The Tortonian reference section at Monte dei Corvi (Italy): evidence for early remanence acquisition in greigite-bearing sediments

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SUMMARY
The reliability of primary natural remanent magnetization (NRM) signals in greigite-bearing sediments has been frequently questioned. Here, we show that the stable NRM in the deep marine Middle to Late Miocene sediments at Monte dei Corvi, northern Italy, is mainly carried by greigite. Combined rock magnetic experiments and scanning electron microscopy successfully enabled discrimination between two greigite populations. One fine-grained and relatively well-dispersed greigite population (grain size between 60 and 200 nm) is most likely of magnetotactic origin. The second greigite population with larger grain sizes (typically 700 nm to 1 μm) is most likely of authigenic (bacterially mediated) origin, and is related to post-depositional sulphidization processes. Greigite is the main magnetic remanence carrier in the older part of the section (12.8 to 8.7 Ma), whereas greigite and fine-grained (presumably magnetotactic) magnetite are present in the younger part of the section (8.7 to 6.9 Ma). Similar remanent magnetization directions of the magnetite and greigite components, and the likelihood of a magnetotactic origin, suggests that the NRM is of syn-depositional age. We suggest that moderate methane seepage from the underlying sediments may have occurred that resulted in the preservation of pristine greigite. This corroborates the reliability of the previously established magnetostratigraphy at Monte dei Corvi.

Key words: Magnetostratigraphy; Rock and mineral magnetism; Europe.

1 INTRODUCTION
Over the last few decades, numerous stratigraphic studies have established high-resolution Neogene chronologies. These studies have employed biostratigraphy, radioisotopic dating, magnetostratigraphy and astronomical tuning in different sedimentary environments. Global Stratotype Sections and Points (GSSPs) have been defined for the Neogene to improve the standard geological timescale.

The Tortonian GSSP, i.e. the Serravallian–Tortonian boundary (Middle–Late Miocene boundary), has been defined at the Monte dei Corvi section in northern Italy (Hilgen et al. 2003, 2005). This section has also been proposed as the Mediterranean reference section and unit stratotype for the Tortonian Stage (Hüsing et al. 2009). Its magnetostratigraphy is calibrated straightforwardly to the interval between 12.5 and 7.2 Ma of the geomagnetic polarity timescale (GPTS), with support from biostratigraphy, radioisotopic dating of ash layers and astronomical tuning of characteristic sedimentary cycle patterns to the precession index (≈21-kyr; Hilgen et al. 2003; Hüsing et al. 2007). Resulting astronomical ages for each reversalsal boundary generally have small uncertainties (1 to 20 kyr). The Monte dei Corvi section is the only marine Miocene section that has such a high-resolution magnetostratigraphy and astronomical dating, therefore its reversal ages have been included into the most recent Neogene geological timescale (Lourens et al. 2004) that provides a basis for worldwide correlation and dating.

For any magnetostratigraphy to be reliable, the magnetic remanence must be a primary palaeomagnetic signal that is stable over geological time. Detrital (fine-grained) magnetite is a reliable magnetic remanence carrier because its magnetization is typically locked in shortly after deposition. Magnetite from bacterial magnetosomes can also carry a reliable primary remanence. Early and late diagenetic processes can, however, alter the primary magnetic mineral assemblage through dissolution and sulphidization processes that lead to the formation of new magnetic minerals, particularly the iron sulphides greigite and pyrrhotite (Berner & Raiswell 1983; Berner 1984; Roberts & Turner 1993; Wilkin et al. 1996; Kao et al. 2004). Pyrrhotite is generally considered to form during late diagenesis (e.g. Dinarès-Turell & Dekkers 1999; Weaver et al. 2002; Horng & Roberts 2006), although it can occur as a detrial magnetic phase (Horng & Roberts 2006). Authigenic pyrrhotite is considered not suitable for palaeomagnetic studies where the syn- or early depositional acquisition of the NRM is crucial. Greigite can...
form authigenically any time after deposition if the necessary reactants are present (Roberts & Weaver 2005), which complicates the interpretation of sedimentary palaeomagnetic records. Therefore, greigite is also considered to be an unreliable magnetic carrier in many cases (Florindo & Sagnotti 1995; Thompson & Cameron 1995; Horng et al. 1998; Richter et al. 1998; Jiang et al. 2001; Roberts et al. 2005; Roberts & Weaver 2005; Sagnotti et al. 2005; Rowan & Roberts 2006). In other cases, early greigite formation has been demonstrated. For example greigite can form within a stagnant water column (e.g. Cutter & Kluckhohn 1999) and sedimentary greigite has been demonstrated to form within years or decades (e.g. Pye 1981; Reynolds et al. 1999). Recently, greigite has also been shown to carry a primary palaeomagnetic signal in Miocene-Pliocene brackish to fresh water environments (Vasiliev et al. 1997).

In sediments of the Monte dei Corvi section, the behaviour of the NRM during thermal demagnetization and preliminary rock magnetic experiments (acquisition of isothermal remanent magnetization; IRM) suggested that beside magnetite the iron sulphide greigite is most likely the main magnetic remanence carrier (Hüsing et al. 2007). Here, we investigate the nature and origin of this carrier by means of detailed rock magnetic experiments and electron microscopic analysis. We discuss the NRM acquisition processes for greigite. These NRM acquisition mechanisms have significant implications for the ages of reversal boundaries, which clearly depend on the type of magnetic remanence carriers present in a sediment.

2 BACKGROUND

2.1 Lithology

The marine, pelagic to hemipelagic, Miocene sediments of the Monte dei Corvi section are exposed along the cliffs between Ancona and Il Trave in the Cònero Riviera, northern Italy (Montanari et al. 1997) (Fig. 1). The section encompasses the upper part of the Serravallian, the entire Tortonian and the lower part of the Messinian stage and is composed of cyclic alternations of marls, marly limestones and sapropels (Fig. 2). Large-scale non-repetitive stratigraphic changes allow discrimination between a Lower, Brownish, Rossini and Euxinic Shale Interval (for more detailed description of the lithology and sedimentary cycles, the reader is referred to Montanari et al. (1997), Hilgen et al. (2003) and Hüsing et al. (2007, 2009)).

Sapropel formation in the Mediterranean has been explained by increased primary production, leading to a higher oxygen demand, and to development of more stagnant conditions resulting in reduced oxygen replenishment of bottom waters (Rossignol-Strick et al. 1982; Calvert et al. 1992; Rohling 1994) related to climate-induced increases in freshwater input from the African and European continents (Rossignol-Strick et al. 1982; Rossignol-Strick 1985; Hilgen 1991; Rohling & Hilgen 1991; Rohling 1994). Distinct sapropel patterns observed at Monte dei Corvi reflect astronomical cyclicity with precession, obliquity and eccentricity all evident in the sedimentary succession (Hilgen et al. 2003; Hüsing et al. 2007). This climatic link has led to correlation of individual ancient sapropels to maxima in (65°N) summer insolation and thus to minima in the precession index using the same phase relations with the orbital parameters as for younger Mediterranean sapropels (Hilgen 1991; Hilgen et al. 2003).

2.2 NRM demagnetization

Initial NRM intensities (at 20°C) are generally low, ranging between 0.001 and 1.804 mAm−1. Higher NRM intensities occur between 78 and 95 m and between 112 and 128 m (Fig. 2). During stepwise thermal demagnetization, a viscous component was removed between room temperature (20°C) and 100°C (Figs 2a–d), which is interpreted to be a secondary post-tilt overprint (Hilgen et al. 2003; Hüsing et al. 2007). A second magnetic component was generally removed up to 260–280°C (Fig. 2d), but where NRM intensities are higher, thermal demagnetization was useful up to ~360°C or even up to 400 to 420°C (Figs 2a and c). The high-temperature component can have either normal or reversed polarity and is interpreted to be the primary component (Hüsing et al. 2007, 2009). The decrease in remanence up to ~360°C (Fig. 2c) is similar to that reported for greigite (Roberts 1995; Chang et al. 2008), with remanence decrease between 250 and 280°C (Fig. 2d) being explained by thermal alteration of greigite (Roberts 1995). To enable identification of the primary magnetization before the onset of thermal breakdown of greigite, selected samples were subjected to alternating field (AF) demagnetization after heating to 280°C. In some samples, the remanence diverged from a linear decay toward the origin above 25 or 30 mT (Fig. 2e), which suggests that the greigite may have acquired a gyroremanent magnetization (GRM) during AF demagnetization (Snowball 1997a,b; Sagnotti & Winkler 1999; Stephenson & Snowball 2001). In other samples, the NRM decay was linear toward the origin up to 100 mT (Fig. 2b), which indicates that greigite has apparently not acquired a GRM during AF demagnetization (see Rowan & Roberts 2006) and suggests the presence of (fine-grained) magnetite.

Plotting the primary directions on an equal area projection reveals two clusters that are located in the SE and NE quarters of the stereographic projection (Fig. 2). The directional non-antipodality can be explained by overlapping blocking temperature spectra of the primary and secondary components, resulting in non-ideal
Figure 2. Lithologic and magnetic stratigraphy and correlation to the GPTS of the Monte dei Corvi section (Hilgen et al. 2003; Hüsing et al. 2007, 2009). The 0 m level is based on the definition of Hilgen et al. (2003). Tortonian GSSP = Tortonian Global Stratotype Section and Point; located in the midpoint of the sapropel in basic cycle 76. T–M denotes the Tortonian–Messinian boundary. Black (white) circles denote reliable (unreliable) ChRM directions. In the polarity column, black (white) zones indicate normal (reversed) polarity intervals. Thermal and AF demagnetization behaviour of selected samples are shown on the right, where temperatures used for thermal demagnetization are indicated in °C and AF demagnetization steps are indicated in mT. (a) COR493.A at 131.07 m; (b) COR667.A at 122.15 m; (c) MCOR1044.A at 81.87 m; (d) MCOR1009.B at 79 m; (e) MCOR1009.A at 79 m. Based on the trend of NRM intensities after thermal treatment at 100 °C and the thermal and AF demagnetization behaviour of the samples (a to e), the section is subdivided into an ‘older interval’ and a ‘younger interval’. A hiatus of ∼80 kyr at ∼133 m was confirmed by astronomical tuning (see Hüsing et al. 2009). Consequently, cycle 237 that contains the last palaeomagnetic sample is astronomically dated at 6.919 Ma.

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identification of the primary magnetization component (Hilgen et al. 2003; Hüsing et al. 2007).

The resulting characteristic polarity pattern (Fig. 2) was correlated straightforwardly to all polarity zones between normal polarity Chron C5Ar.1n and Chron C3Br.1n, which spans the age interval between 12.8 and 7.2 Ma. Even short polarity intervals of 30 to 40 kyr duration were recorded (Hüsing et al. 2007).

Based on the different NRM characteristics during thermal and AF demagnetization, we refer to: (1) the older interval (26 to 112 m; 12.8 to 8.7 Ma), which has generally lower NRM intensities and a marked decrease in remanence between 280 and 360 °C, and (2) the younger interval (112 to 135 m; 8.7 to 6.9 Ma), which has generally higher NRM intensities, higher magnetic susceptibility values, and stable remanences above 360 °C (see Fig. 2).

3 METHODS

Magnetic property analyses were carried out through IRM acquisition, thermal demagnetization of a three-axis IRM (Lowrie 1990), high-temperature thermomagnetic runs and low-temperature magnetic remanence measurements. These were complemented by scanning electron microscope (SEM) analyses.

IRM acquisition curves were obtained for 81 samples in seven intervals (at ~30.4, ~54, ~65.6, ~79.0, 117, 122 and 125 m), each comprising two to four basic cycles. Most samples from the lower four depth intervals had 25 to 30 peak fields applied up to 2 T. Fewer steps were applied in the low-field range because of the inaccuracy of field settings with the PM4 pulse magnetizer. The IRM was subsequently measured using a horizontal 2G Enterprises DC SQUID magnetometer (noise level 3 × 10^{-12} Am²). All samples from the upper three intervals and eight additional samples from the lower four intervals were measured using a robotized SQUID magnetometer (noise level 1–2 × 10^{-12} Am²), which allows measurements of 42 data points after IRM acquisition up to 700 mT. Data acquired from the robotized system were corrected for the tray and sample holder magnetization by (1) subtracting the magnetization of the tray, which was magnetized at 700 mT prior to measurements and (2) subtracting the magnetization of the sample holder including the residual remanence of the sample after AF demagnetization at 300 mT. Each sample was AF demagnetized at 300 mT prior to IRM acquisition so that they were in the AF demagnetizing starting state (Heslop et al. 2004).

All data were subjected to component analysis of cumulative log-Gaussian (CLG) curves (Kruiver et al. 2001), where every IRM curve was decomposed into a number of CLG curves. These can be individually characterized by their saturation IRM (SIRM), remanent acquisition coercive force (B_{r1/2}), and dispersion parameter (DP). Results of the CLG analysis can be used to select suitable peak fields for three-axis thermal demagnetization of the IRM (Lowrie 1990). Component fitting of IRM acquisition curves is best achieved using three components: (1) between 0 and 35 mT; (2) between 35 and 300 mT, and (3) between 300 mT and 2 T (Hüsing et al. 2007). Selected samples were subsequently imparted with an IRM using 2 T, 300 mT and 35 mT fields along three perpendicular axes and were stepwise thermally demagnetized from room temperature up to 600 °C.

Magnetic extracts were obtained from bulk sediment following the set up and separation procedure described by Dekkers (1988b). Heavy liquid extracts were obtained using the protocol of Franke et al. (2007). High-temperature thermomagnetic runs were performed on bulk sediments, magnetic extracts and heavy liquid extracts in air using a modified horizontal translation-type Curie Balance (Mullender et al. 1993). Samples were selected from each lithology and were heated in air using an oscillating field between 150 and 300 mT. The heating run started at room temperature. Heating and cooling cycles were used in which the sample was heated to successive maximum temperatures that were progressively increased by 50 to 100 °C. This was done to discriminate real magnetic behaviour from chemical alteration. Most samples were heated to 720 °C—a few were heated to 640 °C only—with heating rates of 5 °C per min and cooling rates of 10 °C per min.

Low-temperature magnetic remanence measurements were performed on a Quantum Design XL7 Magnetic Properties Measurement System (MPMS) with a noise level of ~10^{-11}Am² at the University of Bremen, Germany. Heavy liquid extracts of three representative samples were selected based on the following criteria: (1) behaviour during thermal demagnetization that suggests the presence of greigite, (2) relatively high NRM intensities, (3) samples from different lithologies, and (4) samples that straddle one basic precession cycle. These selected samples are: MCOR1062 in limestone at 84.65 m, MCOR1064 in marl at 84.86 m and MCOR1066 in a sapropel at 85.02 m. Between 0.05 and 0.25 g of material was fixed in gelatin capsules (for sample preparation and instrument details, see Frederichs et al. 2003). Low-temperature remanence warming curves (10–300 K) were obtained at 1 K increments. For zero-field cooling (ZFC) remanence measurements, the sample was cooled in zero field to 10 K. A 2 T field was then applied and switched off before warming the sample back to room temperature (300 K). For subsequent field cooling (FC) remanence measurements, a 2 T field was applied during initial cooling from room temperature to 10 K. The field was then switched off before warming back to 300 K. The first derivatives of both ZFC and FC remanences versus temperature were calculated to visualize the changes in magnetic behaviour during sample warming. Finally, room temperature SIRM (RT-SIRM) cycles were performed by applying a 5 T field at room temperature (300 K) before the sample was cycled in zero field from 300 to 10 K (cooling) and back to room temperature at 300 K (warming). Secondary electron (SE) and backscattered electron (BSE) imaging were carried out to visualize the magnetic mineral assemblage using a FEI XL SFEG scanning electron microscope (SEM) at the Centre of Electron Microscopy Utrecht (EMU), Utrecht University, The Netherlands. Energy dispersive X-ray spectroscopy (EDS) was used to determine the elemental composition of individual particles in polished thin sections of bulk sediment and dispersed heavy liquid extracts. Particle sizes were estimated using the Scandium imaging software. Atomic ratios of iron to sulphur were compared to distinguish cubic pyrite (FeS₂ = 0.5) and greigite (Fe₃S₄ = 0.75), monoclinic pyrrhotite (Fe₇S₈ = 0.875) and mackinawite (FeS = 1).

4 ROCK MAGNETIC RESULTS

4.1 IRM acquisition component analysis

CLG analysis and interpretation of IRM acquisition curves aims to introduce and fit the smallest number of components to avoid over-interpretation of data. Here, we use results of the thermal demagnetization behaviour of NRM, which indicate that greigite is most likely the main magnetic component. In the younger interval, (fine-grained) magnetite is present in addition to greigite. In all samples, components are labelled the same way starting with the component fitted to the low field range (Fig. 3, Table 1).
Figure 3. Representative examples of CLG interpretation of IRM acquisition curves. (a) and (b) are samples from the older interval with two greigite components (Component 3 = biogenic greigite and Component 4 = authigenic, inorganic greigite), (c) and (d) are samples from the younger interval, with the additional fine-grained (magnetotactic) magnetite Component 2.
Table 1. Results of CLG analysis of IRM acquisition curves.

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>Component 3</th>
<th>Component 4</th>
<th>Component 5</th>
</tr>
</thead>
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<tr>
<td>Thermal activation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level</td>
<td>Total IRM</td>
<td></td>
<td></td>
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<tr>
<td>Sample code</td>
<td>m</td>
<td>(10^-6 Am^2 kg^-1)</td>
<td>(mT)</td>
<td>(log 10 mT)</td>
</tr>
<tr>
<td>Cycle 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCOR 561.B</td>
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<td></td>
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<tr>
<td>Cycle 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>MCOR 751.B</td>
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<tr>
<td>Cycle 3</td>
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<tr>
<td>MCOR 851.A</td>
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<tr>
<td>Cycle 4</td>
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Table 1. (Continued)

<table>
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<tr>
<th>Sample code</th>
<th>Total IRM (mT)</th>
<th>DP Contribution (mT)</th>
<th>Component 1</th>
<th>Component 2</th>
<th>Component 3</th>
<th>Component 4</th>
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</tr>
</thead>
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<tr>
<td>MCOR0106A</td>
<td>78.77</td>
<td>42.3</td>
<td>12.6 (0.32)</td>
<td>23.6 (0.48)</td>
<td>22.4 (0.42)</td>
<td>16.3 (0.30)</td>
<td>12.6 (0.32)</td>
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<td>MCOR0107B</td>
<td>78.79</td>
<td>43.3</td>
<td>12.6 (0.33)</td>
<td>23.6 (0.48)</td>
<td>21.9 (0.41)</td>
<td>16.3 (0.30)</td>
<td>12.6 (0.32)</td>
</tr>
<tr>
<td>MCOR0108B</td>
<td>79.81</td>
<td>53.9</td>
<td>12.6 (0.35)</td>
<td>23.6 (0.48)</td>
<td>21.9 (0.41)</td>
<td>16.3 (0.30)</td>
<td>12.6 (0.32)</td>
</tr>
<tr>
<td>MCOR0109A</td>
<td>79.81</td>
<td>20.8</td>
<td>12.6 (0.30)</td>
<td>23.6 (0.48)</td>
<td>21.9 (0.41)</td>
<td>16.3 (0.30)</td>
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<td>21.9 (0.41)</td>
<td>16.3 (0.30)</td>
<td>12.6 (0.32)</td>
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<tr>
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<td>52.6</td>
<td>12.6 (0.33)</td>
<td>23.6 (0.48)</td>
<td>21.9 (0.41)</td>
<td>16.3 (0.30)</td>
<td>12.6 (0.32)</td>
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<td>Cycle 5</td>
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<td>52.6</td>
<td>15.8 (0.25)</td>
<td>23.6 (0.48)</td>
<td>21.9 (0.41)</td>
<td>16.3 (0.30)</td>
<td>12.6 (0.32)</td>
</tr>
</tbody>
</table>

The total IRM is calculated by adding the SIRM of individual components of respective samples. Asterisk (*) denote that samples were measured by the robotized procedure $B_{p-z}$. The remanent acquisition coercive force $B_{c}$ is interpreted as goethite, is most likely a product of weathering processes. See text for details.
Component 1 was fit in the low field interval, with $B_{1/2} = \sim 12$ mT. The low $B_{1/2}$ value and the relatively small contribution (about 10 per cent of the total IRM) indicates that this component is related to thermal activation resulting in a skewed distribution (Egli 2004a,b; Haslop et al. 2004), and should therefore not be given any physical meaning. Nevertheless, this observation is consistent with that of Rowan & Roberts (2006) who suggested that many greigite samples contain substantial SP contributions.

Component 2 is present only in the younger interval (Fig. 3, Table 1). This component has a $B_{1/2}$ value of $\sim 35$ mT and a narrow grain size distribution indicated by a small DP of $\sim 0.2 \log_{10}$ mT. These values remain relatively constant throughout the younger interval of the section. The $B_{1/2}$ values are typical of magnetite and the narrow gain size distribution is indicative of a magnetotactic (Kruiver et al. 2001) rather than a detrital origin. This magnetotactic magnetite contributes $\sim 15$ per cent to the total IRM and is therefore of minor importance.

Components 3 and 4 are both fitted with the same $B_{1/2}$ values between 49 and 83 mT, but the distribution parameters for component 3 are smaller than for component 4. The $B_{1/2}$ values overlap with remanent coercive force values reported for greigite and pyrrhotite (Dekkers 1988a; Roche et al. 1990; Snowball 1991; Roberts 1995; Snowball 1997a,b; Horng et al. 1998; Sagnotti & Winkler 1999). We interpret this component as greigite rather than pyrrhotite on the basis of the above described thermal behaviour of the NRM and thermomagnetic analysis (see later). Different types of sedimentary greigite formation most likely result in different grain size distributions for different greigite populations (e.g. Vasilyev et al. 2007). We therefore chose to distinguish between two populations of greigite (this interpretation is supported by SEM observations discussed in Section 4.4.). The first population (Component 3) is composed of fine-grained greigite with a narrow DP ($\sim 0.2 \log_{10}$ mT) and high $B_{1/2}$ values. This indicates single-domain (SD) particle sizes (Roberts 1995; Snowball 1997a,b; Horng et al. 1998; Sagnotti & Winkler 1999) that are expected if this greigite component has a biogenic origin (Vasilyev et al. 2008). The relatively constant and higher contribution of Component 3 to the total IRM (between 30 and 60 per cent)—independent of lithology—sugests that this greigite component is the main magnetic carrier throughout the entire section.

The second population (Component 4) is characterized by a wider grain size distribution (DP = $\sim 0.36 \log_{10}$ mT) that would be expected for authigenic greigite resulting from bacterially mediated formation. The contribution of Component 4 ($\sim 30$ per cent) to the total IRM is smaller than that of greigite Component 3, particularly in the younger interval. The survival of fine-grained (magnetotactic) magnetite Component 2 and lower concentrations of greigite Component 4 indicate that sulphidization processes were probably not as severe in the younger sediments as in the older sediments.

Component 5 is fitted to the high-field interval and has $B_{1/2}$ values between 300 mT and 1 T and a large DP ($\sim 0.32 \log_{10}$ mT). Its presence is also indicated by the high field ‘tail’ observed in standardized acquisition plots (SAP). This component is responsible for the non-saturation of IRM in all samples (e.g. Kruiver et al. 2001) and could be carried either by goethite or haematite. The weak NRM intensities and NRM decrease below 500 °C precludes the presence of haematite. Goethite is likely present as a product of weathering processes (Dunlop & Ozdemir 1997; France & Oldfield 2000; Kruiver et al. 2001; Maher et al. 2004) and its contribution (2 to 14 per cent) to the IRM is minor. The $B_{1/2}$ values could indicate a relatively soft goethite component, but the applied maximum fields of only 700 mT and 2 T, respectively, are not sufficient for goethite saturation.

### 4.2 3-axis thermal demagnetization of IRM

For all samples, the medium coercivity (35 and 300 mT) fraction is a constant contributor (Fig. 4). This coercivity range is indicative of magnetite, maghemite, titanomagnetite, greigite and/or pyrrhotite. Based on IRM acquisition curve analysis, thermomagnetic data and SEM observation (see following paragraphs), we can rule out the presence of maghemite, titanomagnetite and pyrrhotite. The soft (0 to 35 mT) and hard (300 mT to 2 T) fractions contribute only a small percentage to the total remanence (Fig. 4).

For the older interval (Figs 4a and b) and some samples from the younger interval (Fig. 4c), the medium and soft fractions have virtually the same thermal characteristics. The main inflection of the thermal demagnetization curves of the medium coercivity fraction at around 350 °C is indicative of the thermal alteration of greigite (Roberts 1995; Chang et al. 2008). The persistence of a remanence to $\sim 500$–550 °C indicates a contribution of fine-grained (titanomagnetite). Backward extrapolation of the thermal demagnetization curves after the inflection point at $\sim 350$ °C suggests that the contribution of the greigite and magnetite component is 50 per cent each to the total IRM. This is in contrast with NRM intensities being close to the noise level of the magnetometer after thermal demagnetization above 360 °C. It indicates that after thermal alteration of greigite at about 360 °C, it appears that a magnetite contribution to the NRM is minimal, for which we do not have a straightforward explanation. Note that the magnetite NRM is low with respect to greigite, but that the magnetite IRM is appreciable with respect to greigite. The sharp decrease in remanence of the hard coercivity fraction at $\sim 120$ °C (Fig. 4b) indicates the presence of goethite. Not all samples contain a goethite component. We conclude that the main magnetic remanence in samples from the older interval is therefore carried by greigite. This is consistent with the IRM component analysis for greigite Components 3 and 4 (with a $B_{1/2}$ between 50 and 80 mT) and NRM decrease between 280 and 360 °C during thermal demagnetizations.

For the younger interval (Figs 4c and d), inflection of the thermal demagnetization curve for the intermediate and low coercivity fraction at around 350 °C indicates the presence of greigite (Figs 4a and d; relatively small decrease in samples MCOR525). The IRM of the intermediate coercivity fraction steadily decreases up to 600 °C, whereas the IRM of the low coercivity fraction decreases at $\sim 450$ °C (Fig. 4d) or at 580 °C (Fig. 4e). The low coercivity fraction ranges from 0 to 35 mT and therefore includes contributions from magnetite. The maximum unblocking temperature of both fractions just below 600 °C indicates the presence of relatively pure magnetite. The small increase at around 500 °C in the low coercivity fraction may indicate pyrite oxidation (Passier et al. 2001). Magnetite and greigite appear to be the main contributors to the remanence, and in samples like MCOR525 (Fig. 4d) the IRM contribution of magnetite is higher than of greigite. This interpretation is supported by the NRM decrease up to $\sim 400$ °C during thermal demagnetization and GRM acquisition up to 100 mT during AF demagnetization.

### 4.3 Thermomagnetic experiments

#### 4.3.1 High-temperature Curie balance measurements

Heating curves for bulk sediment samples (Fig. 5a—older interval; 5b—younger interval) are characterized by a hyperbolic decrease up to 420 °C that indicates the dominance of paramagnetic material. Between 420 and 500 °C, the magnetization increases significantly and is subsequently removed at 580 °C. The considerable
Figure 4. Representative examples of thermal demagnetization of composite three-axis IRM. (a) and (b) Samples from the older interval, (c) and (d) samples from the younger interval. The significant NRM decrease at $\sim 360^\circ$C indicates thermal alteration of greigite. The persistence of a remanence to 500–550$^\circ$C indicates the presence of magnetite that is not observed for samples (a) and (b) during thermal demagnetization of the NRM (see Fig. 2 and text for discussion). The data are more noisy in the high temperature range.

Magnetization increase between 420 and 500$^\circ$C is due to the formation of magnetic iron oxides and thermal breakdown of paramagnetic pyrite (Krs et al. 1992; Passier et al. 2001). The Curie temperature ($T_c$) of this newly formed iron oxide ($T_c = 580^\circ$C) is indicative of magnetite. Between 580 and 700$^\circ$C, the warming and cooling curves do not undergo further changes and are reversible. Thermal alteration to form magnetite has resulted in generally higher magnetizations after heating compared to unheated samples.

Samples obtained from magnetic and heavy liquid extracts generally have higher starting magnetizations than bulk sediments, but have the same hyperbolic shape and magnetization increase above 420$^\circ$C, which indicates that the contribution of paramagnetic minerals in the extracts is still relatively high. The thermomagnetic data are irreversible above 250$^\circ$C, as indicated by warming and cooling sub-cycles (see insets in Fig. 5). This irreversibility indicates the presence of greigite, and excludes the presence of pyrrhotite. The considerable magnetization increase between 420 and 500$^\circ$C is less pronounced in the magnetic extract than in the heavy liquid extract. This is related to the extraction method, whereby pyrite is not extracted in the magnetic procedure but is present after heavy liquid separation.

4.3.2 Low-temperature measurements

Low-temperature magnetic experiments were performed to distinguish between magnetite, pyrrhotite, and greigite. Magnetite and pyrrhotite can be positively identified by the low-temperature Verwey transition at 117 K for stoichiometric magnetite (Özdemir et al. 1993; Kosterov 2001) and the 34 K transition for pyrrhotite (Dekkers et al. 1989; Rochette et al. 1990), whereas no low-temperature transition has been reported for greigite (e.g. Roberts 1995; Chang et al. 2009). The heavy liquid extracts obtained from the sapropel, marl and limestone lithologies have similar ZFC and FC remanence curves (Fig. 6). This suggests that the magnetic mineral assemblage is more or less the same for each lithology. A plausible explanation for the rapid decrease in ZFC and FC remanence between 20 and 40 K (Fig. 6) is the presence of ultra-fine superparamagnetic (SP) greigite particles (Roberts 1995; Chang et al. 2009). Similar behaviour has been observed in oxidized synthetic magnetite with low unblocking temperatures (Özdemir et al. 1993) and natural magnetite (Smirnov & Tarduno 2000). Magnetic interaction, surface effects in ultra-fine grains, or the presence of surface layers around coarser magnetic particles may also account for this rapid decrease in remanence (Pike et al. 2000; Passier & Dekkers 2002). Both ZFC and FC warming curves contain no evidence for any low-temperature transition, which indicates that neither magnetite nor pyrrhotite is present (Dekkers et al. 1989; Rochette et al. 1990; Fig. 7). The difference between the ZFC and FC curves is largest at 10 K; it decreases upon warming and disappears completely at room temperature. This difference is largest in the sapropel sample (Fig. 6a) and could be caused by the presence of goethite (Smirnov & Tarduno 2000; Liu et al. 2006; Franke et al. 2007).
The RT-SIRM curve for the sapropel sample (Fig. 7a) increases linearly upon cooling to 10 K, whereas the remanence of the marl and limestone samples increases distinctively below 20 K (Figs 7b and c). The increase in the low-temperature range (~10 K) might be due to magnetic ordering of paramagnetic (clay-) minerals (Coey & Ghose-Subrata 1988). The considerably higher absolute SIRM values for the sapropel sample and the significant gain and loss of remanence during RT-SIRM cycling compared to the other two lithologies (marl and limestone) indicates that the sapropel sample contains a higher concentration of magnetic minerals. This has also been observed in other deep-sea sapropels (e.g. Roberts et al. 1999).

### 4.4 Scanning electron microscopy results

SEM observations coupled with EDS analysis can provide important information for identifying magnetic minerals. The magnetic fraction usually represents less than 1% of the bulk sediment. Observed minerals are mostly clays and partially dissolved microfossils. Framboidal pyrite spherules (~10 μm), which usually occur in the vicinity of fossil remnants (e.g. foraminifera), were observed in dispersed heavy liquid extracts (Fig. 8a) and in polished bulk sediment sections (Fig. 9). Larger (between 1.5 and 2 μm) single crystals of euhedral pyrite were also observed (Figs 8a and d, Figs 9a and b). Early pyrite formation is supported by the typical size of the framboids (~10 μm) (Figs 9a, b and c), which indicates syngenic formation of iron sulphides and rapid pyrite precipitation from solution (Wilkin & Barnes 1996). Euhedral pyrite also fills space around framboids, which indicates a second phase of diagenetic pyrite formation (Suits & Wilkin 1998; Figs 9b and c). The presence of dispersed euhedral pyrite in the limestones and marls indicates that the initial rate of pyritization was low and that the crystals formed within the sediment where sulphide had more time to react with the detrital minerals (Wilkin & Barnes 1996; Morse & Wang 1997).

The distinct monoclinic morphology of pyrrhotite and its typical occurrence as plates (Weaver et al. 2002; Larrasoaña et al. 2007) was not observed in the studied sediments. In contrast, greigite is a cubic mineral and occurs as octahedral crystals (Roberts & Weaver 2005), which were clearly detected, particularly in the dispersed samples (Figs 8b, c and d). EDS elemental analysis of small cubic minerals with grain sizes of ~0.06–1 μm indicate Fe:S ratios close to the respective value for greigite (Fig. 8, Figs 9a and b). Discrepancies between measured and stoichiometric Fe:S ratios for greigite (0.75) and pyrite (0.5) can be explained by uncertainties in the position of the beam and the beam size exceeding the particle size, which leads to spectral contributions from the surrounding minerals. For framboidal pyrite, clay mineral coatings can additionally account for Mg, Al, Si, K and Ca contaminations (Figs 8a). Irregular particle surfaces in the dispersed heavy liquid extracts also lead to scattering of X-rays, whereas elemental analysis of particles in polished sections is more reliable. The representative elemental spectra for greigite and pyrite from the polished section (Fig. 9) are therefore used as a reference for evaluating other iron sulphide spectra, especially those in the dispersed heavy liquid extracts.
Figure 6. Low-temperature magnetic remanence behaviour of heavy liquid extracts from the older, greigite-only-bearing sediments. No magnetic phase transitions are evident, either for magnetite (\(\sim 120\) K), or for pyrrhotite (\(\sim 34\) K). ZFC and FC remanence curves were measured between 300 and 10 K. For comparison, curves are normalized to the magnitude of the respective ZFC value at 10 K for each sample.

The typical size of individual fine-grained greigite in the heavy liquid separates ranges between 0.06 and 0.1 \(\mu\)m (Fig. 8). Crystals as small as 80 to 180 nm were also observed (Fig. 8b), which is within the expected SD size range (35 to 120 nm; Mann et al. 1990; Snowball 1997b; Chang et al. 2008). Fe:S ratios of the dispersed ultra-fine-grained particles are close to the composition of greigite (Figs 8b and 9). In polished thin sections, ultra-fine-grained greigite particles \(< 200\) nm occur well-dispersed in the sediment (Fig. 9d). Larger crystals with sizes of \(\sim 1\) \(\mu\)m have Fe:S ratios typical of pyrite (Figs 8a, 9a, b and c). Massive accumulations of iron sulphides (e.g. Fig. 9c) are relatively uncommon in the studied samples. Greigite particles with sizes of \(\sim 700\) nm to 1 \(\mu\)m occur in close vicinity of pyrite frambois (\(\sim 10\) \(\mu\)m; Fig. 9c).

Two greigite populations can be distinguished. The first has ultra-fine-grained particles in the range of 60 to 200 nm, which are widespread in all samples. The dispersed distribution of these grains suggests that they formed early, either in the water column (which would have been anoxic during times of sapropel formation), at the sediment–water interface, or within relatively uncompacted shallow
sediment. These greigite particles could be biogenic or they could have resulted from early diagenetic sulphide precipitation. SEM observations do not allow us to distinguish between these different origins. The second greigite population is characterized by particles that have grown authigenically near pyrite framboids and in close vicinity of fossil fragments and have observed particles sizes of typically 700 nm to 1 μm (Figs 9a, b and c). This population is likely to have formed slightly later during post-depositional sulphidization that resulted in inorganic precipitation of greigite and pyrite (Jiang et al. 2001; Roberts & Weaver 2005; Rowan & Roberts 2006).

Particles (~40 μm) with mixed composition containing iron oxide and iron sulphide minerals are also frequently present (Fig. 10). Detailed spot EDS analyses on the particle shown in Fig. 10(a) indicates an iron oxide (IO) composition for the lower area with decreased electron backscatter, a transitional area with mixed composition (IOIS) and iron sulphide (IS) composition in the brighter upper part of the particle. In contrast, the particle shown in Fig. 10(b) is entirely an iron sulphide. These particles might represent detritus eroded from older material that was deposited in environments where detrital iron oxides were sulphidized and replaced by iron sulphide minerals. Regardless, these detrital grains are so large that they are unlikely to be aligned by the geomagnetic field and are therefore unlikely to be palaeomagnetically important.

5 DISCUSSION

5.1 Testing for climatic control on magnetic mineralogy

The total IRM, $B_{1/2}$ and their contributions to the total remanence were plotted for seven intervals—each comprising three to six precession cycles (Fig. 11)—to check for magnetic mineral variations with lithology, and therefore with varying climatic conditions. At Monte dei Corvi, the link between climatic changes and lithology is given by the relation between sapropel formation and insolation maxima (Fig. 11; Hilgen et al. 2003; Hüssing et al. 2007). Although the varying climatic conditions presumably had profound effects on
the lithology at Monte dei Corvi, the rock magnetic parameters are relatively constant throughout the entire section. The higher IRM and NRM intensities in the younger sediments can be explained by the additional presence of fine-grained (magnetotactic) magnetite along with greigite. These observations indicate that the magnetic mineralogy is essentially independent of climate forcing and palaeoceanographic changes, and that it is not controlled by detrital input. This supports an authigenic origin of the greigite and magnetite components, and confirms the importance of early diagenetic processes within the studied sediments.

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Figure 9. SEM micrographs of polished sections from: (a) sample MCOR1065 (limestone) with greigite particles of $\sim 700$ nm, Pyrite of $\sim 1$ $\mu$m, (b) sample MCOR1065 (limestone) with greigite (Gr*) particle sizes of $\sim 700$ nm and Gr of $\sim 900$ nm, (c) sample MCOR1063 (marl) with fine greigite particles ($\sim 700$ nm to $1$ $\mu$m) authigenically grown near pyrite framboids of $\sim 10$ $\mu$m and (d) sample MCOR1063 (marl) showing ultra-fine-grained iron sulphides, likely greigite particles $<200$ nm that are well-dispersed; examples are indicated by white arrows (length $\sim 2$ $\mu$m). All samples originate from the older greigite-bearing sediments. Py denotes pyrite and Gr denotes greigite. EDS spectra are shown for representative analyses of pyrite (left) and greigite (right), respectively.
5.2 Greigite formation

Sapropel formation at Monte dei Corvi indicates that anoxic (sulfidic) bottom water conditions existed (e.g. Passier et al. 1999). Anoxic bottom water has been linked to stratification of the water column as a result of increased freshwater discharge from rivers during insolation maxima (Rossignol-Strick et al. 1982; Rossignol-Strick 1985; Rohling & Hilgen 1991; Hilgen 1991; Rossignol-Strick 1993; Rohling 1994) that increased the preservation of organic matter. It is well known that diagenetic processes in organic-rich sediments may produce new magnetic iron sulphide minerals, such as greigite (Hilton & Lishman 1985; Snowball & Thompson 1988; Hu et al. 1993; Rohling 1994) that increased the preservation of organic matter. It is well known that diagenetic processes in organic-rich sediments may produce new magnetic iron sulphide minerals, such as greigite (Hilton & Lishman 1985; Snowball & Thompson 1988; Hu et al. 1993; Rohling 1994). Marls and limestones were generally deposited in more oxygenated bottom waters. However, poor fossil preservation in all lithologies (marls, limestones and sapropels) at Monte dei Corvi suggests that suboxic conditions in the sediment resulted in at least partial dissolution of calcareous fossils that will also have caused iron oxide dissolution and iron sulphide formation. Reductive dissolution explains the reduced amount of iron oxides in the older sediments at Monte dei Corvi. In the younger interval, sapropels are less frequently developed, NRM intensities are often higher (Fig. 2) and AF and thermal demagnetization diagrams indicate the co-occurrence of fine-grained greigite and magnetite, although anoxic conditions should have caused the dissolution of fine-grained magnetite. This suggests that anoxic conditions were less severely developed or that non-steady-state diagenesis occurred (cf. Passier et al. 2001; Larrasoña et al. 2003), which might have played a significant role in the preservation of greigite and fine-grained magnetite components.

5.2.1 Possible biogenic origin of greigite

Two greigite populations are identified in the Monte dei Corvi sediments. Greigite component 3 (with a small DP and high $B_1$ values) can be of biogenic origin. Biogenic greigite mineralization occurs either in the water column or near the sediment–water interface and would thus produce a syn-sedimentary recording of the geomagnetic field (Kopp & Kirschvink 2008). Fossil magnetotactic greigite has not been reported in ancient sediments until the recent demonstration by Vasiliev et al. (2008). These authors also demonstrated that early diagenetic (inorganic) greigite records a stable syn-depositional palaeomagnetic signal in Miocene–Pliocene sediments of the Paratethys domain (Vasiliev et al. 2007, 2008). Greigite formation in the Monte dei Corvi section might be analogous to modern processes in the Black Sea (e.g. Reitner et al. 2005). We suggest that the smallest greigite particles (60 to 200 nm) observed during SEM analysis might represent the inferred biogenic (magnetotactic) greigite component (sizes between ~30 and 80 nm; e.g. Bazylinksi et al. 1995; Posfai et al. 1998; Reitner et al. 2005; Vasiliev et al. 2008), although we cannot unambiguously confirm a biogenic origin for greigite Component 3.

5.2.2 Post-depositional magnetization

Inorganic early diagenetic and much later formation of greigite has been frequently postulated in various marine sediments (e.g. Horng et al. 1998; Roberts et al. 1999; Roberts et al. 2005; Roberts & Weaver 2005). The second greigite population identified by SEM analysis and IRM acquisition experiments (with larger DP than greigite Component 3) can be associated with authigenic greigite growth. It seems that later diagenetic sulfidization processes were limited, as indicated by the lack of massive euhedral overgrowth of iron sulfides and of sulfides between cleavages of detrital iron-bearing phyllosilicates. Lack of evidence for these processes suggest that later diagenetic sulfidization events (e.g. Canfield et al. 1992) and remagnetization events (e.g. Roberts & Weaver 2005; Rowan & Roberts 2006) did not occur at Monte dei Corvi.

5.2.3 Methane seepage from underlying sediments

The traditional scenario of pyritization arrest (e.g. Berner 1970; Berner 1984; Wilkin & Barnes 1996; Kao et al. 2004) can account for inorganic greigite formation and its preservation in all three studied lithologies at Monte dei Corvi. After greigite formation,
Early remanence acquisition in Tortonian greigite-bearing sediments

Figure 11. Rock magnetic parameters derived from IRM acquisition curve analysis of seven intervals spanning several basic cycles: Cycle 1 at \( \sim 30.4 \) m, cycle 2 at \( \sim 54 \) m, cycle 3 at \( \sim 65.5 \) m, cycle 4 at \( \sim 79 \) m, cycle 5 at \( \sim 117 \) m, cycle 6 at \( \sim 122 \) m and cycle 7 at \( \sim 125 \) m of the stratigraphic section. The \( B_{1/2} \) values and contributions of greigite Component 3, greigite Component 4 and magnetite Component 2 are plotted in stratigraphic order, which reveals no significant changes in values throughout the entire section or between the various lithologies. The insolation curve of La2004(1,1) (Laskar et al. 2004) is plotted next to lithology to indicate the relationship between climatic and lithological changes. Sapropel formation occurred during insolation maxima.

Reducing conditions were maintained in the sediments that aided its preservation. Methane seepage from underlying sediments is inferred to be an important factor that controls the anaerobic oxidation of methane (AOM) in the sediment and water column as is the case in the Black Sea (e.g. Reitner et al. 2005; Krüger et al. 2008). A source of significant additional organic matter to form widespread and longstanding reducing conditions in the Monte dei Corvi sediments may be related to moderate and/or episodic upward migration of methane-rich interstitial fluids, or to diffusion of methane from the underlying sediment, particularly organic-rich sapropels, into the bottom water (Michaelis et al. 2002; Krüger et al. 2008). This flux might have been moderate or periodic, enough to establish only slightly anoxic to suboxic conditions in the sediment column. We speculate that this process preserved the original iron sulphides in the Monte dei Corvi sediments and that it accounts for post-depositional dissolution of calcareous microfossils in marls and limestones, although these sediments were deposited in oxygenated bottom waters. However, further geochemical analyses are required to test this hypothesis.

5.3 Timing of remanence acquisition

The younger intervals of the Monte dei Corvi section can be considered to carry a reliable primary NRM signal because fine-grained magnetite is present along with fine-grained greigite. Both components carry the same palaeomagnetic directions. It is therefore reasonable to assume that NRM acquisition for both minerals was

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roughly coeval. Although magnetite Component 2 seems to be absent in the older interval, a fine-grained magnetic component is indicated by other rock magnetic experiments. The greigite Component 3 is the dominant carrier of the palaeomagnetic signal for these sediments.

The following observations and interpretations indicate syn-sedimentary or early diagenetic formation of pyrite and greigite in the sulphide-bearing sediments of the older interval at Monte dei Corvi.

1. The occurrence of pyrite framboids indicates that pyrite formed rapidly during or shortly after deposition within the top few centimetres of the sediment or in the water column (Sweeney & Kaplan 1973; Berner 1984; Canfield & Berner 1987; Wilkin et al. 1996; Wilkin & Barnes 1997).

2. Magnetite iron oxides, which react rapidly with dissolved sulphide (the half-life of magnetite in anoxic marine sediments ranges from 50 to 1000 yr; Canfield & Berner 1987) are not evidently present, which suggests that they were rapidly dissolved to form iron sulphides during early diagenesis.

3. Iron sulphides have not been observed between cleavages of detrital sheet silicates (cf. Jiang et al. 2001; Roberts & Weaver 2005). Phyllisilicates react much more slowly than iron oxides (the half-life of sheet silicates when in contact with 1 mM concentration of pore water sulphide is ~120 kyr; Canfield et al. 1992). Overall, slow diagenetic reactions that produce iron sulphides are not observed (Canfield et al. 1992; Raiswell & Canfield 1996; Passier & de Lange 1998), which provides indirect evidence against complications from later magnetizations.

Based on the assumption that slightly anoxic or suboxic conditions prevailed after deposition in the Monte dei Corvi sediments, it is reasonable to expect preservation of an early diagenetic NRM carried by greigite. Similar scenarios have been suggested for younger sediments (e.g. Pye 1981; Tric et al. 1991; Roberts & Turner 1993; Reynolds et al. 1999; Vasiliev et al. 2007, 2008).

Reversal ages can be compared to those from other marine and continental sections spanning the same time interval as the Monte dei Corvi section. Suitable sections include the marine Metochia section on Gavdos (Hilgen et al. 1995) and the continental Orera section in Spain (Abdul Aziz et al. 2003). Differences of reversal ages derived from the Monte dei Corvi, Metochia and Orera sections are only minor (between 3 and 41 kyr for the younger Monte dei Corvi interval). These small discrepancies can be explained by uncertainties in the position of the reversal boundaries. These uncertainties are related to the large spacing between age calibration points and to the precision with which reversal boundaries can be identified, and to the use of different astronomical target curves for the tuning (for a more detailed discussion see Hüsing et al. 2007, 2009). If remanence acquisition at Monte dei Corvi was delayed for tens to hundreds of kyr, the recorded polarity pattern would have been distorted (e.g. Horng et al. 1998) and would not be as easily recognized as it is. Therefore, it seems much more likely that remanence acquisition at Monte dei Corvi took place shortly after deposition, with a maximum delay of only a few thousand years (<10 kyr), particularly for the older greigite-bearing sediments (cf. Vasiliev et al. 2008).

6 CONCLUSIONS
The Monte dei Corvi section is one amongst few marine sections so far identified where greigite appears to be responsible for a syn-sedimentary to early diagenetic NRM acquisition. Rock magnetic analysis and SEM observations indicate that two distinct populations of greigite are present throughout the section. The greigite component with a narrow (SD) grain size distribution is interpreted to be of biogenic (magnetotactic) origin, whereas the greigite component with a wider size distribution is attributed to larger authigenic (bacterially mediated) greigite crystals. Increased NRM and total IRM intensities in the younger sediments are related to the elevated amount of fine-grained (magnetotactic) magnetite. The consistent magnetic mineralogy throughout precession-induced lithological variations indicates no significant link between mineralogy and climatic changes on the precessional scale. This supports an authigenic origin for the greigite and magnetite components and emphasizes the importance of early diagenetic processes within the sediment. In addition to the traditional scenario for iron sulphide formation in marine sediments (sulphidization under reducing conditions), we suggest that moderate or occasional methane seepage from the underlying sediment might have helped to maintain (slightly) reducing conditions, which can account for greigite preservation. This is supported by the occurrence of greigite and pyrite, and the poor preservation of calcareous microfossils throughout the sedimentary succession. Any delayed remanence acquisition resulting from the authigenic greigite component must have a maximum delay of <10 kyr because there is no evidence of distortion of the expected palaeomagnetic reversal pattern in the Monte dei Corvi sediments. The primary origin of the palaeomagnetic signal at Monte dei Corvi attests to the reliability of the high-resolution magnetostratigraphy and supports the use of the determined astronomical ages of reversal boundaries (Hüsing et al. 2007, 2009).

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REFERENCES


