Paleomagnetic imprints of sulfate reduction pathways in continental shelf sediments: organoclastic versus anaerobic oxidation of methane

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Abstract

Marine continental shelf sediments with high deposition rates may provide useful archives of rapid geomagnetic secular variation as long as the primary magnetization is not altered substantially by diagenesis. To quantify the effects of sulfate (SO$_4^{2-}$) reduction, which is a dominant early diagenetic process in such sediments, on paleomagnetic recording, we analyzed four \textsim 6-m long sediment cores from the Mediterranean shelf. Two cores did not reach the methanogenic zone and are characterized by continuous organoclastic sulfate reduction (OSR), while the other two have a distinctive shallow sulfate-methane transition zone (SMTZ). Depth-age models based on 28 radiocarbon ages show that deposition was mostly non-synchronous, suggesting that different parts of the shelf stopped accumulating sediments at different times during the Holocene. The upper sediment column in all cores is dominated by detrital titanomagnetite and biogenic magnetite. OSR-affected sediments record continuous dissolution of the (titano)magnetites, resulting in a steady decrease in magnetic susceptibility and remanent magnetic properties. For cores that reach the methanogenic zone, similar behavior is observed at or above the STMZ, but the magnetic properties stabilize at greater depths. Paleomagnetic directions in these sediments are more coherent, with better agreement with geomagnetic models than sediments affected by OSR. We suggest that methane-rich sediments with a shallow SMTZ and high sedimentation rates can better preserve primary paleomagnetic signals than OSR-dominated sediments due to a lack of dissolved sulfide in the main methanogenic zone, and that a susceptibility decline with depth should be a warning sign for paleomagnetic studies.
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Key Points:
- Correlation between early diagenetic zones and mineral magnetic properties is observed in Holocene eastern Mediterranean shelf sediments
- Continuous organoclastic sulfate reduction (OSR) smooths rapid paleomagnetic secular variation recorded by the sediments
- Shallow sulfate-methane transition zones and intense sulfate reduction by anaerobic oxidation of methane may preserve better paleomagnetic records than continuous OSR
Abstract

Marine continental shelf sediments with high deposition rates may provide useful archives of rapid geomagnetic secular variation as long as the primary magnetization is not altered substantially by diagenesis. To quantify the effects of sulfate ($\text{SO}_4^{2-}$) reduction, which is a dominant early diagenetic process in such sediments, on paleomagnetic recording, we analyzed four ~6-m long sediment cores from the Mediterranean shelf. Two cores did not reach the methanogenic zone and are characterized by continuous organoclastic sulfate reduction (OSR), while the other two have a distinctive shallow sulfate-methane transition zone (SMTZ). Depth-age models based on 28 radiocarbon ages show that deposition was mostly non-synchronous, suggesting that different parts of the shelf stopped accumulating sediments at different times during the Holocene. The upper sediment column in all cores is dominated by detrital titanomagnetite and biogenic magnetite. OSR-affected sediments record continuous dissolution of the (titano)magnetites, resulting in a steady decrease in magnetic susceptibility and remanent magnetic properties. For cores that reach the methanogenic zone, similar behavior is observed at or above the STMZ, but the magnetic properties stabilize at greater depths. Paleomagnetic directions in these sediments are more coherent, with better agreement with geomagnetic models than sediments affected by OSR. We suggest that methane-rich sediments with a shallow SMTZ and high sedimentation rates can better preserve primary paleomagnetic signals than OSR-dominated sediments due to a lack of dissolved sulfide in the main methanogenic zone, and that a susceptibility decline with depth should be a warning sign for paleomagnetic studies.

Plain Language Summary

It has long been recognized that marine seafloor sediments provide continuous records of variations of Earth’s magnetic field. Marine sediments have, thus, been used to explore Earth’s magnetic field behavior throughout geological history. The classical view on how sediments acquire a magnetization in aquatic environments involves physical forces that rotate magnetic particles toward the field direction as they sink. However, biochemical processes associated with microbial respiration may distort the primary depositional magnetic information and even remagnetize it. We explore here how sulfate reduction, which is one of the most dominant diagenetic biochemical processes in global continental shelf marine environments, affects sediment magnetic properties and the ability to accurately record magnetic information. We analyzed four sediment cores from the Southeastern Mediterranean shelf, which were deposited under different sulfate reduction regimes. We show that continuous sulfate reduction significantly changes the magnetic mineralogy and, therefore, hampers preservation of sedimentary paleomagnetic records. We also show that to obtain reliable high-resolution sedimentary paleomagnetic data, sulfate should be consumed as early as possible after deposition. Such conditions occur when methane fluxes from below reach shallow sulfate-rich sediments.

1. Introduction

Marine continental shelf sediments are an important source of global paleomagnetic data owing to their high sedimentation rates and availability of datable materials. Over recent decades, marine sediments from continental shelves and shallow basins have provided essential information on spatial and temporal global geomagnetic field evolution (e.g. (Lisé-Pronovost et al., 2009; Reilly
Early diagenesis encompasses a range of biochemical reactions associated with microbial organic matter degradation coupled to reduction of electron acceptors, which is assumed to occur in order of decreasing free energy yield (Berner, 1981; Canfield & Thamdrup, 2009; Roberts, 2015). The following order of electron acceptor use is predicted (with corresponding diagenetic zones): oxygen (oxic zone), nitrate (nitrogenous zone), manganese oxides (manganous zone), iron (oxyhydro)oxides (ferruginous zone), sulfate (sulfidic zone), and finally organic matter itself (methanogenic zone). In many aquatic sedimentary profiles, however, different diagenetic zones with different magnitudes, may overlap partly, or may not appear at all. Sulfate reduction is one of the most dominant early diagenetic processes in marine environments, and is responsible for over half of organic carbon degradation (Bowles et al., 2014). Two main sulfate consumption pathways are via continuous organoclastic sulfate reduction (OSR) or through a diffusive flux to the sulfate-methane transition zone (SMTZ), and intensive reduction there by anaerobic oxidation of methane (AOM) with a narrow sulfidic zone (Jorgensen et al., 2019). The second mode occurs mainly within areas dominated by intensive methanogenesis that causes SMTZ shallowing (Sivan et al., 2007).

The effect of sulfate reduction on sediment magnetic properties is the main focus of this study. This topic has been discussed for both marine and lacustrine environments (e.g. Amiel et al., 2020; Canfield & Berner, 1987; Chang et al., 2014; Ebert et al., 2018; Karlin & Levi, 1983; Karlin et al., 1987; Kars & Kodama, 2015; Larrasoña et al., 2007; Nowaczyk, 2011; Reilly et al., 2020; Roberts et al., 2011; Roberts & Weaver, 2005; Rowan & Roberts, 2006; Rowan et al., 2009). On one hand, dissolved sulfide is released during sulfate reduction and triggers dissolution of detrital or authigenic magnetite, which causes a decrease in bulk magnetic properties and loss of primary paleomagnetic information. On the other hand, reaction of dissolved sulfide with Fe$^{2+}$ ions can cause formation of different iron sulfides, including mainly mackinawite, greigite, and pyrite, where greigite formation may lead to secondary magnetization acquisition. The stoichiometry and magnetic properties of authigenic iron sulfides are controlled by several factors, including the
availability and reactivity of organic matter for degradation, the sulfate reduction rate, and the reactive iron concentration in pore waters.

The purpose of this study is to obtain empirical data on the effect of the two sulfate reduction modes – OSR, which occurs continuously in the sulfidic zone of so-called ‘OSR sediments’, versus AOM at the SMTZ of so-called ‘methanogenic sediments’ – on sedimentary magnetic properties and on of paleomagnetic recording quality. In a field-test approach, we explore shallow marine continental shelf sediments located both within and outside localized methane pockets. This allows us to compare the magnetic properties of sediments, which differ only in their diagenetic pathways along the upper few meters of the sediment column. Our analysis combines paleomagnetic, mineral-magnetic, and geochemical data.

**Geological setting**

The sampling area is located on the continental shelf offshore of Israel at water depths ranging between 46 and 81 m (Table 1, Figure 1). This area comprises the northeastern Nile littoral cell with deposition of silts and clays that were transported from the Nile via counter-clockwise shore-parallel currents (Schattner, 2021; Schattner et al., 2015). The sedimentation regime at these depths stabilized during the mid-late Holocene subsequent to slowing of post-glacial sea level rise (Grant et al., 2012; Schattner, 2021; Sivan et al., 2004; Sivan et al., 2001), creating a geomorphologically and tectonically stable low-relief belt. The study area, as part of the eastern Mediterranean Sea, has oligotrophic conditions (Herut et al., 2000; Kress & Herut, 2001) with poor nutrient availability and low sedimentary organic matter contents. Under these constraints, methanogenesis is not expected, and OSR is the main diagenetic process in shallow sediments (Wurgaft et al., 2019). However, despite the oligotrophic conditions, several shallow methane pockets have been identified by seismic surveys (Lazar et al., 2016; Schattner, 2021; Schattner et al., 2012). The seismic data reveal evidence for methane migration from depth horizons that correspond to the last glacial maximum shoreline (Fig. 1c,e) probably in response to continuous sediment loading. Pore-water chemistry of sediments from these localities confirms the presence of methane at 1-4 m depths and a shallow SMTZ (Amiel et al., 2020; Sela-Adler et al., 2015; Vigderovich et al., 2019; Wurgaft et al., 2019). Based on carbon isotope compositions of dissolved inorganic carbon (DIC) and methane, Sela-Adler et al. (2015) concluded that the methane is produced microbially. Antler et al. (2015) and Wurgaft et al. (2019) then suggested the dominance of sulfate AOM versus continuous sulfate reduction in these methane-rich sediments. Here, we took advantage of geographically confined shallow methane pockets to develop a sampling strategy to collect sediments from both within and outside methane-rich zones, at nearby spots that differ only in their diagenetic profiles. Locations of sampling spots and seismic profiles that indicate the presence of localized gas fronts are shown in Figure 1. Furthermore, the availability of well dated paleosecular variation records from the Levant (Ebert et al., 2018; Shaar et al., 2018) and well-constrained geomagnetic field models for the Holocene (Nilsson et al., 2022; Osete et al., 2020; Pavon-Carrasco et al., 2021; Schanner et al., 2022) suggests that this region is an ideal natural laboratory for assessing the impacts of laterally and stratigraphically varying early diagenetic effects on paleomagnetic recording.
Figure 1: Location map. a-b) Bathymetric maps of the eastern Mediterranean with locations of studied cores (bold fonts) and previously studied cores mentioned in the text (italic fonts). c-d) CHIRP shallow seismic reflection profiles collected near the core locations. Estimated core locations are indicated with red arrows. Yellow arrows in (c) and (d) indicate methane gas fronts.

Table 1: Sampling locations

<table>
<thead>
<tr>
<th>Station</th>
<th>Water depth (m)</th>
<th>Core length (m)</th>
<th>Latitude (N°)</th>
<th>Longitude (E°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC3</td>
<td>81</td>
<td>5.8</td>
<td>32.92584</td>
<td>34.90472</td>
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</tbody>
</table>
2. Methods

2.1. Sampling

Sediments were collected using the Bat-Galic Research Vessel with a 9-m long Benthos piston corer. At each sampling spot (Figure 1, Table 1), we collected two piston cores, the longer of which was labeled ‘B’. ‘B’ core lengths are 5.8–6.8 m. Cores PC3/PC3B and PC6/PC6B were collected at locations where Sela-Adler et al. (2015) detected a shallow SMTZ at ~1 m sediment depth. The locations of cores HUG1/ HUG1B and T5/ T5B were selected based on seismic data, as close as possible to the methanogenic sediments, but outside the methane pockets. On board, the 8-m fiberglass liners were cut to 1.2-m long segments. Pore-waters were extracted from cores segments immediately after recovery along with sediment for methane analysis. Core segments were then refrigerated until they were split and sampled for paleomagnetism (within days of collection). Upon splitting, paleomagnetic samples were collected using non-magnetic plastic sample boxes (outer dimension 23 × 23 × 19 mm) at ~25-mm resolution. Freeze-dried sediments for bulk mineral magnetic analysis were collected from ‘B’ cores at 20-cm stratigraphic intervals.

2.2. Paleo- and mineral- magnetic analyses

All paleomagnetic and mineral magnetic measurements were made at the paleomagnetic laboratory, Institute of Earth Sciences, The Hebrew University of Jerusalem, except for low temperature measurements, which were made at the Institute for Rock Magnetism (IRM), University of Minnesota. Oriented paleomagnetic samples were weighed and subjected to the following procedures in order: alternating field (AF) demagnetization of the natural remanent magnetization (NRM), acquisition of an anhysteretic remanent magnetization (ARM), susceptibility ($\chi$) measurement at two frequencies, and isothermal remanent magnetization (IRM) acquisition. Stepwise AF demagnetization was carried out at 4 mT steps to 20 mT, in 10 mT steps to 50 mT and in 15 mT steps to 110 mT. ARM was imparted using a 0.1 mT bias field and 100 mT AF. Magnetization measurements and ARM acquisition were done with a 2G Enterprises RAPID superconducting rock magnetometer (SRM) system. An IRM was imparted in a 1.5-T induction using an ASC pulse magnetizer and was measured with a MAG-Instruments Portable Spinning Magnetometer (PSM-1). Mass-specific susceptibility was measured using an AGICO MFK-1 Kappabridge at low (976 Hz) ($\chi_{LF}$) and high (15616 Hz) frequencies ($\chi_{HF}$).

About 150 mg of freeze-dried sample was weighed and packed tightly in gelatin capsules for hysteresis loop, back-field demagnetization, first-order reversal curve (FORC), and low temperature measurements. Hysteresis and backfield curves were measured for all ‘B’ cores at 20-cm stratigraphic resolution and FORC measurements were made for selected samples. Six-hundred equally spaced FORCs were measured in the space defined by: $0 < B_c < 100$ mT and $-100$ mT <
$B_a < 100 \text{ mT}$, with $1.5 \text{ T}$ saturation field and $150$-ms averaging time. Measurements were made with a LakeShore 8600 series vibrating sample magnetometer.

Low temperature measurements were made on capsules from cores PC3B and HUG1B using a Quantum Design Magnetic Properties Measurements System (MPMS3) in VSM mode. Procedures included: warming of a $2.5 \text{ T}$ SIRM from $5 \text{ K}$ to $300 \text{ K}$ after cooling in zero-field (‘zero-field-cooled’, ZFC curves), warming of a $2.5 \text{ T}$ SIRM from $5 \text{ K}$ to $300 \text{ K}$ after cooling in $2.5 \text{ T}$ field (‘field-cooled’, FC curves) and low-temperature cycling of room-temperature SIRM from $300 \text{ K}$ to $5 \text{ K}$ and back to $300 \text{ K}$. Heating and warming curves were measured at $5 \text{ K}$ steps at $5 \text{ K/min}$.

Paleomagnetic data analysis was done using the Demag GUI program, which is part of the PmagPy software package (Tauxe et al., 2016). The characteristic remanent magnetization (ChRM) was calculated from principal component analysis (PCA) (Kirschvink, 1980) using the maximum angular deviation (MAD) to quantify parametrically the ChRM quality. FORCs were processed with the FORCinel (Harrison & Feinberg, 2008) and FORCTool (Surovitskii et al., 2022) software, which uses the statistical machine learning framework of Heslop et al. (2020) to find optimal VARIFORC (Egli, 2013) smoothing parameters. First point artefact and drift corrections were applied in all cases before smoothing.

To prepare samples for scanning electron microscope (SEM) observations, we used a rare-earth magnet to extract magnetic particles from freeze-dried sediment. Magnetic extracts were dispersed on carbon tape and were imaged using an XHR-SEM Magellan 400L SEM equipped with energy-dispersive spectrometer (EDS) detectors, in both secondary electron (SE) and backscattered (BS) electron modes. Analyses were made at the Hebrew University Center for Nanoscience and Nanotechnology.

### 2.3. Pore-water chemistry

Holes in Perspex core liners were used for methane sampling and pore-water extraction. Approximately $1.5 \text{ mL}$ of sediment was sampled using a cut syringe and was transferred immediately into $\text{N}_2$-flushed crimped bottles containing $5 \text{ mL}$ of $1.5 \text{ N} \text{ NaOH}$ for headspace methane measurements. Pore waters were extracted using Rhizons through a $0.22$-mm filter and were kept without air until measurement. Ferrozine solution was used to fix immediately $1 \text{ mL}$ of water for $\text{Fe}^{2+}$ measurement.

Headspace methane concentrations were measured with a Thermo Scientific gas chromatography (GC) system equipped with a flame ionization detector (FID) at $2 \text{ mmolL}^{-1}$ precision. Ferrous iron was measured with a spectrophotometer at $562$ nm absorbance (Stookey, 1970) with an error of less than $7 \text{ mmolL}^{-1}$. Sulfate concentrations were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES-720-ES, VARIAN) with an accuracy of $2\%$.

### 2.4. Radiocarbon dating

Radiocarbon dating (e.g. (Reimer et al., 2020) was used to determine the age of twenty-eight selected samples along the four studied piston cores. Tens of the best-preserved shells of the benthic foraminiferal genera *Ammonia* and *Elphidium* (> $150 \mu\text{m}$ size fraction) were handpicked under a binocular microscope to obtain at least $\sim 1 \text{ mg}$ of $\text{CaCO}_3$ per sample. The pretreatment procedure included cleaning of calcareous shells by ultrasonication and ethanol to remove any fine
sediment residues from within the shells. Radiocarbon dating was conducted at the AMS MICADAS (Mini Carbon Dating System) radiocarbon laboratory at the Alfred Wegener Institute (AWI), Helmholtz Centre for Polar and Marine Research, Germany. Radiocarbon ages were calibrated and modeled using the Oxcal program v4.4.4 (Ramsey, 2009) and IntCal20 calibration curve (Heaton et al., 2020). Correction for local reservoir effects follows Heaton et al. (2020) and uses an average of six published ages from offshore Israel (Boaretto et al., 2010; Reimer & McCormac, 2002), which results in a reservoir correction $\Delta R_{\text{marine20}}$ of $-139 \pm 73$.

3. Results

3.1. Radiocarbon ages

Obtaining a sufficient mass of datable material was sometimes a challenge. In most cases, sorting sediments across a 1-2 cm thickness resulted in 1.5 mg of foraminiferal shells, which is the minimum weight for age determination. In some depth intervals, larger volumes that span a few centimeters thickness were required to achieve the minimal weight, due to poorly preserved (reworked), broken, or small shells. In general, the radiocarbon ages increase with depth (Fig. 2, Table 2). After rejecting five samples as outliers, age-depth models were calculated using five samples from core PC3B, six samples from core HUG1B, eight samples from core PC6B, and four samples from core T5B. Depositional models were calculated using the P_sequence (Poisson) function in the Oxcal program (Ramsey, 2008) with k factor of 1 and interpolation every 10 cm. Based on depositional models, the age of paleomagnetic samples was calculated by interpolating between the means of the modeled age distributions.

Age models for the cores (Fig. 2) indicate fairly steady deposition, where average deposition rates in the methanogenic sediments (cores PC3B, PC6B) are 3.5-3.6 mm/year, which is higher than the rate for the OSR sediments (cores HUG1B, T5), which is only 1.9 mm/year. The age range spanned by the four cores is significantly different with little overlap among them. Extrapolation of ages toward the surface yields apparent core top ages ranging between 5.1 ky BP for core HUG1B to 1.4 ky BP for core PC6B. The difference between extrapolated surface ages for cores PC3B and HUG1B, which were collected only 1.5 km apart, and the difference between those for cores PC6B and T5, which are located at the same water depth but 25 km away from each other is more than 1000 years. This probably indicates a non-synchronous and non-continuous sedimentation regime in which nearby parts of the shelf stopped accumulating sediments at different times during the Holocene. This result is discussed further in section 4.4.

Table 2: Radiocarbon ages for the studied sediment cores.

<table>
<thead>
<tr>
<th>Core</th>
<th>Sample name: core, depth range</th>
<th>$^{14}$C age (BP)</th>
<th>Cal. age (BP) (68%)</th>
<th>Cal. age (BP) (95%)</th>
<th>Modeled age (BP) (68%)</th>
<th>Modeled age (BP) (95%)</th>
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</thead>
<tbody>
<tr>
<td>PC3B</td>
<td>PC3B 50-54</td>
<td>3827±29</td>
<td>3908-3652</td>
<td>4054-3536</td>
<td>3894-3658</td>
<td>4044-3553</td>
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<tr>
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<td>PC3B 101-102*</td>
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<td>4731-4428</td>
<td>4854-4274</td>
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<td>2869-2699</td>
<td>2932-2386</td>
</tr>
<tr>
<td></td>
<td>PC 6B 550-555</td>
<td>2853±61</td>
<td>2730-2465</td>
<td>2840-2328</td>
<td>3110-2918</td>
<td>3169-2623</td>
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<tr>
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<td>PC 6B 650-660</td>
<td>3279±64</td>
<td>3250-2960</td>
<td>3376-2813</td>
<td>3391-3180</td>
<td>3456-2889</td>
</tr>
</tbody>
</table>

### 3.2. Diagenetic zones

Combined geochemical-magnetic depth profiles for all studied cores are shown in Figures 3 and 4, with selected magnetic parameters and dissolved sulfate, methane, and iron concentrations. The upper several centimeters of the sediment might have not been fully recovered by coring, which possibly masks our view of the uppermost sediments. From the diagenetic zones summarized by Roberts (2015), as outlined in Section 1, only the sulfidic and methanogenic zones can be identified directly from our geochemical measurements. This is because the oxic zone is restricted to a narrow layer at the water-sediment interface (Wurgaft et al., 2019) and the nitrogenous, manganese, and ferruginous zones may overlap with the upper sulfidic zone. The sulfate concentration in the upper sediment section is 25-30 mM and gradually decreases in OSR sediments (HUG1B, T5B, Figure 3) to ~10 mM at a depth of ~4 m. Methanogenic sediments (cores PC3B, PC6B, Figure 4) have a steeper, mostly diffusive, sulfate concentration gradient to depletion.
at the SMTZ at depths of 1.6 m in core PC3B and 4 m in core PC6B. As expected, the methane concentration is non-measurable in OSR-sediments (Figure 3), whereas in core PC3B (Figure 4a) methane increases from nearly zero to ~1 mM at 1.6 m and reaches almost 3 mM at 2.5 m. In core PC6B (Figure 4b), methane starts to increase at ~4.5 m and at the core bottom at 6.8 m it is >1.2 mM. Based on sulfate and methane data, the SMTZ is clearly defined at a narrow interval between ~1 m and ~1.8 m in core PC3B. In core PC6B, the SMTZ seems to be wider, between ~3.5 m and 6.3 m. SMTZ positions are marked with gray in Figure 4.
Ferrous iron concentration provides valuable information on iron reduction processes. Iron concentration in core PC3B, which best represents methanogenic sediments, has a small-scale local maximum above the STMZ at ~0.5 m, a further small increase at the top of the SMTZ (~1.1 m) to 15 μM, and a sharp increase to ~50 μM at the SMTZ base (~1.8 m). Below the SMTZ, in the methanogenic zone, iron concentrations vary between 40 and 80 μM. Core PC6B has a similar, although more complicated, picture with a wider SMTZ, small-scale fluctuations above the SMTZ (1.8-3.2 m) and another increase to ~3 μM at the top of the SMTZ. Core PC6B did not penetrate the deeper methanogenic zone, so we cannot know if ferrous iron has higher concentrations similar to those in core PC3B at greater depths. In the OSR-affected sediments, iron concentrations are much lower. In core HUG1B, iron contents increase from 0.4 μM at the top of the core to 1.1 μM at 4 m. In core T5B, iron measurements failed to produce coherent data and are not shown.

3.3. Bulk magnetic properties

Magnetic parameters are sensitive to iron bearing mineral changes; variations are consistent with geochemical parameters and the diagenetic zones outlined above. All of the parameters shown in Figures 3-4 are sensitive to distinct magnetic property variations (Liu et al., 2012). Mass normalized ARM and SIRM represent concentration changes of low (<100 mT) and high (> 100 mT) coercivity ferrimagnetic minerals, respectively. The mass-normalized susceptibility (χLF) is a bulk measurement that can serve as a proxy for large magnetic mineralogy changes. Frequency-dependent susceptibility (χFD = 100 ∙ χLF−χHF χLF) is sensitive to variations in nanometer-scale superparamagnetic (SP) particles and is, therefore, a proxy for authigenic mineral formation in this environment. The hysteresis ratios MTR/MS and BCR/Bc provide a measure of bulk grain size variations. The presence of a gyromagnetic magnetization (GRM) during AF demagnetization is typical of stable single domain (SD) greigite (Snowball, 1997; Sagnotti & Winkler, 1999). ∆GRM (Just et al., 2019) is < 1% for almost all specimens, so it is not shown in Figures 3-4.

In all of the studied cores, χLF, SIRM, and ARM variations have similar trends, which indicates that bulk magnetic property changes are primarily controlled by low-coercivity ferrimagnetic minerals. In the OSR sediments (cores HUG1B, T5B; Figure 3), there is a decreasing bulk parameter (ARM, IRM, χLF) trend, with IRM and χLF decreasing to half of their maximum values over a < 6 m depth interval. In both cores, we observe a ~2-m-thick region (at 2-4 m in T5B and 3-5 m in T5B) with a slight ARM (but not IRM) increase, large χFD and BCR/Bc increases, and a MTR/MS decrease. These observations indicate authigenic mineral formation in the SD-SP size range within the sulfidic interval. Below this interval in core T5B, there is a downward χFD decrease, accompanied by increased IRM and ARM, which may suggest that a small authigenic particle fraction grew above the SP-SD threshold volume.

The magnetic behavior of the methanogenic sediments (cores PC3B, PC6B; Figure 4) is different than for the OSR-sediments. In core PC3B, which has a shallow and narrow SMTZ, all magnetic parameters change above the top of the SMTZ, expressed first as an IRM, ARM, χLF, and MTR/MS increase and a BCR/Bc decrease. Then, at the SMTZ, these parameters change to an opposite trend. Most importantly, below the SMTZ, all bulk parameters stabilize. In core PC6B, where the SMTZ is wider and deeper, a sharp magnetic parameter change occurs in the upper 50 cm, and then a more gradual change occurs with IRM, ARM, χLF, BCR/Bc decreasing, and MTR/MS.
increasing. At the SMTZ $\chi_{FD}$ decreases, followed by an increase; other parameter trends do not change, but their gradient increases.

Figure 3: Depth profiles from cores HUG1B and T5B (OSR-affected sediments) of pore water chemistry and selected magnetic parameters. See text for details of the interpretation of various parameters. In general, concentration-dependent parameters (IRM, ARM, $\chi_{LF}$) decrease with depth and hysteresis parameters move toward the multi-domain (MD) region. Increased $\chi_{FD}$ suggests the occurrence of an ultrafine authigenic SP phase.
Figure 4: Depth profiles from cores PC3B and PC6B (methanogenic sediments) of pore water chemistry and selected magnetic parameters. The SMTZ is indicated by gray shading. See text for details of the interpretation of various parameters. Magnetic properties change abruptly at the SMTZ with little variation in the methanogenic zone below the SMTZ.

3.4. First-order reversal curves (FORCs)

FORC measurements were used to quantify depth variations of ferrimagnetic minerals with different domain states (Egli, 2021; Pike et al., 2001; Roberts et al., 2014). To find optimal VARIFORC smoothing parameters (Egli, 2013), we applied the statistical machine learning optimization method of Heslop et al. (2020) on all samples separately. The results are similar, and the parameters used are: $S_{b0} = S_{c0} = 4$, $S_{b1} = S_{c1} = 6$, $\lambda_b = \lambda_c = 0.04$. All FORC diagrams can be interpreted as containing 3-4 components (e.g. Fig. 5a-b, e-f). The most prominent feature is a vortex state component expressed as “triangular” contours with asymmetry along the $B_u$ axis and hints of negative diagonal bands in the lower quadrant of the diagram. For all cases, the background
reflects a weak SD component with a narrow central ridge extending to 100 mT. The large $B_u$ dispersion at $B_c = 0$ indicates multi-domain (MD) properties. Also, a local maximum at the origin of the diagrams may be interpreted as due to SP particles (Pike et al., 2001).

To illustrate graphically depth changes in FORC data, we present in Figure 5c, g central ridge profiles for all samples, with $\rho$ values (mass-normalized FORC distribution second derivative) at $B_u = 0$, and in Fig. 5d, i we plot the $\rho$ maximum ($\rho_{\text{max}}$) versus depth. For both cores PC3B (methanogenic sediments) and HUG1 (OSR-sediments), the central ridge and $\rho_{\text{max}}$ have similar trends as bulk magnetic parameters (IRM, ARM, $\chi$; Figs. 3-4). In the OSR sediments (core HUG1B; Figure 5a-d), there is a noticeable central ridge profile and $\rho_{\text{max}}$ decay. Between 2 and 3 m there is a slight FORC, ARM, and $X_{FD}$ increase (Fig. 3a). In the methanogenic sediments (core PC3B; Figure 5e-h), $\rho_{\text{max}}$ increases in the upper 50 cm, decreases sharply at the SMTZ, and then fluctuates with depth in the methanogenic zone, but with smaller fluctuations than in the OSR-sediments. Overall, the FORC data are consistent with the bulk magnetic data in Figures 3-4.

**Figure 5**: FORC data for OSR-affected (a-d) and methanogenic sediments (e-h). a-b, e-f) Representative FORC diagrams with contributions from SP-SD, vortex state, and MD components. c, g) Central ridge profile over $B_u = 0$. d, h) Depth profiles for the maximum $\rho$ value in (c, g). In the OSR sediments, the central ridge intensity decreases with depth. In the methanogenic sediments there is a sharp drop at the SMTZ and stabilization in the methanogenic zone.
3.5. Low-temperature magnetic measurements

Representative mass-normalized low temperature data are shown in Figure 6a-b, e-f. The Verwey transition ($T_v$) due to magnetite causes a detectable gradient change in FC and ZFC warming curves between $\sim$100 K and $\sim$120 K where $T_v$ in biogenic magnetite is closer to 100 K (Jackson & Moskowitz, 2021). Following Chang et al. (2016b), who used ZFC/FC data to distinguish between biogenic ($T_v$ $\sim$100 K) and inorganic ($T_v$ $\sim$120 K) magnetite in marine sediments, we show in Figure 6c-g the FC curve derivative for methanogenic (PC3B) and OSR (HUG1B) sediments. In the OSR sediments, the derivative curve becomes smoother with increasing depth, with a peak near $\sim$100 K observed only in the uppermost sediments, below which $T_v$ is not observed. In core PC3B, the 100-110 K derivative peak is observed at all depths. The maximum derivative value between 100 and 120 K plotted versus depth in Figures 6d, h is a proxy for magnetite concentration changes. In both cores there is an increase in the uppermost meter. Magnetite is continuously depleted in the OSR sediments until it cannot be detected below $\sim$3.5 m. In the methanogenic zone, however, a fraction of biogenic magnetite survives below the SMTZ and remains stable. Overall, the results suggest the presence of biogenic magnetite in all cores. In the OSR-sediments, magnetite dissolves with depth, while it survives as it passes through the SMTZ in methanogenic sediments.

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**Figure 6:** Low temperature magnetic measurements for OSR-affected (a–d) and methanogenic sediments (e–h). a–h, e–f) Representative FC/ZFC warming curves and room-temperature SIRM cooling-heating cycles. c, g) First-derivative of the FC curves, where colors represent depths. Vertical dashed lines indicate the Verwey transition ($T_v$) for biogenic ($\sim$100 K) and inorganic ($\sim$120 K) magnetite. d, h) Depth profiles of the maximum first derivative from (c, g) in the 100-120 K range. The
magnetite signal gradually diminishes in the OSR sediments, whereas magnetite is still detectable below the SMTZ in the methanogenic sediments.

3.6. Electron microscopy

Representative electron microscope images of titanomagnetite and iron sulfides from different depths in OSR-sediments (core HUG1B) are shown in Figure 7. Iron sulfides are widespread and easily detectable. Multiple generations of frambooids and other clusters vary in size, shape, and Fe:S ratio. Micron-sized detrital titanomagnetites occur at all depths. At greater depths (e.g. Figure 7h-i), signs of preliminary titanomagnetite dissolution are observed. The titanomagnetite is likely responsible for vortex state and MD behavior in FORC diagrams. We could not identify microscopic evidence for biogenic magnetite, possibly owing to their small concentrations and small (nanometer-scale) size. The ferrimagnetic mineralogy in core PC3B is similar to that in core HUG1B. Representative images of titanomagnetites and iron sulfides are shown in Figure 8. The only difference between the core PC3B and HUG1B sediments is that we could not identify hints of titanomagnetite dissolution.

Figure 7: Representative SEM images for magnetic mineral extracts from core HUG1B. (a, b, g-i) Coarse, MD detrital titanomagnetite; at 550 cm depth (g-i), there are preliminary signs of reductive dissolution. (c-f) Different appearances of authigenic iron sulfides.
3.7. Paleomagnetic directions

Representative demagnetization results are shown in Figure 9. Typically, > 90% of the NRM is removed at 60 mT, and the average median destructive field (MDF) for all specimens is 19.6 mT. For most specimens, straight lines are observed on Zijderveld (Zijderveld, 1967) plots with MAD < 5°. Other specimens with noisy or non-straight trajectories and MAD > 5° were discarded from further analysis. We could not find any systematic difference between AF demagnetization data for OSR and methanogenic sediments. Overall, 953 specimens from cores HUG1B, T5B, PC3B, and PC6B were analyzed. The percentage of specimens with MAD < 5° in OSR sediments is 91% and 79% for cores HUG1B and T5B, respectively, which is lower than for methanogenic sediments, which are 97% and 93% for cores PC3B and PC6B, respectively. Although the demagnetization experiments seem to yield successful results, paleomagnetic directions plotted versus depth (Fig. S1, supplementary material) have considerable scatter and sharp declination and/or inclination swings in some intervals. These non-geomagnetic behaviors are likely due to sediment distortion during coring. Therefore, we ignored the following intervals: 500-570 cm in core HUG1B, 400-560 cm in core T5B, 400-594 cm in core PC3B, and 0-100 cm in core PC6B.
Figure 10: Paleomagnetic data with comparison between sedimentary paleomagnetic directions, geomagnetic model results, and archaeomagnetic data. a-b) Declination and inclination data from the studied sediment cores. c) Corrected paleomagnetic inclinations after finding the optimal inclination shallowing coefficient and lock-in time that produces the best agreement between the models and archaeomagnetic data. Data for the methanogenic sediments (PC3B, PC6B) correlate better with the models than those for OSR-affected sediments (HUG1B, T5B).
4. Discussion

4.1. Effects of sulfate reduction mode on bulk sedimentary magnetic properties

Our results demonstrate a strong correlation between diagenetic zones defined by pore-water chemistry (sulfate, methane, and ferrous iron) and magnetic properties. Magnetic analysis includes bulk concentration-dependent proxies (Figures 3-4), hysteresis (Figures 3-4), FORC (Figure 5), and low temperature measurements (Figure 6), along with electron microscopy (Figure 7). In OSR sediments, we observe a gradual sulfate concentration decrease accompanied by weaker magnetism. All bulk concentration-dependent magnetic parameters (IRM, ARM, $\chi$, FORC $\rho_{max}$) generally decrease downward with depth, which indicates that the decline is associated with low coercivity ferrimagnetic minerals. The FORC central ridge profile associated with the SD and vortex states decrease with depth, and hysteresis parameters ($B_{cr}/B_{c}$ and $M_r/M_S$) mark a trend to more MD-like values. Sulfate reduction effects on iron-bearing minerals are observed by electron microscopy, with various iron-sulfide types and generations. SEM images reveal signs of partial dissolution of micrometer-scale titanomagnetite particles, indicating that dissolved Fe$^{2+}$ for precipitating authigenic sulfides is sourced from reduction of low solubility ferric (Fe$^{3+}$) iron oxides. Also, low-temperature data indicate that biogenic magnetite that forms in the uppermost sediments dissolves with depth. Authigenic sulfide mineralogy is heterogenous, with a large pyrite population, and Fe:S ratios that can be attributed to greigite. Thus, although we cannot identify ferrimagnetic greigite clearly from GRM signals or from closed concentric FORC contours, we cannot exclude its presence in the sediments. All observations lead us to conclude that the ferrimagnetic phase in the OSR sediments includes vortex state to MD titanomagnetite and SP-SD biogenic magnetite. Both vortex state and SD particles can efficiently record the paleomagnetic field. Yet, they dissolve gradually with depth, with smaller magnetite particles dissolving first. The decline of concentration dependent magnetic parameters to about 50% of their maximum value over 6 m might result in a significant primary paleomagnetic signal loss, and perhaps even remagnetization.

Methanogenic sediments have a more complex correlation between diagenetic zones and magnetic data. In core PC3B, which best represents the methanogenic sediments, all concentration-dependent bulk magnetic parameters (IRM, ARM, $\chi$, FORC $\rho_{max}$) drop sharply across the SMTZ, which corresponds to a sharp magnetite concentration decrease in the FC derivative, and a hysteresis parameter change. We observe three features below the SMTZ. First, sediment magnetic properties stabilize in the methanogenic zone, with much smaller magnetic variability. Second, biogenic magnetite that formed in the uppermost sediment column survives the dissolution front at the SMTZ, and a $T_v$ signature due to magnetite remains throughout the methanogenic zone. Third, the ferrous iron concentration remains high in the methanogenic zone. These observations are discussed further below in Section 4.3.

The process of reductive dissolution of iron-bearing minerals by sulfate reduction is common in marine environments. Sulfate reduction can significantly affect sediment magnetic properties, causing a downward decrease in ARM, IRM, susceptibility, and SD-sensitive properties (Brachfeld et al., 2009; Chang et al., 2016b; Karlin, 1990a, 1990b; Karlin & Levi, 1983; Larrasoña et al., 2007; Liu et al., 2004; Qian et al., 2020; Reilly et al., 2020; Roberts et al., 2013; Roberts & Weaver, 2005; Rowan & Roberts, 2006; Rowan et al., 2009). The magnetization decrease is caused by reductive dissolution of ferrimagnetic magnetite and precipitation of the
paramagnetic iron sulfide pyrite. Magneto geochemical studies of methanogenic sediments that
directly measured pore water methane and sulfate have reported similar results to ours. Regardless
of location, sedimentation rate, and specific local conditions, there is typically a magnetization
decrease, correlated with a magnetite decrease at the SMTZ as observed, for example, in the
Eastern Mediterraenean (Amiel et al., 2020), Bay of Bengal (Badesab et al., 2020; Badesab et al.,
2023; Dewangan et al., 2013), Labrador Sea (Kawamura et al., 2012), Indian Ocean (März et al.,
2008), Weddell Sea (Reilly et al., 2020), and western Argentine Basin (Riedinger et al., 2005). In
many cases, the SMTZ can have a marked effect on paleomagnetic recording and can distort the
primary paleomagnetic signal and even cause remagnetization (Roberts & Weaver, 2005; Rowan
& Roberts, 2006; Rowan et al., 2009), depending on sedimentation rate and organic carbon
availability (Chang et al., 2016a). Our Eastern Mediterranean data suggest that when the SMTZ is
shallow and sedimentation rates are high, magnetic properties can stabilize and preserve a primary
magnetization.

4.2. Comparing OSR and AOM effects on paleomagnetic recording

In this study, we explore sulfate reduction effects, either via continuous OSR or AOM, on the
quality of sedimentary paleomagnetic recording, with emphasis on short term secular variation
recorded by rapidly deposited marine sediments. We assess the degree of paleomagnetic
smoothing, potential lock in depths, and inclination shallowing. Declination and inclination data
for all the cores are shown in Figure 9a-b. The cores were not oriented, so relative declination data
are corrected by subtracting the average declination. Also shown for comparison, are geomagnetic
data calculated from recent geomagnetic models: ARCHKALMG14 (Schanner et al., 2022),
pfm9k.2 (Nilsson et al., 2022), SHAWQ (Campuzano et al., 2019; Osete et al., 2020), and
SCHA.DIF.4k (Pavon-Carrasco et al., 2021) and archaeomagnetic data from archaeological burnt
structures in Israel and Cyprus (Shaar et al., 2018; Tema et al., 2021). All paleomagnetic directions
are allocated to the coordinates of Jerusalem (31.78°N,35.23°E). Comparison of sedimentary data
with models and archaeomagnetic data reveal significant discrepancies in both declination and
inclination. Declinations have the most pronounced difference with large amplitude changes that
cannot be associated with geomagnetic field behavior, for example, the younger part of cores
PC6B and T5B. Inclination data are more consistent with the models and archaeomagnetic data
than declination data. These results suggest that parts of the sediment rotated within the core tubes
before sampling. Thus, for further analysis, we mainly focus on inclination data.

To account for the unknown effects of inclination shallowing and magnetization lock in depth, we
wrote an optimization algorithm to find the optimal shallowing coefficient (f) (King, 1955) and
the lock in time, searching for values that yield a minimum root mean square of the difference
between sedimentary data, geomagnetic models, and archaeomagnetic data. The corrected
inclination time series (after optimization) is shown in Figure 9c. Data for core T5B are not shown
because even after optimization, the data are much noisier than for the other cores. The optimal
lock in time in all other cores is similar and is around 250 years. This time corresponds to depths
of 71 cm in cores PC3B and PC6B (methanogenic sediments) and to 131 cm in core HUG1B (OSR
sediments). The inclination shallowing coefficient ranges between 0.73 in core PC3B and 0.89 in
core PC6B. This indicates that inclination shallowing is non negligible, which is consistent with
usual inclination shallowing values estimated in paleomagnetic studies (Kodama, 2012a).

Paleomagnetic data for the methanogenic sediments are more coherent than for the OSR
sediments, and are more consistent with geomagnetic models and archaeomagnetic data (Figure
9). Also, as noted in Section 3.7, the paleomagnetic stability of methanogenic sediments in AF demagnetization experiments is superior, with stable single-component magnetizations compared to OSR sediments. Considering the mineral magnetic data discussed above, we conclude that methanogenic sediments below a shallow SMTZ with rapid deposition may better record primary paleomagnetic directions than sediments with continuous OSR.

4.3. Magnetite and ferrous iron occurrences in the methanogenic zone

Comparison of low-temperature and FORC data from core PC3B (Figures 5h, 6h) indicate the occurrence of non-detrital SD magnetite deep in the methanogenic zone. The magnetite concentration is high at the top of the core, and increases in the meter above the SMTZ before decreasing sharply at the SMTZ. Below the SMTZ, magnetite remains detectable. The presence of nanometer-scale magnetite in the methanogenic zone is important because this fraction is expected to dissolve at the SMTZ. Moreover, the dissolved iron concentration is high below the SMTZ. Two scenarios could explain these observations. First, due to the high deposition rate, there was insufficient time for the magnetite that formed in the uppermost sediment, either as magnetosomes or via bacterial dissimilatory iron reduction, to dissolve. The second explanation is that a new generation of magnetite is forming in the presence of methanogenic archaea (Shang et al., 2020). Authigenic magnetite precipitation in methanogenic sediments has been suggested in several studies (Amiel et al., 2020; Badesab et al., 2023; Beaver et al., 2021; Lin et al., 2021). Our results provide further support for this hypothesis. Yet, more work is needed to resolve the microbiological mechanism associated with this process.

4.4. Geomorphological implications for shelf development

Although our main focus is on the paleomagnetic properties of southeastern Mediterranean shelf sediments, radiocarbon analysis provides insights into mid-late Holocene temporal evolution of the shelf. All cores were collected from the horizontal shelf segment, where seismic reflectors dip negligibly, at 46-49 m and 67-81 m water depths for the northern and southern study area, respectively (Figure 1). The time span covered by the studied sediments is 7.5 - 1.5 ky BP, during which Mediterranean sea level rise decreased and stabilized at ~6 ky BP (Lambeck et al., 2014; Sivan et al., 2004; Sivan et al., 2001). Radiocarbon age models indicate a nearly constant sedimentation rate, and, thus, steady sediment accumulation related to shelf buildup. The sedimentary succession is truncated by an unconformity at depths < 50 cm, where the unconformity age increases northward. In the southernmost location (core PC6B), the sediment age at 50 cm depth is 1.6 ky and in core T5B (25 km northward), it is 3.2 ky. In the northern study area, near Haifa bay, the sediment age at 50 cm is 3.8 and 5.4 ky for cores PC3B and HUG1B, respectively. The absence of young sediments in the northern study area may be associated with the Carmel structure, which blocks sediment transport by shore-parallel currents. A similar unconformity was found in studies of Holocene shelf cores (see Figure 1b for core locations), but until this study it was not certain whether this is a characteristic feature of the shelf or a local phenomenon. Avnaim-Katav et al. (2019) dated core V4, which was collected from a 47 m water depth between the locations of cores T5B and PC6B, and reported an unconformity at a depth of ~25 cm with 2.4 ky sediment age. Bookman et al. (2021) studied a more sandy lithology at shallower water depths of 33-36 m and reported unconformities in cores V101 and V115 (Figure 1b). The unconformity seems to be a characteristic shelf feature that spans over at least 100 km from southern Israel to Haifa bay. Given that the sedimentation rate is steady below the
unconformity and that sea level changes since 6 ky BP have been minor, it is unlikely that a thick
sediment column (6.5-9.5 m, based on the above-reported sedimentation rates) was deposited and
then eroded in a single event. Instead, it possibly marks a time during which shelf build-up
stabilized and stopped accumulating sediments, possibly after eroding previously deposited
sediments or by multiple deposition-erosion cycles. This hypothesis requires non-synchronous
shelf stabilization, where different parts stopped accumulating sediments at different times in the
late Holocene, and that the northern shelf stabilized before the southern part. We note that deeper
open continental slope deposits include late Holocene sediments (e.g. (Schilman et al., 2001),
which were likely deposited on the shelf and then eroded within submarine canyons offshore of
northern Israel (Moshe et al., 2024). Therefore, the sedimentation regime along different shelf
segments is more complex and site-dependent and requires further study.

5. Conclusions

We compare paleomagnetic, mineral-magnetic, and pore water chemical properties of four ~6-m-
long sediment cores from the Holocene Eastern Mediterranean continental shelf to study sulfate
reduction effects on the quality and preservation of paleomagnetic recording. Sediments affected
by continuous organoclastic sulfate reduction undergo a continuous magnetization decrease and
coarsening of the dominant magnetic mineral. This magnetic property change results from
dissolution of detrital titanomagnetite and fine-grained biogenic magnetite. Sediments affected by
continuous OSR, thus, significantly smooth short-term geomagnetic secular variations. In contrast,
sediments with intensive upward methane fluxes cause shallowing of the sulfate-methane
transition zone and anaerobic oxidation of methane consumes most of the sulfate there leaving a
narrow sulfidic zone. This probably leads to preservation of primary paleomagnetic signals in the
methanogenic zone.

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Paleomagnetic imprints of sulfate reduction pathways in continental shelf sediments: organoclastic versus anaerobic oxidation of methane

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Key Points:

- Correlation between early diagenetic zones and mineral magnetic properties is observed in Holocene eastern Mediterranean shelf sediments
- Continuous organoclastic sulfate reduction (OSR) smooths rapid paleomagnetic secular variation recorded by the sediments
- Shallow sulfate-methane transition zones and intense sulfate reduction by anaerobic oxidation of methane may preserve better paleomagnetic records than continuous OSR
Abstract

Marine continental shelf sediments with high deposition rates may provide useful archives of rapid geomagnetic secular variation as long as the primary magnetization is not altered substantially by diagenesis. To quantify the effects of sulfate (SO$_4^{2-}$) reduction, which is a dominant early diagenetic process in such sediments, on paleomagnetic recording, we analyzed four ~6-m long sediment cores from the Mediterranean shelf. Two cores did not reach the methanogenic zone and are characterized by continuous organoclastic sulfate reduction (OSR), while the other two have a distinctive shallow sulfate-methane transition zone (SMTZ). Depth-age models based on 28 radiocarbon ages show that deposition was mostly non-synchronous, suggesting that different parts of the shelf stopped accumulating sediments at different times during the Holocene. The upper sediment column in all cores is dominated by detrital titanomagnetite and biogenic magnetite. OSR-affected sediments record continuous dissolution of the (titano)magnetites, resulting in a steady decrease in magnetic susceptibility and remanent magnetic properties. For cores that reach the methanogenic zone, similar behavior is observed at or above the STMZ, but the magnetic properties stabilize at greater depths. Paleomagnetic directions in these sediments are more coherent, with better agreement with geomagnetic models than sediments affected by OSR. We suggest that methane-rich sediments with a shallow SMTZ and high sedimentation rates can better preserve primary paleomagnetic signals than OSR-dominated sediments due to a lack of dissolved sulfide in the main methanogenic zone, and that a susceptibility decline with depth should be a warning sign for paleomagnetic studies.

Plain Language Summary

It has long been recognized that marine seafloor sediments provide continuous records of variations of Earth’s magnetic field. Marine sediments have, thus, been used to explore Earth’s magnetic field behavior throughout geological history. The classical view on how sediments acquire a magnetization in aquatic environments involves physical forces that rotate magnetic particles toward the field direction as they sink. However, biochemical processes associated with microbial respiration may distort the primary depositional magnetic information and even remagnetize it. We explore here how sulfate reduction, which is one of the most dominant diagenetic biochemical processes in global continental shelf marine environments, affects sediment magnetic properties and the ability to accurately record magnetic information. We analyzed four sediment cores from the Southeastern Mediterranean shelf, which were deposited under different sulfate reduction regimes. We show that continuous sulfate reduction significantly changes the magnetic mineralogy and, therefore, hampers preservation of sedimentary paleomagnetic records. We also show that to obtain reliable high-resolution sedimentary paleomagnetic data, sulfate should be consumed as early as possible after deposition. Such conditions occur when methane fluxes from below reach shallow sulfate-rich sediments.

1. Introduction

Marine continental shelf sediments are an important source of global paleomagnetic data owing to their high sedimentation rates and availability of datable materials. Over recent decades, marine sediments from continental shelves and shallow basins have provided essential information on spatial and temporal global geomagnetic field evolution (e.g. (Lisé-Pronovost et al., 2009; Reilly...
Early diagenesis encompasses a range of biochemical reactions associated with microbial organic matter degradation coupled to reduction of electron acceptors, which is assumed to occur in order of decreasing free energy yield (Berner, 1981; Canfield & Thamdrup, 2009; Roberts, 2015). The following order of electron acceptor use is predicted (with corresponding diagenetic zones): oxygen (oxic zone), nitrate (nitrogenous zone), manganese oxides (manganous zone), iron (oxyhydro)oxides (ferruginous zone), sulfate (sulfidic zone), and finally organic matter itself (methanogenic zone). In many aquatic sedimentary profiles, however, different diagenetic zones with different magnitudes, may overlap partly, or may not appear at all. Sulfate reduction is one of the most dominant early diagenetic processes in marine environments, and is responsible for over half of organic carbon degradation (Bowles et al., 2014). Two main sulfate consumption pathways are via continuous organoclastic sulfate reduction (OSR) or through a diffusive flux to the sulfate-methane transition zone (SMTZ), and intensive reduction there by anaerobic oxidation of methane (AOM) with a narrow sulfidic zone (Jorgensen et al., 2019). The second mode occurs mainly within areas dominated by intensive methanogenesis that causes SMTZ shallowing (Sivan et al., 2007).

The effect of sulfate reduction on sediment magnetic properties is the main focus of this study. This topic has been discussed for both marine and lacustrine environments (e.g. (Amiel et al., 2020; Canfield & Berner, 1987; Chang et al., 2014; Ebert et al., 2018; Karlin & Levi, 1983; Karlin et al., 1987; Kars & Kodama, 2015; Larrasoaña et al., 2007; Nowaczyk, 2011; Reilly et al., 2020; Roberts et al., 2011; Roberts & Weaver, 2005; Rowan & Roberts, 2006; Rowan et al., 2009). On one hand, dissolved sulfide is released during sulfate reduction and triggers dissolution of detrital or authigenic magnetite, which causes a decrease in bulk magnetic properties and loss of primary paleomagnetic information. On the other hand, reaction of dissolved sulfide with Fe$^{2+}$ ions can cause formation of different iron sulfides, including mainly mackinawite, greigite, and pyrite, where greigite formation may lead to secondary magnetization acquisition. The stoichiometry and magnetic properties of authigenic iron sulfides are controlled by several factors, including the...
availability and reactivity of organic matter for degradation, the sulfate reduction rate, and the
reactive iron concentration in pore waters.

The purpose of this study is to obtain empirical data on the effect of the two sulfate reduction
modes – OSR, which occurs continuously in the sulfidic zone of so-called ‘OSR sediments’, versus
AOM at the SMTZ of so-called ‘methanogenic sediments’ – on sedimentary magnetic properties
and on of paleomagnetic recording quality. In a field-test approach, we explore shallow marine
continental shelf sediments located both within and outside localized methane pockets. This allows
us to compare the magnetic properties of sediments, which differ only in their diagenetic pathways
along the upper few meters of the sediment column. Our analysis combines paleomagnetic,
mineral-magnetic, and geochemical data.

Geological setting

The sampling area is located on the continental shelf offshore of Israel at water depths ranging
between 46 and 81 m (Table 1, Figure 1). This area comprises the northeastern Nile littoral cell
with deposition of silts and clays that were transported from the Nile via counter-clockwise shore-
parallel currents (Schattner, 2021; Schattner et al., 2015). The sedimentation regime at these depths
stabilized during the mid-late Holocene subsequent to slowing of post-glacial sea level rise (Grant
et al., 2012; Schattner, 2021; Sivan et al., 2004; Sivan et al., 2001), creating a geomorphologically
and tectonically stable low-relief belt. The study area, as part of the eastern Mediterranean Sea,
has oligotrophic conditions (Herut et al., 2000; Kress & Herut, 2001) with poor nutrient availability
and low sedimentary organic matter contents. Under these constraints, methanogenesis is not
expected, and OSR is the main diagenetic process in shallow sediments (Wurgaft et al., 2019).
However, despite the oligotrophic conditions, several shallow methane pockets have been
identified by seismic surveys (Lazar et al., 2016; Schattner, 2021; Schattner et al., 2012). The
seismic data reveal evidence for methane migration from depth horizons that correspond to the last
glacial maximum shoreline (Fig. 1c,e) probably in response to continuous sediment loading. Pore-
water chemistry of sediments from these localities confirms the presence of methane at 1-4 m
depths and a shallow SMTZ (Amiel et al., 2020; Sela-Adler et al., 2015; Vigderovich et al., 2019;
Wurgaft et al., 2019). Based on carbon isotope compositions of dissolved inorganic carbon (DIC)
and methane, Sela-Adler et al. (2015) concluded that the methane is produced microbially. Antler
et al. (2015) and Wurgaft et al. (2019) then suggested the dominance of sulfate AOM versus
continuous sulfate reduction in these methane-rich sediments. Here, we took advantage of
geographically confined shallow methane pockets to develop a sampling strategy to collect
sediments from both within and outside methane-rich zones, at nearby spots that differ only in
their diagenetic profiles. Locations of sampling spots and seismic profiles that indicate the
presence of localized gas fronts are shown in Figure 1. Furthermore, the availability of well dated
paleosecular variation records from the Levant (Ebert et al., 2018; Shaar et al., 2018) and well-
constrained geomagnetic field models for the Holocene (Nilsson et al., 2022; Osete et al., 2020;
Pavon-Carrasco et al., 2021; Schanner et al., 2022) suggests that this region is an ideal natural
laboratory for assessing the impacts of laterally and stratigraphically varying early diagenetic
effects on paleomagnetic recording.
Figure 1: Location map. a-b) Bathymetric maps of the eastern Mediterranean with locations of studied cores (bold fonts) and previously studied cores mentioned in the text (italic fonts). c-d) CHIRP shallow seismic reflection profiles collected near the core locations. Estimated core locations are indicated with red arrows. Yellow arrows in (c) and (d) indicate methane gas fronts.

Table 1: Sampling locations

<table>
<thead>
<tr>
<th>Station</th>
<th>Water depth (m)</th>
<th>Core length (m)</th>
<th>Latitude (N°)</th>
<th>Longitude (E°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC3</td>
<td>81</td>
<td>5.8</td>
<td>32.92584</td>
<td>34.90472</td>
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</table>
### 2. Methods

#### 2.1. Sampling

Sediments were collected using the *Bat-Galim* Research Vessel with a 9-m long Benthos piston corer. At each sampling spot (Figure 1, Table 1), we collected two piston cores, the longer of which was labeled ‘B’. ‘B’ core lengths are 5.8–6.8 m. Cores PC3/PC3B and PC6/PC6B were collected at locations where Sela-Adler et al. (2015) detected a shallow SMTZ at ~1 m sediment depth. The locations of cores HUG1/ HUG1B and T5/ T5B were selected based on seismic data, as close as possible to the methanogenic sediments, but outside the methane pockets. On board, the 8-m fiberglass liners were cut to 1.2-m long segments. Pore-waters were extracted from cores segments immediately after recovery along with sediment for methane analysis. Core segments were then refrigerated until they were split and sampled for paleomagnetism (within days of collection). Upon splitting, paleomagnetic samples were collected using non-magnetic plastic sample boxes (outer dimension 23 × 23 × 19 mm) at ~25-mm resolution. Freeze-dried sediments for bulk mineral magnetic analysis were collected from ‘B’ cores at 20-cm stratigraphic intervals.

#### 2.2. Paleo- and mineral- magnetic analyses

All paleomagnetic and mineral magnetic measurements were made at the paleomagnetic laboratory, Institute of Earth Sciences, The Hebrew University of Jerusalem, except for low temperature measurements, which were made at the Institute for Rock Magnetism (IRM), University of Minnesota. Oriented paleomagnetic samples were weighed and subjected to the following procedures in order: alternating field (AF) demagnetization of the natural remanent magnetization (NRM), acquisition of an anhysteretic remanent magnetization (ARM), susceptibility (χ) measurement at two frequencies, and isothermal remanent magnetization (IRM) acquisition. Stepwise AF demagnetization was carried out at 4 mT steps to 20 mT, in 10 mT steps to 50 mT and in 15 mT steps to 110 mT. ARM was imparted using a 0.1 mT bias field and 100 mT AF. Magnetization measurements and ARM acquisition were done with a 2G Enterprises RAPID superconducting rock magnetometer (SRM) system. An IRM was imparted in a 1.5-T induction using an ASC pulse magnetizer and was measured with a MAG-Instruments Portable Spinning Magnetometer (PSM-1). Mass-specific susceptibility was measured using an AGICO MFK-1 Kappabridge at low (976 Hz) (χ_{LF}) and high (15616 Hz) frequencies (χ_{HF}).

About 150 mg of freeze-dried sample was weighed and packed tightly in gelatin capsules for hysteresis loop, back-field demagnetization, first-order reversal curve (FORC), and low temperature measurements. Hysteresis and backfield curves were measured for all ‘B’ cores at 20-cm stratigraphic resolution and FORC measurements were made for selected samples. Six-hundred equally spaced FORCs were measured in the space defined by: 0 < B_c < 100 mT and -100 mT <

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
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<td>32.28361</td>
<td>34.74556</td>
</tr>
<tr>
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</tr>
<tr>
<td>T5B</td>
<td>46</td>
<td>5.7</td>
<td>32.50333</td>
<td>34.83417</td>
</tr>
</tbody>
</table>
B₀ < 100 mT, with 1.5 T saturation field and 150-ms averaging time. Measurements were made with a LakeShore 8600 series vibrating sample magnetometer.

Low temperature measurements were made on capsules from cores PC3B and HUG1B using a Quantum Design Magnetic Properties Measurements System (MPMS3) in VSM mode. Procedures included: warming of a 2.5 T SIRM from 5 K to 300 K after cooling in zero-field (‘zero-field-cooled’, ZFC curves), warming of a 2.5 T SIRM from 5 K to 300 K after cooling in 2.5 T field (‘field-cooled’, FC curves) and low-temperature cycling of room-temperature SIRM from 300 K to 5 K and back to 300 K. Heating and warming curves were measured at 5 K steps at 5 K/min.

Paleomagnetic data analysis was done using the Demag GUI program, which is part of the PmagPy software package (Tauxe et al., 2016). The characteristic remanent magnetization (ChRM) was calculated from principal component analysis (PCA) (Kirschvink, 1980) using the maximum angular deviation (MAD) to quantify parametrically the ChRM quality. FORCs were processed with the FORCinel (Harrison & Feinberg, 2008) and FORCTool (Surovitskii et al., 2022) software, which uses the statistical machine learning framework of Heslop et al. (2020) to find optimal VARIFORC (Egli, 2013) smoothing parameters. First point artefact and drift corrections were applied in all cases before smoothing.

To prepare samples for scanning electron microscope (SEM) observations, we used a rare-earth magnet to extract magnetic particles from freeze-dried sediment. Magnetic extracts were dispersed on carbon tape and were imaged using a XHR-SEM Magellan 400L SEM equipped with energy-dispersive spectrometer (EDS) detectors, in both secondary electron (SE) and backscattered (BS) electron modes. Analyses were made at the Hebrew University Center for Nanoscience and Nanotechnology.

### 2.3. Pore-water chemistry

Holes in Perspex core liners were used for methane sampling and pore-water extraction. Approximately 1.5 ml of sediment was sampled using a cut syringe and was transferred immediately into N₂-flushed crimped bottles containing 5 ml of 1.5 N NaOH for headspace methane measurements. Pore waters were extracted using Rhizons through a 0.22-mm filter and were kept without air until measurement. Ferrozine solution was used to fix immediately 1 mL of water for Fe²⁺ measurement.

Headspace methane concentrations were measured with a Thermo Scientific gas chromatography (GC) system equipped with a flame ionization detector (FID) at 2 mmolL⁻¹ precision. Ferrous iron was measured with a spectrophotometer at 562 nm absorbance (Stookey, 1970) with an error of less than 7 mmolL⁻¹. Sulfate concentrations were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES-720-ES, VARIAN) with an accuracy of 2%.

### 2.4. Radiocarbon dating

Radiocarbon dating (e.g. (Reimer et al., 2020) was used to determine the age of twenty-eight selected samples along the four studied piston cores. Tens of the best-preserved shells of the benthic foraminiferal genera *Ammonia* and *Elphidium* (> 150 μm size fraction) were handpicked under a binocular microscope to obtain at least ~1 mg of CaCO₃ per sample. The pretreatment procedure included cleaning of calcareous shells by ultrasonication and ethanol to remove any fine
sediment residues from within the shells. Radiocarbon dating was conducted at the AMS MICADAS (Mini Carbon Dating System) radiocarbon laboratory at the Alfred Wegener Institute (AWI), Helmholtz Centre for Polar and Marine Research, Germany. Radiocarbon ages were calibrated and modeled using the Oxcal program v4.4.4 (Ramsey, 2009) and IntCal20 calibration curve (Heaton et al., 2020). Correction for local reservoir effects follows Heaton et al. (2020) and uses an average of six published ages from offshore Israel (Boaretto et al., 2010; Reimer & McCormac, 2002), which results in a reservoir correction ΔRmarine20 of -139 ± 73.

3. Results

3.1. Radiocarbon ages

Obtaining a sufficient mass of datable material was sometimes a challenge. In most cases, sorting sediments across a 1-2 cm thickness resulted in 1-5 mg of foraminiferal shells, which is the minimum weight for age determination. In some depth intervals, larger volumes that span a few centimeters thickness were required to achieve the minimal weight, due to poorly preserved (reworked), broken, or small shells. In general, the radiocarbon ages increase with depth (Fig. 2, Table 2). After rejecting five samples as outliers, age-depth models were calculated using five samples from core PC3B, six samples from core HUG1B, eight samples from core PC6B, and four samples from core T5B. Depositional models were calculated using the P_sequence (Poisson) function in the Oxcal program (Ramsey, 2008) with k factor of 1 and interpolation every 10 cm. Based on depositional models, the age of paleomagnetic samples was calculated by interpolating between the means of the modeled age distributions.

Age models for the cores (Fig. 2) indicate fairly steady deposition, where average deposition rates in the methanogenic sediments (cores PC3B, PC6B) are 3.5-3.6 mm/year, which is higher than the rate for the OSR sediments (cores HUG1B, T5), which is only 1.9 mm/year. The age range spanned by the four cores is significantly different with little overlap among them. Extrapolation of ages toward the surface yields apparent core top ages ranging between 5.1 ky BP for core HUG1B to 1.4 ky BP for core PC6B. The difference between extrapolated surface ages for cores PC3B and HUG1B, which were collected only 1.5 km apart, and the difference between those for cores PC6B and T5, which are located at the same water depth but 25 km away from each other is more than 1000 years. This probably indicates a non-synchronous and non-continuous sedimentation regime in which nearby parts of the shelf stopped accumulating sediments at different times during the Holocene. This result is discussed further in section 4.4.

Table 2: Radiocarbon ages for the studied sediment cores.

<table>
<thead>
<tr>
<th>Core</th>
<th>Sample name: core, depth range</th>
<th>(^{14}C) age (BP)</th>
<th>Cal. age (BP) (68%)</th>
<th>Cal. age (BP) (95%)</th>
<th>Modeled age (BP) (68%)</th>
<th>Modeled age (BP) (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC3B</td>
<td>PC3B 50-54</td>
<td>3827±29</td>
<td>3908-3652</td>
<td>4054-3536</td>
<td>3894-3658</td>
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<tr>
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<td>PC3B 101-102*</td>
<td>4429±70</td>
<td>4731-4428</td>
<td>4854-4274</td>
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<tr>
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<td>PC3B 200-202</td>
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<td>4300-4112</td>
<td>4426-4020</td>
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<tr>
<td></td>
<td>PC3B 301-302</td>
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<tr>
<td></td>
<td>PC3B 400-402</td>
<td>4459±70</td>
<td>4786-4491</td>
<td>4889-4304</td>
<td>4845-4676</td>
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</table>
274

<table>
<thead>
<tr>
<th></th>
<th>PC3B 550-551</th>
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<tr>
<td>HUG1B</td>
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<td>5512-5301</td>
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<tr>
<td>HUG1B</td>
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<td>5213±73</td>
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<tr>
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<tr>
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<tr>
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</tr>
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</table>

### 3.2. Diagenetic zones

Combined geochemical-magnetic depth profiles for all studied cores are shown in Figures 3 and 4, with selected magnetic parameters and dissolved sulfate, methane, and iron concentrations. The upper several centimeters of the sediment might have not been fully recovered by coring, which possibly masks our view of the uppermost sediments. From the diagenetic zones summarized by Roberts (2015), as outlined in Section 1, only the sulfidic and methanogenic zones can be identified directly from our geochemical measurements. This is because the oxic zone is restricted to a narrow layer at the water-sediment interface (Wurgaft et al., 2019) and the nitrogenous, manganous, and ferruginous zones may overlap with the upper sulfidic zone. The sulfate concentration in the upper sediment section is 25-30 mM and gradually decreases in OSR sediments (HUG1B, T5B, Figure 3) to ~10 mM at a depth of ~4 m. Methanogenic sediments (cores PC3B, PC6B, Figure 4) have a steeper, mostly diffusive, sulfate concentration gradient to depletion.
at the SMTZ at depths of 1.6 m in core PC3B and 4 m in core PC6B. As expected, the methane concentration is non-measurable in OSR-sediments (Figure 3), whereas in core PC3B (Figure 4a) methane increases from nearly zero to ~1 mM at 1.6 m and reaches almost 3 mM at 2.5 m. In core PC6B (Figure 4b), methane starts to increase at ~4.5 m and at the core bottom at 6.8 m it is >1.2 mM. Based on sulfate and methane data, the SMTZ is clearly defined at a narrow interval between ~1 m and ~1.8 m in core PC3B. In core PC6B, the SMTZ seems to be wider, between ~3.5 m and 6.3 m. SMTZ positions are marked with gray in Figure 4.

Figure 2: Radiocarbon age-depth models. Probability density functions of calibrated and modeled ages are shown in light and dark gray, respectively; colored ages mark outliers. The 95% probability density range of age-depth models are shown in colors. Although collected from nearby locations, the age spans of the cores are different, where northern cores (HUG1B, PC3B) have older ages than the southern cores (T5B, PC6B).
Ferrous iron concentration provides valuable information on iron reduction processes. Iron concentration in core PC3B, which best represents methanogenic sediments, has a small-scale local maximum above the STMZ at ~0.5 m, a further small increase at the top of the SMTZ (~1.1 m) to 15 μM, and a sharp increase to ~50 μM at the SMTZ base (~1.8 m). Below the SMTZ, in the methanogenic zone, iron concentrations vary between 40 and 80 μM. Core PC6B has a similar, although more complicated, picture with a wider SMTZ, small-scale fluctuations above the SMTZ (1.8-3.2 m) and another increase to ~3 μM at the top of the SMTZ. Core PC6B did not penetrate the deeper methanogenic zone, so we cannot know if ferrous iron has higher concentrations similar to those in core PC3B at greater depths. In the OSR-affected sediments, iron concentrations are much lower. In core HUG1B, iron contents increase from 0.4 μM at the top of the core to 1.1 μM at 4 m. In core T5B, iron measurements failed to produce coherent data and are not shown.

### 3.3. Bulk magnetic properties

Magnetic parameters are sensitive to iron bearing mineral changes; variations are consistent with geochemical parameters and the diageneric zones outlined above. All of the parameters shown in Figures 3-4 are sensitive to distinct magnetic property variations (Liu et al., 2012). Mass normalized ARM and SIRM represent concentration changes of low (<100 mT) and high (> 100 mT) coercivity ferrimagnetic minerals, respectively. The mass-normalized susceptibility (χ<sub>LF</sub>) is a bulk measurement that can serve as a proxy for large magnetic mineralogy changes. Frequency-dependent susceptibility (χ<sub>FD</sub> = 100 · χ<sub>LF</sub> - χ<sub>HF</sub> / χ<sub>LF</sub>) is sensitive to variations in nanometer-scale superparamagnetic (SP) particles and is, therefore, a proxy for authigenic mineral formation in this environment. The hysteresis ratios M<sub>r</sub>/M<sub>s</sub> and B<sub>cr</sub>/B<sub>c</sub> provide a measure of bulk grain size variations. The presence of a gyroremanent magnetization (GRM) during AF demagnetization is typical of stable single domain (SD) greigite (Snowball, 1997; Sagnotti & Winkler, 1999). ∆GRM (Just et al., 2019) is < 1% for almost all specimens, so it is not shown in Figures 3-4.

In all of the studied cores, χ<sub>LF</sub>, SIRM, and ARM variations have similar trends, which indicates that bulk magnetic property changes are primarily controlled by low-coercivity ferrimagnetic minerals. In the OSR sediments (cores HUG1B, T5B; Figure 3), there is a decreasing bulk parameter (ARM, IRM, χ<sub>LF</sub>) trend, with IRM and χ<sub>LF</sub> decreasing to half of their maximum values over a < 6 m depth interval. In both cores, we observe a ~2-m-thick region (at 2-4 m in T5B and 3-5 m in T5B) with a slight ARM (but not IRM) increase, large χ<sub>FD</sub> and B<sub>cr</sub>/B<sub>c</sub> increases, and a M<sub>r</sub>/M<sub>s</sub> decrease. These observations indicate authigenic mineral formation in the SD-SP size range within the sulfidic interval. Below this interval in core T5B, there is a downward χ<sub>FD</sub> decrease, accompanied by increased IRM and ARM, which may suggest that a small authigenic particle fraction grew above the SP-SD threshold volume.

The magnetic behavior of the methanogenic sediments (cores PC3B, PC6B; Figure 4) is different than for the OSR-sediments. In core PC3B, which has a shallow and narrow SMTZ, all magnetic parameters change above and at the top of the SMTZ, expressed first as an IRM, ARM, χ<sub>LF</sub>, and M<sub>r</sub>/M<sub>s</sub> increase and a B<sub>cr</sub>/B<sub>c</sub> decrease. Then, at the SMTZ, these parameters change to an opposite trend. Most importantly, below the SMTZ, all bulk parameters stabilize. In core PC6B, where the SMTZ is wider and deeper, a sharp magnetic parameter change occurs in the upper 50 cm, and then a more gradual change occurs with IRM, ARM, χ<sub>LF</sub>, B<sub>cr</sub>/B<sub>c</sub> decreasing, and M<sub>r</sub>/M<sub>s</sub> increasing.
increasing. At the SMTZ $\chi_{FD}$ decreases, followed by an increase; other parameter trends do not change, but their gradient increases.

Figure 3: Depth profiles from cores HUG1B and T5B (OSR-affected sediments) of pore water chemistry and selected magnetic parameters. See text for details of the interpretation of various parameters. In general, concentration-dependent parameters (IRM, ARM, $\chi_{LF}$) decrease with depth and hysteresis parameters move toward the multi-domain (MD) region. Increased $\chi_{FD}$ suggests the occurrence of an ultrafine authigenic SP phase.
Figure 4: Depth profiles from cores PC3B and PC6B (methanogenic sediments) of pore water chemistry and selected magnetic parameters. The SMTZ is indicated by gray shading. See text for details of the interpretation of various parameters. Magnetic properties change abruptly at the SMTZ with little variation in the methanogenic zone below the SMTZ.

3.4. First-order reversal curves (FORCs)

FORC measurements were used to quantify depth variations of ferrimagnetic minerals with different domain states (Egli, 2021; Pike et al., 2001; Roberts et al., 2014). To find optimal VARIFORC smoothing parameters (Egli, 2013), we applied the statistical machine learning optimization method of Heslop et al. (2020) on all samples separately. The results are similar, and the parameters used are: $S_{b0} = S_{c0} = 4$, $S_{b0} = S_{c1} = 6$, $\lambda_b = \lambda_c = 0.04$. All FORC diagrams can be interpreted as containing 3-4 components (e.g. Fig. 5a-b, e-f). The most prominent feature is a vortex state component expressed as “triangular” contours with asymmetry along the $B_u$ axis and hints of negative diagonal bands in the lower quadrant of the diagram. For all cases, the background
reflects a weak SD component with a narrow central ridge extending to 100 mT. The large $B_u$ dispersion at $B_c = 0$ indicates multi-domain (MD) properties. Also, a local maximum at the origin of the diagrams may be interpreted as due to SP particles (Pike et al., 2001).

To illustrate graphically depth changes in FORC data, we present in Figure 5c, g central ridge profiles for all samples, with $\rho$ values (mass-normalized FORC distribution second derivative) at $B_u = 0$, and in Fig. 5d, i we plot the $\rho$ maximum ($\rho_{\text{max}}$) versus depth. For both cores PC3B (methanogenic sediments) and HUG1 (OSR-sediments), the central ridge and $\rho_{\text{max}}$ have similar trends as bulk magnetic parameters (IRM, ARM, $\chi$; Figs. 3-4). In the OSR sediments (core HUG1B; Figure 5a-d), there is a noticeable central ridge profile and $\rho_{\text{max}}$ decay. Between 2 and 3 m there is a slight FORC, ARM, and $X_{FD}$ increase (Fig. 3a). In the methanogenic sediments (core PC3B; Figure 5e-h), $\rho_{\text{max}}$ increases in the upper 50 cm, decreases sharply at the SMTZ, and then fluctuates with depth in the methanogenic zone, but with smaller fluctuations than in the OSR-sediments. Overall, the FORC data are consistent with the bulk magnetic data in Figures 3-4.

Figure 5: FORC data for OSR-affected (a-d) and methanogenic sediments (e-h). a-b, e-f) Representative FORC diagrams with contributions from SP-SD, vortex state, and MD components. c, g) Central ridge profile over $B_u = 0$. d, h) Depth profiles for the maximum $\rho$ value in (c, g). In the OSR sediments, the central ridge intensity decreases with depth. In the methanogenic sediments there is a sharp drop at the SMTZ and stabilization in the methanogenic zone.
3.5. Low-temperature magnetic measurements

Representative mass-normalized low temperature data are shown in Figure 6a-b, e-f. The Verwey transition ($T_v$) due to magnetite causes a detectable gradient change in FC and ZFC warming curves between ~100 K and ~120 K where $T_v$ in biogenic magnetite is closer to 100 K (Jackson & Moskowitz, 2021). Following Chang et al. (2016b), who used ZFC/FC data to distinguish between biogenic ($T_v$ ~100 K) and inorganic ($T_v$ ~120 K) magnetite in marine sediments, we show in Figure 6c, g the FC curve derivative for methanogenic (PC3B) and OSR (HUG1B) sediments. In the OSR sediments, the derivative curve becomes smoother with increasing depth, with a peak near ~100 K observed only in the uppermost sediments, below which $T_v$ is not observed. In core PC3B, the 100-110 K derivative peak is observed at all depths. The maximum derivative value between 100 and 120 K plotted versus depth in Figures 6d, h is a proxy for magnetite concentration changes. In both cores there is an increase in the uppermost meter. Magnetite is continuously depleted in the OSR sediments until it cannot be detected below ~3.5 m. In the methanogenic zone, however, a fraction of biogenic magnetite survives below the SMTZ and remains stable. Overall, the results suggest the presence of biogenic magnetite in all cores. In the OSR-sediments, magnetite dissolves with depth, while it survives as it passes through the SMTZ in methanogenic sediments.

Figure 6: Low temperature magnetic measurements for OSR-affected (a-d) and methanogenic sediments (e-h). a-h, e-f) Representative FC/ZFC warming curves and room-temperature SIRM cooling-heating cycles. c, g) First-derivative of the FC curves, where colors represent depths. Vertical dashed lines indicate the Verwey transition ($T_v$) for biogenic (~100 K) and inorganic (~120 K) magnetite. d, h) Depth profiles of the maximum first derivative from (c, g) in the 100-120 K range. The
magnetite signal gradually diminishes in the OSR sediments, whereas magnetite is still detectable below the SMTZ in the methanogenic sediments.

3.6. Electron microscopy

Representative electron microscope images of titanomagnetite and iron sulfides from different depths in OSR-sediments (core HUG1B) are shown in Figure 7. Iron sulfides are widespread and easily detectable. Multiple generations of framboids and other clusters vary in size, shape, and Fe:S ratio. Micron-sized detrital titanomagnetites occur at all depths. At greater depths (e.g. Figure 7h-i), signs of preliminary titanomagnetite dissolution are observed. The titanomagnetite is likely responsible for vortex state and MD behavior in FORC diagrams. We could not identify microscopic evidence for biogenic magnetite, possibly owing to their small concentrations and small (nanometer-scale) size. The ferrimagnetic mineralogy in core PC3B is similar to that in core HUG1B. Representative images of titanomagnetites and iron sulfides are shown in Figure 8. The only difference between the core PC3B and HUG1B sediments is that we could not identify hints of titanomagnetite dissolution.

Figure 7: Representative SEM images for magnetic mineral extracts from core HUG1B. (a, b, g-i) Coarse, MD detrital titanomagnetite; at 550 cm depth (g-i), there are preliminary signs of reductive dissolution. (c-f) Different appearances of authigenic iron sulfides.
Representative SEM images of magnetic mineral extracts from core PC3B. Detrital titanomagnetite and diagenetic iron sulfides from above (a-c) and below (d-f) the SMTZ.

3.7. Paleomagnetic directions

Representative demagnetization results are shown in Figure 9. Typically, > 90% of the NRM is removed at 60 mT, and the average median destructive field (MDF) for all specimens is 19.6 mT. For most specimens, straight lines are observed on Zijderveld (Zijderveld, 1967) plots with MAD < 5°. Other specimens with noisy or non-straight trajectories and MAD > 5° were discarded from further analysis. We could not find any systematic difference between AF demagnetization data for OSR and methanogenic sediments. Overall, 953 specimens from cores HUG1B, T5B, PC3B, and PC6B were analyzed. The percentage of specimens with MAD < 5° in OSR sediments is 91% and 79% for cores HUG1B and T5B, respectively, which is lower than for methanogenic sediments, which are 97% and 93% for cores PC3B and PC6B, respectively. Although the demagnetization experiments seem to yield successful results, paleomagnetic directions plotted versus depth (Fig. S1, supplementary material) have considerable scatter and sharp declination and/or inclination swings in some intervals. These non-geomagnetic behaviors are likely due to sediment distortion during coring. Therefore, we ignored the following intervals: 500-570 cm in core HUG1B, 400-560 cm in core T5B, 400-594 cm in core PC3B, and 0-100 cm in core PC6B.

Figure 8: Representative SEM images of magnetic mineral extracts from core PC3B. Detrital titanomagnetite and diagenetic iron sulfides from above (a-c) and below (d-f) the SMTZ.

Figure 9: Orthogonal vector component (Zijderveld, 1967) plots. Straight lines converge to the origin above and below the SMTZ in methanogenic sediments (a-b) and in upper and lower parts of OSR-affected sediments (c-d).
Figure 10: Paleomagnetic data with comparison between sedimentary paleomagnetic directions, geomagnetic model results, and archaeomagnetic data. a-b) Declination and inclination data from the studied sediment cores. c) Corrected paleomagnetic inclinations after finding the optimal inclination shallowing coefficient and lock-in time that produces the best agreement between the models and archaeomagnetic data. Data for the methanogenic sediments (PC3B, PC6B) correlate better with the models than those for OSR-affected sediments (HUG1B, T5B).
4. Discussion

4.1. Effects of sulfate reduction mode on bulk sedimentary magnetic properties

Our results demonstrate a strong correlation between diagenetic zones defined by pore-water chemistry (sulfate, methane, and ferrous iron) and magnetic properties. Magnetic analysis includes bulk concentration-dependent proxies (Figures 3-4), hysteresis (Figures 3-4), FORC (Figure 5), and low temperature measurements (Figure 6), along with electron microscopy (Figure 7). In OSR sediments, we observe a gradual sulfate concentration decrease accompanied by weaker magnetism. All bulk concentration-dependent magnetic parameters (IRM, ARM, χ, FORC ρ_max) generally decrease downward with depth, which indicates that the decline is associated with low coercivity ferrimagnetic minerals. The FORC central ridge profile associated with the SD and vortex states decrease with depth, and hysteresis parameters (Bcr/BC and Mr/MS) mark a trend to more MD-like values. Sulfate reduction effects on iron-bearing minerals are observed by electron microscopy, with various iron-sulfide types and generations. SEM images reveal signs of partial dissolution of micrometer-scale titanomagnetite particles, indicating that dissolved Fe^{2+} for precipitating authigenic sulfides is sourced from reduction of low solubility ferric (Fe^{3+}) iron oxides. Also, low-temperature data indicate that biogenic magnetite that forms in the uppermost sediments dissolves with depth. Authigenic sulfide mineralogy is heterogenous, with a large pyrite population, and Fe:S ratios that can be attributed to greigite. Thus, although we cannot identify ferrimagnetic greigite clearly from GRM signals or from closed concentric FORC contours, we cannot exclude its presence in the sediments. All observations lead us to conclude that the ferrimagnetic phase in the OSR sediments includes vortex state to MD titanomagnetite and SP-SD biogenic magnetite. Both vortex state and SD particles can efficiently record the paleomagnetic field. Yet, they dissolve gradually with depth, with smaller magnetite particles dissolving first. The decline of concentration dependent magnetic parameters to about 50% of their maximum value over 6 m might result in a significant primary paleomagnetic signal loss, and perhaps even remagnetization.

Methanogenic sediments have a more complex correlation between diagenetic zones and magnetic data. In core PC3B, which best represents the methanogenic sediments, all concentration-dependent bulk magnetic parameters (IRM, ARM, χ, FORC ρ_max) drop sharply across the SMTZ, which corresponds to a sharp magnetite concentration decrease in the FC derivative, and a hysteresis parameter change. We observe three features below the SMTZ. First, sediment magnetic properties stabilize in the methanogenic zone, with much smaller magnetic variability. Second, biogenic magnetite that formed in the uppermost sediment column survives the dissolution front at the SMTZ, and a T_v signature due to magnetite remains throughout the methanogenic zone. Third, the ferrous iron concentration remains high in the methanogenic zone. These observations are discussed further below in Section 4.3.

The process of reductive dissolution of iron-bearing minerals by sulfate reduction is common in marine environments. Sulfate reduction can significantly affect sediment magnetic properties, causing a downward decrease in ARM, IRM, susceptibility, and SD-sensitive properties (Brachfeld et al., 2009; Chang et al., 2016b; Karlin, 1990a, 1990b; Karlin & Levi, 1983; Larrasoña et al., 2007; Liu et al., 2004; Qian et al., 2020; Reilly et al., 2020; Roberts et al., 2013; Roberts & Weaver, 2005; Rowan & Roberts, 2006; Rowan et al., 2009). The magnetization decrease is caused by reductive dissolution of ferrimagnetic magnetite and precipitation of the
paramagnetic iron sulfide pyrite. Magneto-geochemical studies of methanogenic sediments that
directly measured pore water methane and sulfate have reported similar results to ours. Regardless
of location, sedimentation rate, and specific local conditions, there is typically a magnetization
decrease, correlated with a magnetite decrease at the SMTZ as observed, for example, in the
Eastern Mediterranean (Amiel et al., 2020), Bay of Bengal (Badesab et al., 2020; Badesab et al.,
2023; Dewangan et al., 2013), Labrador Sea (Kawamura et al., 2012), Indian Ocean (März et al.,
2008), Weddell Sea (Reilly et al., 2020), and western Argentine Basin (Riedinger et al., 2005). In
many cases, the SMTZ can have a marked effect on paleomagnetic recording and can distort the
primary paleomagnetic signal and even cause remagnetization (Roberts & Weaver, 2005; Rowan
& Roberts, 2006; Rowan et al., 2009), depending on sedimentation rate and organic carbon
availability (Chang et al., 2016a). Our Eastern Mediterranean data suggest that when the SMTZ is
shallow and sedimentation rates are high, magnetic properties can stabilize and preserve a primary
magnetization.

**4.2. Comparing OSR and AOM effects on paleomagnetic recording**

In this study, we explore sulfate reduction effects, either via continuous OSR or AOM, on the
quality of sedimentary paleomagnetic recording, with emphasis on short-term secular variation
recorded by rapidly deposited marine sediments. We assess the degree of paleomagnetic
smoothing, potential lock-in depths, and inclination shallowing. Declination and inclination data
for all the cores are shown in Figure 9a-b. The cores were not oriented, so relative declination data
are corrected by subtracting the average declination. Also shown for comparison, are geomagnetic
data calculated from recent geomagnetic models: ARCHKALMG14 (Schanner et al., 2022),
pfm9k.2 (Nilsson et al., 2022), SHAWQ (Campuzano et al., 2019; Osete et al., 2020), and
SCHA.DIF.4k (Pavon-Carrasco et al., 2021) and archaeomagnetic data from archaeological burnt
structures in Israel and Cyprus (Shaar et al., 2018; Tema et al., 2021). All paleomagnetic directions
are allocated to the coordinates of Jerusalem (31.78°N,35.23°E). Comparison of sedimentary data
with models and archaeomagnetic data reveal significant discrepancies in both declination and
inclination. Declinations have the most pronounced difference with large amplitude changes that
cannot be associated with geomagnetic field behavior, for example, the younger part of cores
PC6B and T5B. Inclination data are more consistent with the models and archaeomagnetic data
than declination data. These results suggest that parts of the sediment rotated within the core tubes
before sampling. Thus, for further analysis, we mainly focus on inclination data.

To account for the unknown effects of inclination shallowing and magnetization lock-in depth, we
wrote an optimization algorithm to find the optimal shallowing coefficient ($f$) (King, 1955) and
the lock-in time, searching for values that yield a minimum root mean square of the difference
between sedimentary data, geomagnetic models, and archaeomagnetic data. The corrected
inclination time-series (after optimization) is shown in Figure 9c. Data for core T5B are not shown
because even after optimization, the data are much noisier than for the other cores. The optimal
lock-in time in all other cores is similar and is around 250 years. This time corresponds to depths
of 71 cm in cores PC3B and PC6B (methanogenic sediments) and to 131 cm in core HUG1B (OSR
sediments). The inclination shallowing coefficient ranges between 0.73 in core PC3B and 0.89 in
core PC6B. This indicates that inclination shallowing is non-negligible, which is consistent with
typical inclination shallowing values estimated in paleomagnetic studies (Kodama, 2012a).

Paleomagnetic data for the methanogenic sediments are more coherent than for the OSR
sediments, and are more consistent with geomagnetic models and archaeomagnetic data (Figure
9). Also, as noted in Section 3.7, the paleomagnetic stability of methanogenic sediments in AF demagnetization experiments is superior, with stable single-component magnetizations compared to OSR sediments. Considering the mineral magnetic data discussed above, we conclude that methanogenic sediments below a shallow SMTZ with rapid deposition may better record primary paleomagnetic directions than sediments with continuous OSR.

### 4.3. Magnetite and ferrous iron occurrences in the methanogenic zone

Comparison of low-temperature and FORC data from core PC3B (Figures 5h, 6h) indicate the occurrence of non-detrital SD magnetite deep in the methanogenic zone. The magnetite concentration is high at the top of the core, and increases in the meter above the SMTZ before decreasing sharply at the SMTZ. Below the SMTZ, magnetite remains detectable. The presence of nanometer-scale magnetite in the methanogenic zone is important because this fraction is expected to dissolve at the SMTZ. Moreover, the dissolved iron concentration is high below the SMTZ. Two scenarios could explain these observations. First, due to the high deposition rate, there was insufficient time for the magnetite that formed in the uppermost sediment, either as magnetosomes or via bacterial dissipatory iron reduction, to dissolve. The second explanation is that a new generation of magnetite is forming in the presence of methanogenic archaea (Shang et al., 2020). Authigenic magnetite precipitation in methanogenic sediments has been suggested in several studies (Amiel et al., 2020; Badesab et al., 2023; Beaver et al., 2021; Lin et al., 2021). Our results provide further support for this hypothesis. Yet, more work is needed to resolve the microbiological mechanism associated with this process.

### 4.4. Geomorphological implications for shelf development

Although our main focus is on the paleomagnetic properties of southeastern Mediterranean shelf sediments, radiocarbon analysis provides insights into mid-late Holocene temporal evolution of the shelf. All cores were collected from the horizontal shelf segment, where seismic reflectors dip negligibly, at 46-49 m and 67-81 m water depths for the northern and southern study area, respectively (Figure 1). The time span covered by the studied sediments is 7.5 - 1.5 ky BP, during which Mediterranean sea level rise decreased and stabilized at ~6 ky BP (Lambeck et al., 2014; Sivan et al., 2004; Sivan et al., 2001). Radiocarbon age models indicate a nearly constant sedimentation rate, and, thus, steady sediment accumulation related to shelf buildup. The sedimentary succession is truncated by an unconformity at depths < 50 cm, where the unconformity age increases northward. In the southernmost location (core PC6B), the sediment age at 50 cm depth is 1.6 ky and in core T5B (25 km northward), it is 3.2 ky. In the northern study area, near Haifa bay, the sediment age at 50 cm is 3.8 and 5.4 ky for cores PC3B and HUG1B, respectively. The absence of young sediments in the northern study area may be associated with the Carmel structure, which blocks sediment transport by shore-parallel currents. A similar unconformity was found in studies of Holocene shelf cores (see Figure 1b for core locations), but until this study it was not certain whether this is a characteristic feature of the shelf or a local phenomenon. Avnaim-Katav et al. (2019) dated core V4, which was collected from a 47 m water depth between the locations of cores T5B and PC6B, and reported an unconformity at a depth of ~25 cm with 2.4 ky sediment age. Bookman et al. (2021) studied a more sandy lithology at shallower water depths of 33-36 m and reported unconformities in cores V101 and V115 (Figure 1b). The unconformity seems to be a characteristic shelf feature that spans over at least 100 km from southern Israel to Haifa bay. Given that the sedimentation rate is steady below the
unconformity and that sea level changes since 6 ky BP have been minor, it is unlikely that a thick sediment column (6.5-9.5 m, based on the above-reported sedimentation rates) was deposited and then eroded in a single event. Instead, it possibly marks a time during which shelf build-up stabilized and stopped accumulating sediments, possibly after eroding previously deposited sediments or by multiple deposition-erosion cycles. This hypothesis requires non-synchronous shelf stabilization, where different parts stopped accumulating sediments at different times in the late Holocene, and that the northern shelf stabilized before the southern part. We note that deeper open continental slope deposits include late Holocene sediments (e.g. (Schilman et al., 2001), which were likely deposited on the shelf and then eroded within submarine canyons offshore of northern Israel (Moshe et al., 2024). Therefore, the sedimentation regime along different shelf segments is more complex and site-dependent and requires further study.

5. Conclusions

We compare paleomagnetic, mineral-magnetic, and pore water chemical properties of four ~6-m-long sediment cores from the Holocene Eastern Mediterranean continental shelf to study sulfate reduction effects on the quality and preservation of paleomagnetic recording. Sediments affected by continuous organoclastic sulfate reduction undergo a continuous magnetization decrease and coarsening of the dominant magnetic mineral. This magnetic property change results from dissolution of detrital titanomagnetite and fine-grained biogenic magnetite. Sediments affected by continuous OSR, thus, significantly smooth short-term geomagnetic secular variations. In contrast, sediments with intensive upward methane fluxes cause shallowing of the sulfate-methane transition zone and anaerobic oxidation of methane consumes most of the sulfate there leaving a narrow sulfidic zone. This probably leads to preservation of primary paleomagnetic signals in the methanogenic zone.

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Open Research

Paleomagnetic, rock-magnetic, and geochemical data are available in Zenodo (doi: 10.5281/zenodo.11221956)
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