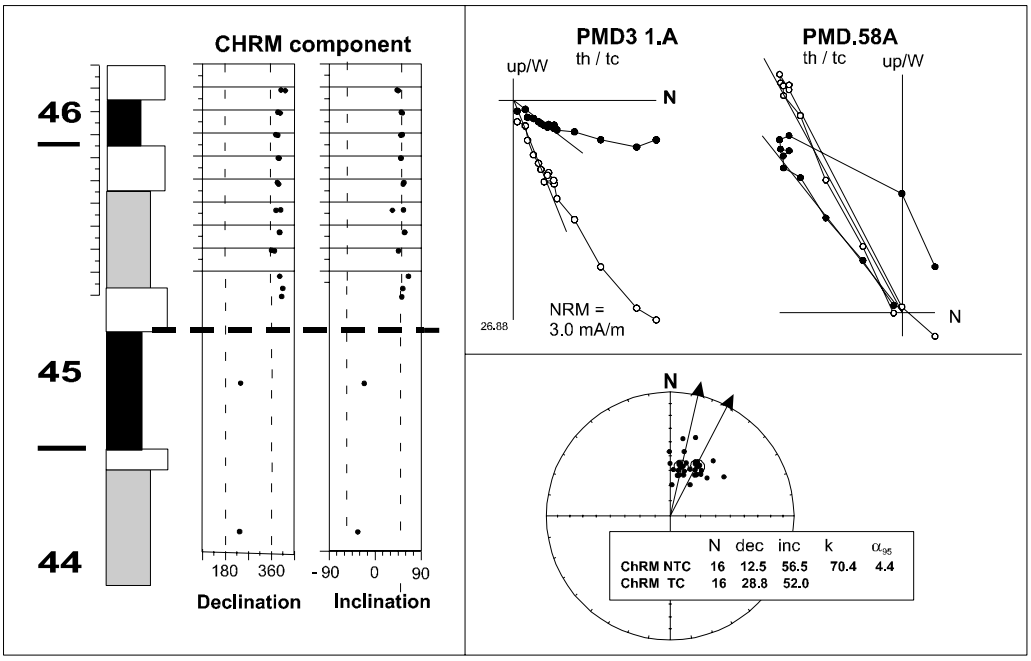

Fig. 7. Paleomagnetic data for the PMD track. (a) Bedding-corrected orthogonal thermal demagnetization diagrams. (b) ChRM declination and inclination record showing that a reverse to normal transition (lower Cochiti) occurs in cycle 45 (showed by a dashed thick line between G45 and B45). c) Equal-area projection of the ChRM components after bedding correction.

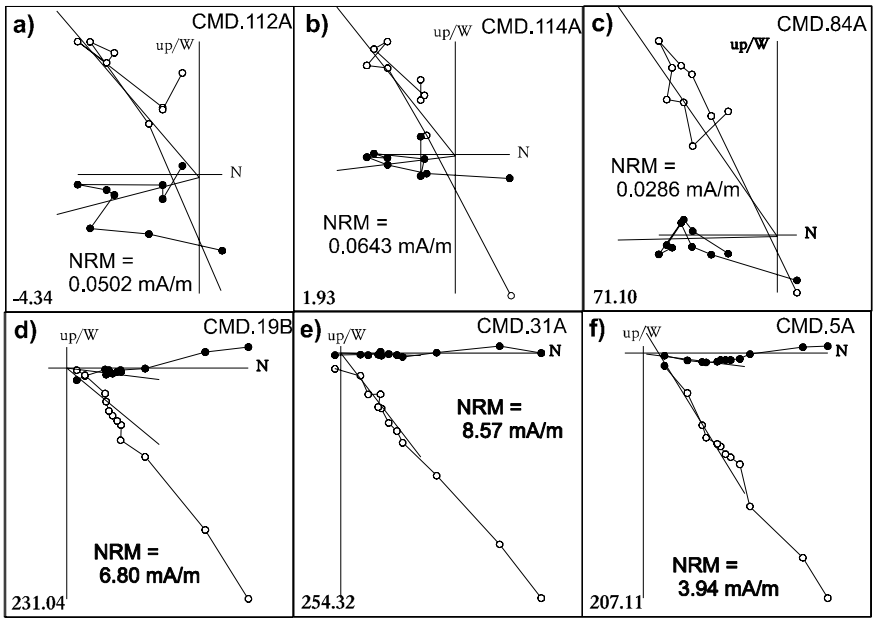

Fig. 8. Bedding-corrected orthogonal projections of stepwise thermal demagnetization of selected samples from the CMD record. Steps of 100, 150, 180, 210, 240, 270, 300, 320, 340 °C were used for the top three samples. Steps of 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 585 °C were used for the three lower diagrams. Note that the low-temperature unblocking reverse samples (a, b and c) are located in cycles 43 and 44 whereas the high-temperature unblocking normal samples (d, e, and f) belong to the overlying cycles 45 and 46 (see Fig. 9).

demagnetization of the IRM, for samples from the lower domain (Fig. 4e), shows the presence of unblocking temperatures typical of iron sulfides (330°C). However, in some samples, 30-40 % of the remanence is lost at higher temperatures (up to 580°C) indicating that magnetite must also contribute to the IRM (they likely correspond to the "mixed" category outlined before). The demagnetization behaviour of samples from the upper domain is characterized by a progressive loss in magnetization with a relative sharp decay around 550-580°C indicating that magnetite is the predominant carrier (Fig. 4e). These samples also display a drop in intensity at about 150°C. This feature was also observed along the upper Cochiti record at Punta di Maiata (van Hoof et al. 1993) and in samples from Eraclea Minoa (van Velzen & Zijderveld 1995). The latter authors conclude that this decay of IRM intensity at 150°C, and also other magnetic changes at this temperature, are related to weathering and release of stresses in the magnetic grains as explained in the introductory part.

A more noticeable difference between the magnetic behaviour from both domains is the variation in susceptibility upon heating (the susceptibility is measured at room temperature) (Fig. 4f). Samples from the lower domain show a constant susceptibility after heating up to temperatures of 350-400°C where an abrupt increase occurs. This increase can be related to the breakdown of iron sulfides (pyrite) and formation of new mineral phases (magnetite) that, after further heating, probably converts to hematite that explains the decrease of susceptibility at high temperatures. In contrast, samples from the upper domain show a substantially different behaviour. They are characterised by a much less pronounced increase at ~350-400°C and by a subtle but noticeable increase of susceptibility at ~150°C. As mentioned before, this is a peculiar feature related to weathering. We have used the normalised susceptibility to the room temperature at 150°C as an index for the weathering stage/mineralogy along the CMD record (Fig. 5b). It is evident that the upper domain displays higher values (up to 1.3) than in the lower domain where values remain close to one. This indicates that more weathering has occurred in the upper part and coincides with the field observations of two distinct domains with different colouring profile as outlined before.

The ARM/IRM ratio from the CMD record (Fig. 5b) ranges from 1 x 10-2 to 5 x 10-2 and the actual variations are difficult to interpret. In the lower domain, the lowest values are observed in cycle 44 beige. Seemingly, low values are also observed in the beige layers of cycles 45 and 46 from the upper domain. The highest values are observed in cycle 46 grey but also in several samples from the lower domain. The predominance of either of the magnetic minerals evidenced in the IRM experiments (iron-sulfide, magnetite, hematite) might explain to some extent the actual observations. The B_{cr} values are around 40 mT along the lower domain with the exception of the lowermost 30 cm and in cycle 44 white1 that display higher values (80-100 mT). In the upper domain, B_{cr} values are higher in the central part. The presence of a mixed mineralogy at the CMD record including a high-coercivity mineral precludes straightforward use of B_{cr} as a mineralogical proxy.

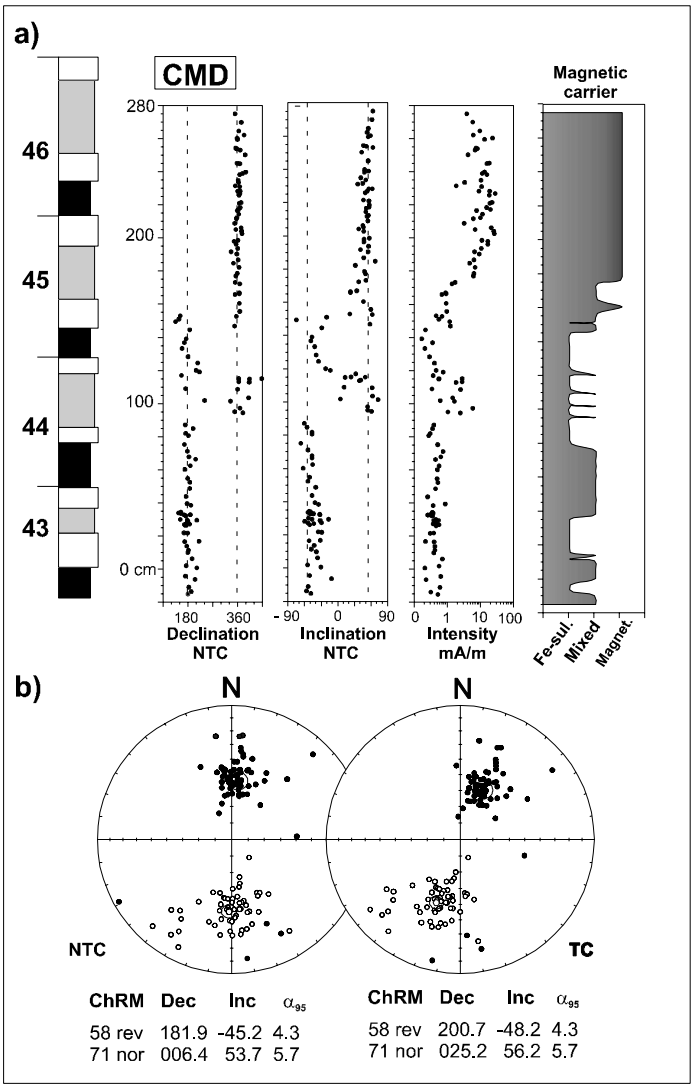

Fig. 9. Paleomagnetic data for the CMD record. (a) ChRM declination, inclination and intensity record. The reversal boundary located in W1-45 also delimits a lower domain with low unblocking temperatures assigned to Fe-sulfide or mixed Fe-sulfide/magnetite with respect to an upper domain characterized by higher unblocking temperatures typical of magnetite. (b) Equal-area projections the ChRM components before (NTC) and after bedding correction (TC).

Comparison of the Profiles

The low-field susceptibility depends on the concentration, grain-size and composition of the magnetic minerals as well as the proportion of diamagnetic and paramagnetic minerals. In the freshest LCM profile (Fig. 5a), the susceptibility minima (30-50 μSI) correlated with peaks of carbonate content, indicating that the contribution from diamagnetic carbonate might be the controlling factor. The maximum susceptibilities occurred in the grey and beige layers, typically 70 μSI. In contrast, the higher susceptibilities in the weathered PMD profile (not illustrated) and in the weathered CMD profile (Figure 5b) were associated with the beige layers. Cycles 45 and 46 in the CMD profile had values around 150 μSI, but the beige layers from cycles 43 and 44 were only slightly higher (c.80 μSI) than their corresponding grey layers. Previous studies of the Trubi marls (van Hoof 1993, van Hoof et al. 1993) showed always prominent susceptibility maxima in the beige layers (e.g. the beige layers of cycles 44 and 45 at Capo Bianco were 250 μSI). These were then interpreted as corresponding to both a relative higher clay content, i.e. a higher paramagnetic contribution, and a higher ferromagnetic contribution (van Hoof et al., 1993) because the high-field (mostly paramagnetic) susceptibility did not adequately account for the maxima in the low-field susceptibility. In the profiles reported here, it can only be noted that the relative contributions of the diamagnetic, paramagnetic and ferromagnetic phases probably vary. However, it is important to note that the same beds at the different profiles show marked differences, suggesting that the rocks and hence their magnetic properties have been differentially affected by some non-depositional processes.

The main R-N transition located at cycle 45 white1 in the CMD profile is consistent with previously established lower Cochiti reversal at cycle 45. In our PMD profile it is also located at this level. Unfortunately, this reversal boundary coincides with the boundary that separates two domains with distinct magnetic properties and therefore casts some doubt on its genuine validity as recorded in the CMD profile (Fig. 9a). The normal 'excursion' observed at cycle 44 beige is difficult to understand as a delayed remanence because is not only holded by iron-sulfides but also to the fact that seems to be recorded throughout the entire beige layer. Previous observations of delayed remanences of different polarity along reversal boundaries (van Hoof et al. 1993) were accounted for by the iron-migration model (or early diagenetic model). In such a model secondary (delayed) magnetite and not magnetic iron-sulfides will form away from the grey layers and therefore the central part of the beige layers will still hold the primary polarity. Consequently, we regard the CMD record as a hybrid situation of the different diagenetic/weathering processes affecting the Trubi marls (see below). The coincidence of the differential complex magnetic signature with the location of the lower Cochiti reversal renders the actual puzzling observations.

The occurrence of unrotated reverse polarities throughout the LCM profile from cycle 43 to 54 is the key element in the present study. The interval sampled in the LCM profile expands both downward and upward the normal Cochiti magnetozone (known to occur between cycles 45 and 49 beige layers) (Fig. 3). The expected normal polarities are not recorded and hence the ChRM directions from the LCM record must pre- or postdate the Cochiti. The fact that the mean direction does not imply any significant clokwise rotation (as would be expected for a Pliocene or older remanence in this region) provides us with a time constraint for its origin, i. e. is post Cochiti and likely to be Pleistocene and pre-Brunhes. Moreover, the presence of pyrrhotite as carrier of such "late" remanence in the LCM record provides a previously unrecognized feature in the Trubi marls that has important implications for the diagenetic pathway undergone by these rocks. The possible mechanism by which the later occurrence of iron-sulpides has occurred in some areas is discussed in the next section and a general diagenetic model will be presented.

As a global conclusion, there seems to be a direct correlation between the general magnetic properties and the expression of the colour profile of the Trubi marls. Generally, lower NRM intensifies and lower unblocking temperatures are observed at locations where the typical grey-white-beige-white colouring profile is less evident or nonexistent (eventually, as in the LCM profile, remanences can entirely be of "late" origin and locally enhanced). When the colouring is more obvious, samples show higher remanence intensifies, presence of magnetite and the peculiar features at low temperature (-150'C) and ascribed earlier to weathering. Despite that, those magnetite remanences appear to be primary as they record the sequence of expected Pliocene reversals derived from the oceanic magnetic anomalies in addition to local tectonic rotations (Hilgen & Langereis 1988, Zachariasse et al. 1989, Langereis & Hilgen 1991, Van Hoof, 1993 & our PMD record).

Discussion

Paleomagnetic and rock-magnetic data for two detailed records along the lower Cochiti reversal (CMD and LCM) and a third less-detailed additional record (PMD) along the same interval at Punta di Maiata has been presented. The data clearly shows the conspicuous occurrence of magnetic iron-sulfides (pyrrhotite) in particular locations along these laterally-equivalent profiles (notably throughout the LCM record). This feature was not known previously, and its particularities add important information that bears on the diagenetic history of the Trubi marls. The observations gathered from the Trubi marls will next be located in a general pathway framed in the syndiagenesis, anadiagenesis, and epidiagenesis global diagenetic stages as defined in Fairbridge (1967) (Fig. 10).

In a normal marine environment, syndiagenesis starts at the time of deposition on the sea floor. Is during this stage that the boundary (Eh = 0), above which the presence of oxygen allows organic activity, will delimit a lower zone where oxygen consumption outreaches the supply by diffusion (the early-burial stage) and

geochemical conditions may become suboxic and finally became anoxic. The cyclic nature of the Trubi marls results through sedimentary variations of this redox boundary as consequence of climatic variations controlled by orbital forcing (chiefly influencing carbonate production and dilution of terrigenous material). The consequences of this periodic changes in sedimentation and geochemical conditions on the magnetic signature has been previosuly modeled under the so called "early diagenetic or iron-migration model" (van Hoof et al. 1993) and described earlier in this paper. In Fig. 10 a schematic representation of this model involving three different time snapshots is given. Both detrital primary magnetite formed at t = 1 through t = 2 and "delayed" secondary magnetite (t = 3) are shown. In this example, two reverse pre-transitional "excursions" (delayed remanences) are explained by migration and later fomation of magnetite away from the lowermost represented grey layer.

In the global diagenetic stage model, Anadiagenesis will follow if sediments become buried to certain depths (i. e. up to 10 km). This would include compaction, dehydration and cementation and eventually metamorphism could initiate if conditions became appropriate. The Trubi marls probably did not got into the anadiagenesis stage and most likely only underwent limited burial of perhaps few kilometers at the most since sedimentation rate for the Trubi marls is estimated to be only 4-5 cm/ky and relatively soon after deposition (~3-4 My) rocks were uplifted and incorporated to the orogenic wedge.

During basin subsidence anadiagenesis will normally be the ongoing diagenetic process. However, if subsidence is replaced by uplift, the sediments may become exposed to the influence of the circulating groundwater. This type of environment is referred to as epidiagenesis and is characterized by the presence of a certain amount of O2 and CO2, and therefore, can be

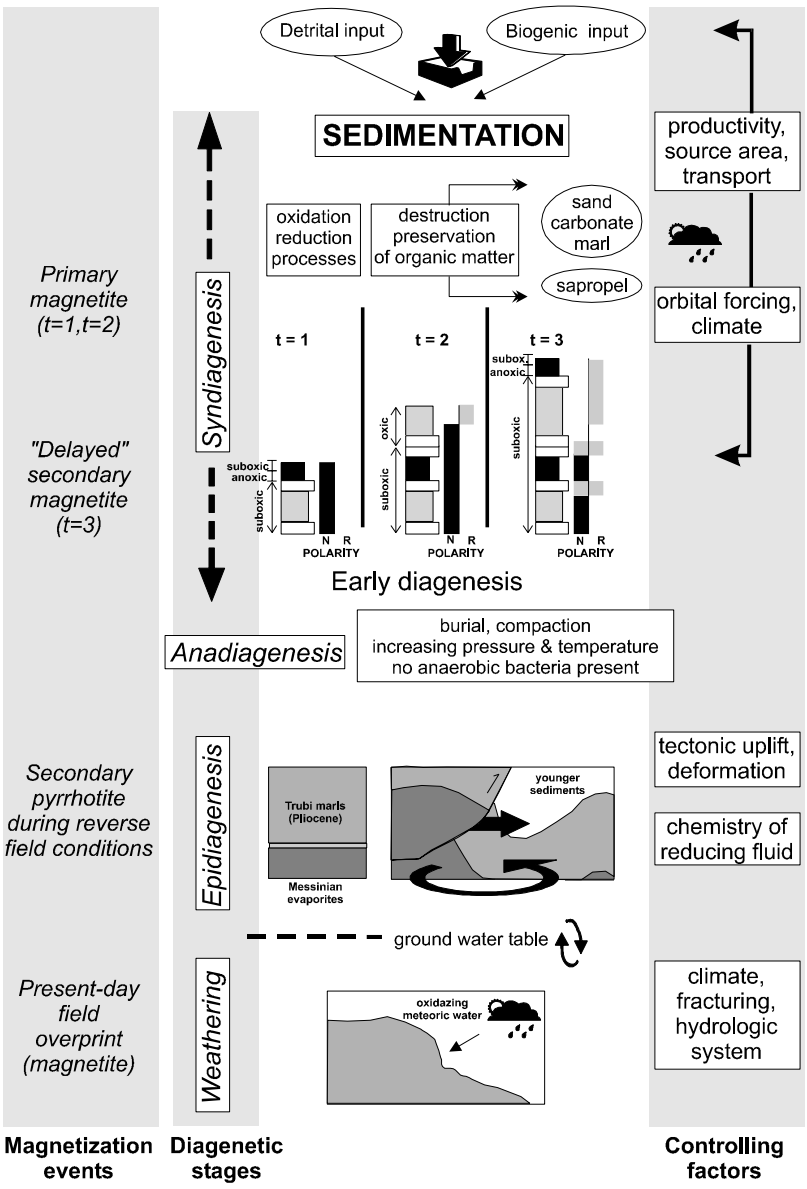

Fig. 10. General diagenetic evolution diagram through time in which the proposed diagenetic pathway for the Trubi marls together with its controlling factors. The different diagenetic stages (syndiagenesis, anadiagenesis and epidiagenesis) arranged from sedimentation to late weathering and including the "early diagenetic model" (van Hoof et al. 1993) are depicted.

aggressive towards mineral phases formed during anadiagenesis and thus, mask or destroy traces of the earlier stages. As described before, the studied outcrops in the southern part of the Caltanissetta basin have been uplifted and therefore placed through epidiagenetic conditions before reaching their actual position above the ground water table (Fig. 10). Is during this stage that we invoke an anoxic event that caused the dissolution of the former magnetite and the formation of magetic iron sulphides (pyrrhotite). This event must have occurred during a reverse period of the geomagnetic field attending the polarity observed at the LCM record. We cannot give further constraints on the age. It may speculatively be linked to a fluid flow related to thrust emplacement during Upper Pliocene or Pleistocene times. Such a fluid could have been enriched in sulphate after percolation and remobilization of the Messinian evaporites. The recording of this anoxic event can be rather irregular depending on the hydrologic system itself, the permeability of the rocks and the actual disposition of the outcrops in relation with the structures. The documentation of advection fluids at the front of the Sicilian subduction complex is not new but linkage to the magnetic signature of the Neogene sediments is not known. Larroque et al (1996) have reported that the frontal Sicilian prism supported localised transient fluid flow of deep freshwater sourced from two different origins: (1) a shallow one, where aqueous fluids locally flowed along the upper décollement and (2) a deeper one where aqueous and hydrocarbon-bearing fluids have been chanelized along the basal décollement from a depth as great as 10 km.

A different and unusual example of reduction in the epidiagenetic stage (otherwise generally oxidizing) occurs in the anhydrite caprock of certain salt domes (e. g. Feely & Kulp 1957, Davis & Kirkland 1979, Sassen et al. 1989). The sulfate reducing bacteria in the sulfate-bearing caprock of a salt dome obtain their sulfate supply from the immediate vicinity. Migration and accumulation of petroleum hydrocarbons favored by the fractured dome structure provides the nutrients for the sulfate-reducing bacteria. Another peculiar sulfate reduction setting and formation of pyrite in the epidiagenetic phase has been described in an English Chalk aquifer (Kimblin & Johnson 1992). In this case, meteoric water, sulfate-reducing bacteria and supply of organic matter from the sediment account for the formation of pyrite in anoxic conditions located in microninches in a dominantly oxic environment. Champ et al. 1979, have also described sulfate reduction in ground water aquifers where the highly oxidized state of the ground waters at recharge change progressively to a reduced state at discharge.

In the case of the Trubi marls under study, we don't unambiguously know the detailed mechanisms and chemical characteristics of the remagnetising fluid/process although it seems reasonable to relate to a late tectonic event perhaps connected to the previosuly described occurrence of fluids in the frontal Sicilian prism. The sulfate concentration of the groundwater or percolating fluid could originate from the aquifer system, i.e., from the dissolution of rock sulfate (gypsum/anhydrite) or from oxidative weathering of sulfides. When sulfate-bearing fluids penetrate strata containing organic matter, sulfate-reducing bacteria will produce H2S. The association of dissolved sulfates and hydrocarbons is thermodynamically unstable in diagenetic environments. Hence, redox reactions occur, either with or without the mediation of bacteria. The regional structure of the organic rich Trubi sediments in a series of thrust slices with local thick Messinian evaporites would propitiate the occurrence of a late sulfate reducing event and dissolution of original magnetite in particular zones (in a setting comparable to that described for the salt caprock situation). The degree of dissolution is a function of the surface area of the magnetite, the concentration of dissolved sulfide and the time together with a wide-range variables such as source rock, sulfate reduction rate, and reactivity of iron minerals contained in the sediment. It is therefore likely to conceive that magnetite dissolution and sulfitization in the Trubi marls at particular locations might have happened later in its diagenetic history when appropiate conditions were met (anoxia event during the epidiagenetic stage).

Upwards in the geological pile, epidiagenesis is replaced by weathering, with the ground water table being the practical boundary between them (Fig. 10). It will be at this stage when the Trubi marls suffer partial oxidation inducing the magnetization of the present day field. This late remagnetization event completes the diagenetic pathway for the Trubi marls as inferred in the present study.

Conclusions

The present research along the Cochiti interval at Punta di Maiata has demostrated the ocurrence of magnetic iron-sulfides that do not record the expected polarities and tectonically-related rotations. Hence, they are believed to have been formed during a late anoxic event during the epidiagenetic stage. Similar or comparable phenomena are already known related to the caprock of several salt domes. The exact geochemical conditions under which the 'anoxia' event in the Trubi marls took place is not known yet, and only the general framework for its occurrence has been put forward. Geochemical analysis, integrated with further petrographic observations and the rock-magnetic data will probably help deciphering the details of these processes. This study also hints on the complexity in which sediments can acquire their NRM and alerts on the necessity to use multidisciplinary approaches to unravel the exact sequence of events along the rock history.

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References

Brand, U. 1994. Morphochemical and replacement diagenesis in biogenic carbonates. In: K. H. Wolf & G. V. Chilingarian (eds), *Diagenesis IV. Developments in Sedimentology* 51. Elsevier, Amsterdam, 217-282.

Catalano, R. & D'Argenio, B. 1982. Schema geologico della Sicilia. In: R. Catalano and B. D'argenio (eds.), Guida alla Geologia della Sicilia Occidentale. Soc. Geol. Ital., Guide Geologiche Regionali, 9-41.

Catalano, R., Di Stefano, P. & Vitale, F. P. 1995. Structural trends and palaeogeography of the central and western Sicily belt: new insights. *Terra Nova*, 7, 189-199.

Champ, D. R., Gulens, J. & Jackson, R. E. 1979. Oxidation-reduction sequences in ground water flow systems. *Canadian Journal of Earth Sciences*, 16, 12-23.

Cita, M. B. & Gartner, S. 1973. The stratotype Zanclean. Foraminiferal and nannofossil biostratigraphy. *Rivista Italiana di Paleontologia*, 79, 503-558.

Davis, J. B. & Kirkland D. W. 1979. Bioepigenetic sulfur deposits. Economic *Geology*, 74, 462-468.

Dekkers, M.J. 1988. Magnetic properties of natural pyrrhotite Part I: Behaviour of initial susceptibility and saturation-magnetization-related rock-magnetic parameters in a grain-size dependent framework. *Physics of the. Earth and Planetary Interiors*, 52: 376-393.

De Visser, J.P., Ebbing, J. H. J., Gudjonsson, L., Hilgen, F. J., Jorinssen, F. J., Verkallen, P. J. J. M. & Zevenboom, D. 1989. The origin of rhythmic bedding in the Pliocene Trubi Formation of Sicily, Southern Italy,. *Palaeogeography, Palaeoclimatology, Palaeocology*, 69, 45-66.

Fairbridge, R. W. 1967. Phases of diagenesis and authigenesis. In: J. G. Larsen & G. V. Chilingar (eds), *Diagenesis in sediments*, Elsevier, Amsterdam, 19-89.

Feely, H. W. & Kulp, J. L. 1957. Origin of Gulf Coast salt-dome sulfur deposits. Bulletin of the American Association of Petroleum Geologists, 41, 1802-1853.

Hilgen, F. J. 1987. Sedimentary rhytms and high-resolution chonostratigraphic correlations in the Mediterranean Pliocene. *Newsletters of Stratigraphy*, 17, 109-127.

Hilgen, F. J. 1991: Extension of the astronomically calibrated (polarity) time scale to the Miocene/Pliocene boundary. *Earth and Planetary Science Letters*, 107, 349-368.

Hilgen, F. J. & Langereis, C. G. 1988: The age of the Miocene-Pliocene boundary in the Capo Rossello area (Sicily). *Earth and Planetary Science Letters*, 91, 214-222.

Hunt, C. P., Banerjee, S. K., Han, J., Solheid, P. A., Oches, E., Sun, W. & Liu, T. 1995. Rock-magnetic proxies of climate change in the loess-paleosol sequences of the western Loess Plateau of China. *Geophysical Journal International*, 123, 232-244.

Kimblin, R. T. & Johnson, A. C. 1992. Recent localised sulphate reduction and pyrite formation in a fissured Chalk aquifer. *Chemical Geology*, 100, 119-127.

Langereis, C. G. & Hilgen, F. J. 1991. The Rossello composite: a Mediterranean and global standard reference section for the Early to early Late Pliocene. *Earth and planetary Science Letters*, 104, 211-225.

Larroque, C., Guilhaumou, N., Stephan, J.F. & Roure, F. 1996. Advection of fluids at the front of the Sicilian Neogene subduction complex. *Tectonophysics*, 254, 41-55.

Lentini, F. and Vezzani, L. 1978. Tentativo di elaborazioni di uno schema structturale della Sicilia orientale. *Memorias. Sococietà. Geologica. Italiana.*, 19: 495-500.

Lourens, L. J., Antonarakou, A., Hilgen, F. J., Van Hoof, A. A. M., Vergnaud-Grazzini, C. & Zachariasse, W. J. 1996. Evaluation of the Plio-Pleistocene astronomical timescale. *Paleoceanography*, 11, 4, 391-413.

Mullender, T. A. T., van Velzen, A. J. & Dekkers, M. J. 1993. Continuous drift correction and separate identification of ferrimagnetic and paramagnetic contribution in thermomagnetic runs. *Geophysical Journal International*, 114, 663-672.

Ogniben, L. 1960. Nota illustrativa dello schema geologico della Sicilia nord-orientale. *Riv. Min. Sicil*., 64-65.

Roberts, A. P. 1995. Magnetic properties of sedimentary greigite (Fe3S4). *Earth and Planetrary Science Letters*, 134, 227-236.

Scheepers, P. J. J. 1994. Tectonic rotations in the Tyrrenian arc system during the Quaternary and late Tertiary, PhD Thesis, Univ. of Utrecht, *Geologica Ultraiectina*, 112, 352 pp.

Scheepers, P. J. J. & Langereis, C. G. 1993. Analysis of NRM-directions from the Rossello composite: implications for tectonic rotations of the Caltanisetta basin (Sicily). *Earth and planetary Science Letters*, 119, 243-258.

Sassen, R, McCabe, C., Kyle, J. R. & Chinn, W. Deposition of magnetic pyrrhotite during alteration of crude oil and reduction of sulfate. *Organic Geochemistry*, 14, 318-392.

van Hoof, A. A. M. 1993: Geomagnetic polarity transitions on the Gilbert and Gauss Chrons recorded in marine marls from Sicily. PhD Thesis, Univ. of Utrecht. *Geologica Ultraiectina*, 100, 123 pp.

van Hoof, A. A. M. & Langereis, C. G. 1991. Reversal records in marine marls and delayed acquisition of remanent magnetization. Nature, 351, 223-224.

van Hoof, A. A. M., van Os, B. J. H., Rademakers, J. G., Langereis, C. G. & de Lange, G. J. 1993. A paleomagnetic and geochemical record of the upper Cochiti reversal and two subsequent precessional cycles from southern Sicily (Italy). *Earth and planetary Science Letters*, 117, 235-250.

van Hoof, A. A. M., van Os, B. J. H. & Langereis, C. G. 1993. The upper and lower Nunivak sedimentary geomagnetic transitional records from Southern Sicily. *Physics of the Earth and Planetary Interiors*, 77, 297-313.

van Velzen, A. J. & Zijderveld, J. D. A. 1995. Effects of weathering on single-domain magnetite in Early Pliocene marine marls. *Geophysical Journal International*, 121, 267-278.

Zachariasse, W. J., Zijderveld, J. D. A., Langereis, C. G., Hilgen, F. J. & Verhallen, P. J. J. M. 1989. Early Late Pliocene biocronology and surface water temperature variations in the Mediterranean. *Marine Micropaleontology*, 14, 339-355.