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## RESEARCH ARTICLE

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### Key Points:

- The last magnetic reversal at Scotia Sea Site U1538 is offset downward by ~20 m compared to the more reliable Site U1537 record
- Ferrous iron enrichment below the sulfate reduction depth is observed at Site U1538
- Anomalous magnetic minerals and porewater differences reveal a geochemical setting conducive to chemical remanent magnetization acquisition

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## A Geochemical Mechanism for >10 m Apparent Downward Offsets of Magnetic Reversals Inferred From Comparison of Two Scotia Sea Drill Sites

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**Abstract** We document an apparent downward displacement of the Matuyama-Brunhes magnetic reversal by ~20 m at Scotia Sea International Ocean Discovery Program Site U1538 (Pirie Basin) by comparison with the well-defined paleomagnetic record at nearby Site U1537 (Dove Basin). Detailed stratigraphic correlation between the two sites is possible due to similar lithologic variations. However, the two sites have distinctly different porewater geochemistry. Notably, Site U1538 indicates a greater demand for electron acceptors to oxidize organic carbon and Fe<sup>2+</sup> enrichment below the depth of SO<sub>4</sub><sup>2-</sup> depletion. Magnetic parameters indicate enrichment of an authigenic magnetic mineral with strong remanence properties around the depth of SO<sub>4</sub><sup>2-</sup> depletion (~46 m at Site U1538) relative to magnetic parameters at correlative depths at Site U1537. Fe<sup>2+</sup> enrichment below the depth of SO<sub>4</sub><sup>2-</sup> depletion is not predicted based on the energetically favorable order of electron acceptors for microbial respiration but is documented here and in other depositional settings. This indicates Fe<sup>2+</sup> production exceeds the production of H<sub>2</sub>S by SO<sub>4</sub><sup>2-</sup> reduction, providing a geochemical environment that favors the production and preservation of ferrimagnetic remanence-bearing iron sulfides over paramagnetic pyrite and, thus, a mechanism for deep chemical remanent magnetization acquisition at depths of tens of meters. The influence of authigenic ferrimagnetic iron sulfides on paleomagnetic signals can be difficult to demonstrate with magnetic properties alone; therefore, this finding has implications for evaluating the fidelity of magnetostratigraphic records with complementary geochemical data. Such situations should be considered in other depositional environments with similar porewater Fe<sup>2+</sup> accumulation below the SO<sub>4</sub><sup>2-</sup> reduction depth.

**Plain Language Summary** Sediment on the seafloor is an archive of Earth history, including past climate variations, ice sheet dynamics, and geomagnetic field variations. The lattermost include a history of when the Earth's magnetic field flipped upside down in the past so that compass needles would have pointed to the South Pole instead of the North Pole. Scientists have a good understanding of when these flips happened and, once identified in sedimentary layers, the flips can be used to identify time horizons—which are useful for dating other events recorded by the sediment. In this study, we present two magnetic reconstructions from nearby locations that initially recorded the same geomagnetic signals. After deposition, one of the magnetic records changed as a result of chemical reactions that modified the magnetic minerals in the sediment, making it difficult to correlate to the geomagnetic time scale. We have a nearby record with minimal chemical modifications so we could identify the chemical reactions were likely responsible for the changes. This observation will provide additional insights into what signals to look for when studying similar complications from other locations in the world.

### 1. Introduction

Sedimentary magnetic mineral assemblages are a reflection of sediment provenance, sediment transport, and diagenetic alteration (Q. Liu et al., 2012). The latter can result in the dissolution of iron oxides like magnetite and/

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or growth of authigenic minerals including ferrimagnetic iron sulfides like greigite and hexagonal 3C pyrrhotite (Hornig, 2018; Karlin & Levi, 1983; Roberts, 2015). Numerous complex factors control the depths at which authigenic ferrimagnetic iron sulfides form (Roberts, 2015). The offset between the sediment-water interface and the depth of ferrimagnetic sulfide formation can make the measured paleomagnetic signal recorded by the chemical remanent magnetization (CRM) appear older than the stratigraphic horizon in which they are found. In some settings, relatively deep formation is indicated, which could complicate polarity interpretations (Jiang et al., 2001) and smooth paleomagnetic signals (Rowan et al., 2009), while in other settings, minimal offset is observed due to shallow greigite formation that would minimally impact or even improve the recording of paleomagnetic signals (Blanchet et al., 2009; Ebert et al., 2021; Reynolds et al., 1999). It is likely that several geochemical scenarios exist in which ferrimagnetic iron sulfides can form that could result in small, large, and/or multiple generations of offsets in the depth of the CRM relative to the primary depositional remanent magnetization (DRM) (Fu et al., 2008; Roberts & Weaver, 2005).

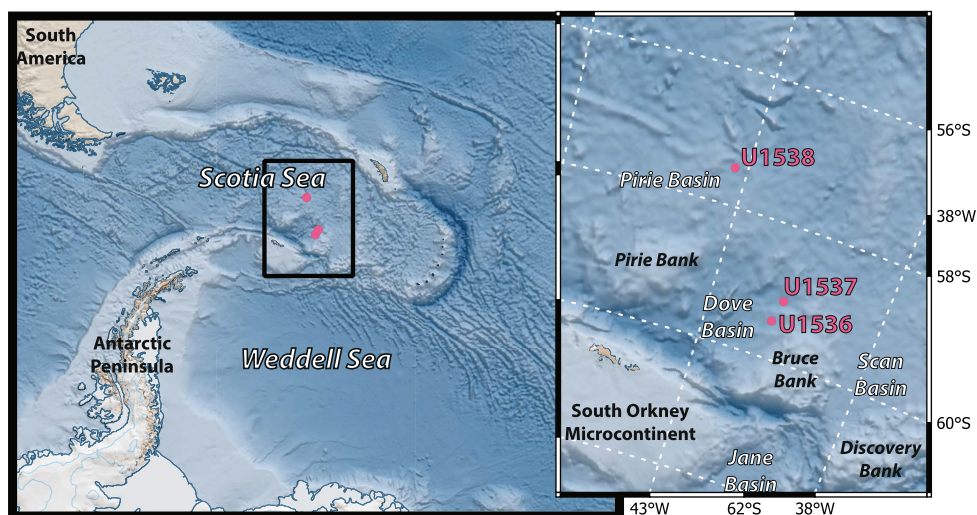
Magnetic mineral authigenesis is largely controlled by porewater geochemistry, particularly through the production of dissolved  $\text{Fe}^{2+}$  during  $\text{Fe}^{3+}$  reduction and the production of  $\text{H}_2\text{S}$  during  $\text{SO}_4^{2-}$  reduction (Amiel et al., 2020; Berner, 1984; Canfield & Berner, 1987; Karlin & Levi, 1983; Reilly et al., 2020). The order in which electron acceptors are used in microbial respiration is governed by their energetic favorability (Froelich et al., 1979), with  $\text{Fe}^{3+}$  being more energetically favorable than  $\text{SO}_4^{2-}$ . In traditional diagenetic models,  $\text{Fe}^{2+}$  accumulates in porewaters at the depth range of  $\text{Fe}^{3+}$  reduction and is consumed by upward  $\text{H}_2\text{S}$  diffusion from deeper  $\text{SO}_4^{2-}$  reduction to create iron sulfides like pyrite. However, in nature, there are mechanisms by which  $\text{Fe}^{3+}$  can also be used as an electron acceptor at greater depths, such as the proposed anaerobic oxidation of methane coupled with iron reduction (Beal et al., 2009; Chuang et al., 2021; Riedinger et al., 2014), in which  $\text{Fe}^{2+}$  can accumulate below the  $\text{SO}_4^{2-}$  reduction zone. These mechanism and others can result in a geochemical environment where  $\text{Fe}^{2+}$  accumulates more rapidly than it can be consumed by  $\text{H}_2\text{S}$ , creating conditions that favor precipitation and preservation of sulfide-limited iron sulfides, including the ferrimagnetic phases greigite and/or hexagonal 3C pyrrhotite, over pyrite (Blanchet et al., 2009; Hornig, 2018; Hornig & Roberts, 2018; Hunger & Benning, 2007; Kao et al., 2004; Reilly et al., 2020; Roberts et al., 2011; Rowan et al., 2009). Direct comparison of high-resolution porewater geochemistry and magnetic measurements has clearly demonstrated ferrimagnetic enrichment where  $\text{Fe}^{2+}$  concentrations are enhanced below the  $\text{SO}_4^{2-}$  reduction zone (Amiel et al., 2020; Reilly et al., 2020).

In 2019, International Ocean Discovery Program (IODP) Expedition 382, *Iceberg Alley and Subantarctic Ice and Ocean Dynamics*, drilled several sites in the Scotia Sea from deep-sea contourite deposits in the Dove and Pirie Basins (Figure 1; Pérez et al., 2021; Weber et al., 2021b). One of the exceptional aspects of these records is the tight relative stratigraphic control made possible between sites due to similar lithologic variability (Bailey et al., 2022; Reilly et al., 2021). In this framework, Dove Basin Sites U1536 (3,220 m) and U1537 (3,713 m) have reproducible, reliable magnetic polarity stratigraphy (Bailey et al., 2022; Reilly et al., 2021; Warnock et al., 2022; Weber et al., 2022); whereas, the initial interpretation of Pirie Basin Site U1538 (3,131 m) inclination data was more ambiguous and indicated apparent normal polarity in sediments that were likely deposited during the reverse Matuyama C1r.1r Chron (Figures 2 and 3; Weber et al., 2021d).

Pirie Basin Site U1538 and Dove Basin Site U1537 have contrasting porewater geochemistry (Weber et al., 2021c, 2021d), which provides a rare opportunity to compare sediment magnetic data from sites with similar lithologic variations but different diagenetic environments, and which are only ~350 km apart. It can be challenging to determine how diagenesis has modified a paleomagnetic signal at a single site using magnetic methods alone, as authigenic ferrimagnetic iron sulfides can have similar magnetic coercivities and properties to other magnetic minerals. Thus, unraveling the factors behind the complicated Site U1538 magnetic signals in the context of Site U1537 variations will offer insight into how the fidelity of magnetostratigraphic records can be evaluated in the context of porewater and sediment geochemistry.

### 1.1. Shipboard Observations and Motivation

Two stratigraphic lines of evidence conflict with the initial Site U1538 Matuyama-Brunhes boundary pick made during IODP Expedition 382 based on paleomagnetic data alone. First, the last occurrence (LO) of the radiolarian *Pterocanium charybdeum trilobum* (Haeckel, 1861) was unexpectedly identified in an apparent normal polarity zone, immediately above the stable reverse polarity horizon at Site U1538 used to initially define the end of the

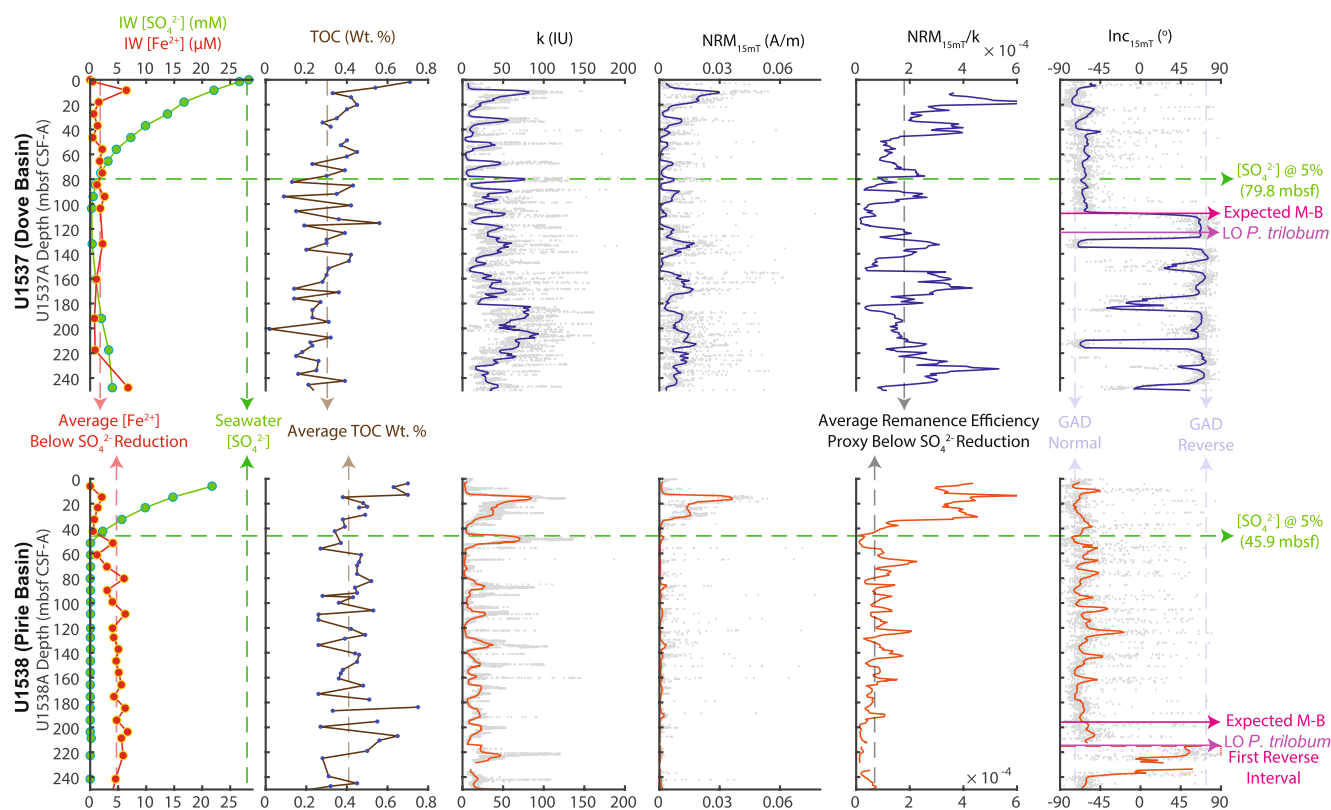


**Figure 1.** International Ocean Discovery Program drill sites from Dove and Pirie Basins in the Scotia Sea are studied here. Sites U1536 and U1537 (Dove Basin) and Site U1538 (Pirie Basin) sampled deep-sea contourite deposits, for which seismic context is documented by Pérez et al. (2021). Map generated using the Quantarctica QGIS package (Matsuoka et al., 2021) using the IBCSO bathymetry (Arndt et al., 2013).

C1r.1r Matuyama Chron (Figure 2; Weber et al., 2021d). The LO of *P. trilobum* in the Southern Ocean is long known to have occurred during the reverse polarity C1r.1r since the earliest magnetic stratigraphy studies (Hays & Opdyke, 1967; Opdyke et al., 1966), dated at approximately 860 ka (Gradstein et al., 2012). Second, leveraging the markedly similar sediment physical property pattern observed between Dove Basin Sites U1536 and U1537 and Pirie Basin Site U1538 (Figures 3 and 4), Bailey et al. (2022) established the correlation of Site U1538 to the Site U1537 depth scale using natural gamma radiation (NGR), which primarily tracks the abundance of terrigenous sediment derived  $K$ , and the  $b^*$  blue-yellow color parameter, which has been shown to correlate with biogenic silica concentrations in the Scotia Sea (Sprenk et al., 2013; Weber et al., 2022). This provides a clear stratigraphic correlation of Pleistocene glacial-interglacial lithologic variability between the two sites but suggests that the initial Matuyama-Brunhes boundary pick was apparently displaced  $\sim 16$ – $22$  m downward relative to its occurrence in marine isotope stage (MIS) 19 at Site U1537 (Figure 3). Based on the correlation to Site U1537, an extended zone of noisy but apparent normal polarity was present below the expected Matuyama-Brunhes transitional interval, with additional noisy data in the reverse polarity intervals bracketing the Jaramillo C1r.1n Subchron (Figure 3).

While these data indicate that the Site U1538 magnetostratigraphy is not reliable, the magnetic polarity stratigraphy of Site U1537 to which we compare is considered robust (Reilly et al., 2021). High-resolution comparisons of Site U1537 stratigraphy to ice core chronologies for the last 800 kyr place the last magnetic reversal in late MIS 19 (Weber et al., 2022), where the reversal is found in other locations when direct benthic  $\delta^{18}\text{O}$  comparisons are possible (Channell et al., 2010; Shackleton & Opdyke, 1973; Tauxe et al., 1996). Additionally, anomalous and reproducible directions that are interpreted as the Iceland Basin event occur at the transition from MIS 7 to MIS 6 at Site U1537, as recognized in both Northern and Southern Hemisphere archives (Figure 4; Channell, 2014; Channell et al., 2017).

Despite the similar lithostratigraphy, the two sites have several notable differences that provide an opportunity to study the factors that might contribute to the less reliable magnetostratigraphy at Site U1538. Accumulation rates are higher at Site U1538, which could be explained by several factors, such as differences in primary productivity and/or sediment focusing factors in these contourite deposits (e.g., Sprenk et al., 2013). Importantly for magnetic minerals, geochemical observations suggest a higher demand on electron acceptors by microbes for organic carbon oxidation at Site U1538 (Figure 2). This demand is manifested as a substantially shallower  $\text{SO}_4^{2-}$  depletion depth, with  $\text{SO}_4^{2-}$  concentrations falling below 5% of sea-level concentrations at around 46 m below sea floor (mbsf) at Site U1538 but not until around 80 mbsf at Site U1537. In the upper 250 mbsf, average total organic carbon (TOC) wt.% at Site U1538 is 0.4% versus 0.3% at Site U1537 (Figure 2). Elevated organic matter

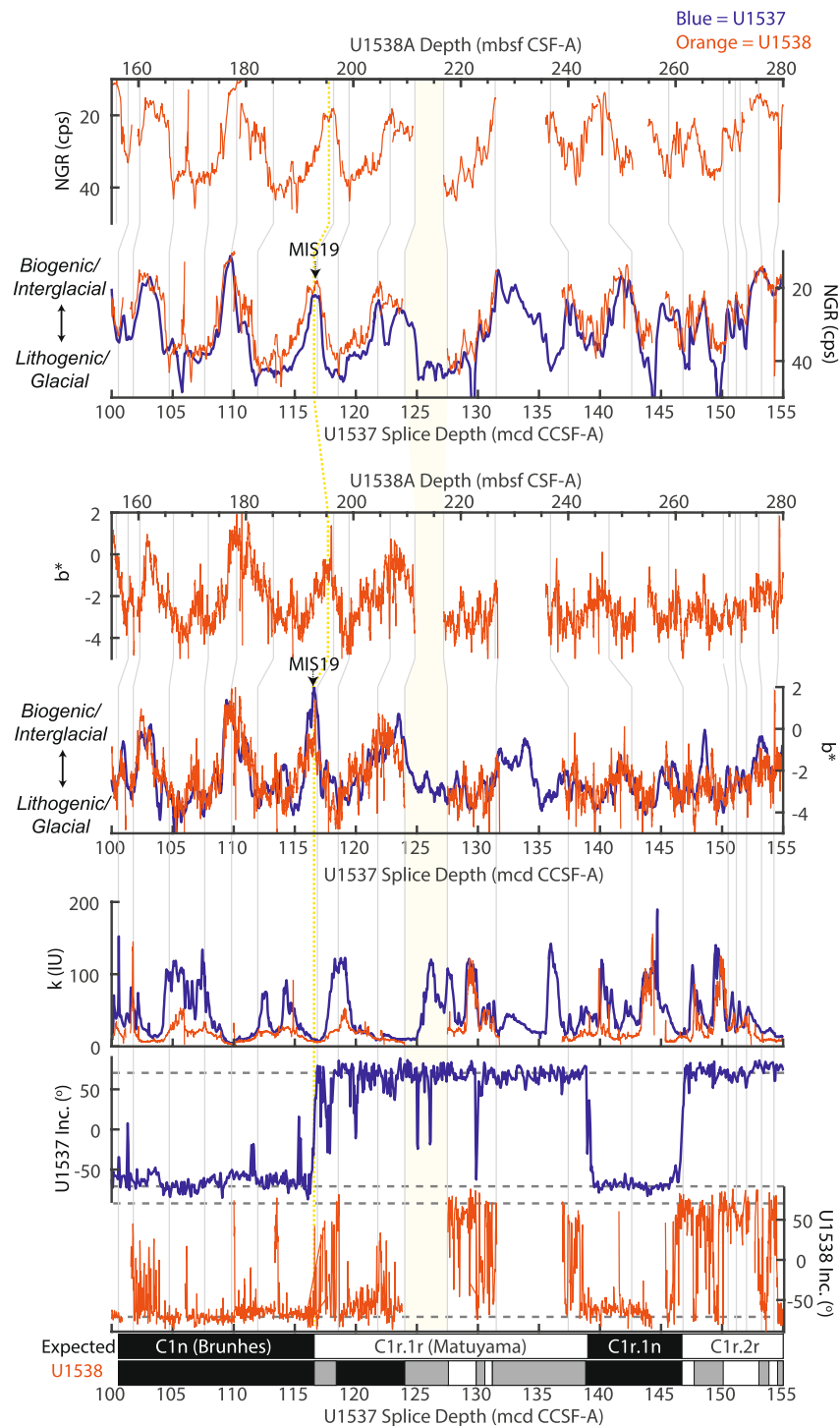


**Figure 2.** Summary of shipboard geochemical and magnetic data. Shipboard data for the upper 250 m at Holes U1537A (top row; Weber et al., 2021c) and U1538A (bottom row; Weber et al., 2021d). From left to right: interstitial water sulfate (green) and ferrous iron (red). The depth of sulfate reduction (horizontal green dashed line) is nominally calculated where sulfate concentrations are 5% of seawater concentrations (~80 m at U1537A and ~46 m at U1538A). Average ferrous iron concentrations below the sulfate reduction zone (vertical red dashed line) are higher in Hole U1538A than U1537A. Total organic carbon weight % (blue) is also on average higher in Hole U1538A, with variability between samples as a function of variable ooze and silty clay lithology. Magnetic susceptibility ( $k$ ) and the natural remanent magnetization after 15 mT alternating field (AF) demagnetization ( $NRM_{15mT}$ ) are plotted as individual measurements (gray dots) and as a 5-m-wide running median (black/red lines).  $NRM_{15mT}/k$  of the running median is plotted as a proxy for remanence efficiency, with U1537A having higher values on average below sulfate reduction depths. Inclination after 15 mT AF demagnetization ( $Inc_{15mT}$ ) with the expected values for a geocentric axial dipole are plotted. The expected Matuyama-Brunhes reversal location is indicated based on assignment of marine isotope stage 19 (Bailey et al., 2022; Weber et al., 2022). The last occurrence of the radiolarian, *P. trilobum*, is also indicated, which is expected to be found in C1r.1r at around 860 ka. Inclination data are all raw, unedited data collected in Hole A at each site, and include ice-rafted debris clasts and disturbed intervals.

degradation at Site U1538 compared to U1537 is also indicated by substantially higher dissolved phosphate and ammonium concentrations in sedimentary interstitial waters (Weber et al., 2021c, 2021d).

Interestingly, neither site has significant porewater dissolved  $CH_4$  concentration at any depth, and thus no clear sulfate-methane transition zone (SMTZ). Average  $CH_4$  concentrations at Sites U1537 and U1538 are 2.3 and 2.9 ppmv, respectively, and there is no concentration trend with respect to depth or  $SO_4^{2-}$  concentrations (Weber et al., 2021c, 2021d). For comparison, Site U1534 was studied using the same shipboard methods and drilled on the same expedition to the north at 604 m water depth on the continental slope ~660 km east of the Strait of Magellan. This site had a clearly defined SMTZ with  $CH_4$  concentrations exceeding 50,000 ppmv below the  $SO_4^{2-}$  reduction depth (Peck et al., 2021). The lack of dissolved  $CH_4$  at Sites U1537 and U1538 will be explored in future work using geochemical modeling, but may result from a combination of low methanogenesis rates and rapid  $CH_4$  oxidation after production.

$SO_4^{2-}$  reduction produces  $H_2S$ , which reacts with  $Fe^{2+}$  sourced first from highly reactive iron species and later from crystalline iron forms such as magnetite, which when dissolved combine to produce iron sulfide minerals (Canfield & Berner, 1987). Thus, the  $H_2S$  concentration that accumulates in porewaters is a balance between the  $SO_4^{2-}$  reduction rate and  $Fe^{2+}$  availability with which to react. The  $H_2S$  concentration is not measured routinely as part of IODP shipboard protocols, and such data are not available for Expedition 382 records. Higher  $SO_4^{2-}$  reduction rates at U1538 and inferred  $H_2S$  concentration indicate the potential, however, for greater detrital



**Figure 3.** Stratigraphic correlation between sites U1538 and U1537 around the Matuyama-Brunhes reversal. Stratigraphic correlation (gray tie lines) of Bailey et al. (2022) of Hole U1538A (orange) to the Site U1537 splice (blue) based on natural gamma radiation data and supported by  $b^*$  reflectance. The location of marine isotope stage 19 is indicated (Weber et al., 2022) along with the location of the Matuyama-Brunhes reversal at Site U1537 (yellow dashed line) and interval of no recovery at Site U1538 for which reverse polarity sediments are below and apparent normal polarity sediments are above (vertical yellow shading). The resulting alignment of down core continuous shipboard magnetic susceptibility ( $k$ ) and archive half inclination after 15 mT measurements (lower three panels) illustrate the differences between the two sites and ambiguity in interpreting the U1538 paleomagnetic data. The expected inclinations for normal and reverse polarity are indicated with horizontal dashed lines. At the bottom, the expected polarity pattern and an interpretation of the U1538 shipboard archive half polarity pattern are indicated (black = normal; white = reverse; gray = undetermined).

magnetic mineral dissolution and are likely responsible for the larger decrease in magnetic susceptibility ( $k$ ) and natural remanent magnetization (NRM) intensity at around the  $\text{SO}_4^{2-}$  reduction depth at Site U1538 relative to Site U1537 (Figure 2). This magnetic mineral diagenesis also has a clear imprint in shipboard data on the paleomagnetic recording potential of sites U1537 and U1538. The ratio of NRM intensity after 15 mT peak alternating field (AF) demagnetization to  $k$  ( $\text{NRM}_{15\text{mT}}/k$ ) is a proxy for remanence efficiency (or remanence preservation), and is significantly lower below  $\text{SO}_4^{2-}$  reduction depths at Site U1538 relative to Site U1537 (Figure 2).

Perhaps the most striking difference from a Fe cycling perspective in the porewater geochemistry of U1537 versus U1538 is that  $\text{Fe}^{2+}$  is present in concentrations well above the analytical detection limit of the shipboard inductively coupled plasma optical emission spectrometry (i.e.,  $>\sim 0.5 \mu\text{M Fe}$ ) below the  $\text{SO}_4^{2-}$  reduction horizon at Site U1538 (Figure 2). We note that sediment porewater sampling was not conducted under oxygen-free conditions as is usually required for dissolved  $\text{Fe}^{2+}$  assessment. As a result, in situ dissolved  $\text{Fe}^{2+}$  concentrations before porewater extraction may have even been higher than shown in Figure 2. While several mechanisms may be responsible for the  $\text{Fe}^{2+}$  profile shown in Figure 2, the presence of dissolved  $\text{Fe}^{2+}$  below  $\text{SO}_4^{2-}$  indicates that its production and/or diffusion rates are greater than its consumption rate by  $\text{H}_2\text{S}$ . This type of geochemical environment, where  $\text{H}_2\text{S}$  is limited with respect to  $\text{Fe}^{2+}$ , is favorable for authigenic ferrimagnetic iron sulfide formation (Amiel et al., 2020; Kao et al., 2004; Reilly et al., 2020), with the sulfide formation depth most likely at the interface between upward diffusing  $\text{Fe}^{2+}$  and downward diffusing  $\text{H}_2\text{S}$  near the base of  $\text{SO}_4^{2-}$  reduction. These conditions occur at approximately 46 mbsf at Site U1538 today, but this sulfide formation depth likely varied through time as environmental conditions changed. For example, as factors such as organic carbon supply, reactive iron supply and sedimentation rate varied, redox zones and key horizons like the  $\text{SO}_4^{2-}$  reduction depth would migrate vertically in response to increased or decreased microbial demand for electron acceptors.

Site U1538 offers an opportunity to test the potential for deep iron sulfide formation that could be responsible for the apparent downward displacement of magnetic reversals of 10s of meters by comparison of rock magnetic properties with U1537 using the detailed physical properties-based stratigraphic correlation of Bailey et al. (2022; Figures 3 and 4). We consider the Brunhes-Matuyama reversal position at Site U1537 to be the correct stratigraphic horizon and assume that the primary detrital magnetic mineral composition was initially similar at Sites U1537 and U1538. These assumptions are based on the observation that a wide array of shallow Scotia Sea piston cores typically have consistent magnetic variations (Diekmann et al., 2000; Pugh et al., 2009; Weber et al., 2012; Xiao et al., 2016) and that the positions of paleomagnetic reversals at Site U1537 relative to lithologic variations are well reproduced at the higher accumulation rate Dove Basin Site U1536 (Reilly et al., 2021) and are consistent with an independent timescale (Weber et al., 2022). Thus, magnetostratigraphic and mineralogical differences can be considered to be due to diagenetic anomalies at Site U1538.

## 2. Methods

Vertically oriented paleomagnetic cubes were taken at intervals of  $\sim 1$  per section ( $\sim 1.5$  m) in the first drilled hole at Sites U1537 and U1538. While at sea, these cubes were studied to understand the sediment NRM. Nearly all cubes were demagnetized and measured to 15 mT peak AF, while some were demagnetized to higher levels. Shipboard methods and results (along with all other data collected during the expedition) are discussed in the expedition proceedings (Weber et al., 2021a, 2021c, 2021d). Following the expedition, the cube specimens were further studied at the Scripps Institution of Oceanography Paleomagnetic Laboratory. Bulk  $k$  was measured on an AGICO KLY-4S Kappabridge and reported values are the mean of three measurements. All remanence measurements were made on a 2G Enterprises three axis superconducting rock magnetometer with direct current Superconducting Quantum Interference Devices. The NRMs were further demagnetized using a static ASC D-2000 AF demagnetizer to measure the remanence before and after demagnetization to peak AFs of 0, 10, 15, 20, 30, 40, 60, 80, and 100 mT (if not previously demagnetized to these levels). Next, anhysteretic remanent magnetizations (ARMs) were imparted using a 100 mT peak AF and 0.05 mT bias field and subsequently demagnetized at 20 and 40 mT peak AF. Finally, isothermal remanent magnetizations (IRMs) were imparted at 100, 300, and 1,000 mT, and then in a  $-300$  mT backfield using an ASC pulse field magnetizer. These data were used to construct a suite of secondary parameters and ratios such as the hard IRM ( $\text{HIRM} = (\text{IRM}_{1,000\text{mT}} + \text{IRM}_{300\text{mT}})/2$ ; Robinson, 1986),  $k_{\text{ARM}}/k$  (Banerjee et al., 1981; King et al., 1982), ARM AF coercivity ratios (e.g.,  $\text{ARM}_{40\text{mT}}/\text{ARM}$ ; Peters & Thompson, 1998), IRM ratios (e.g.,  $\text{IRM}_{100\text{mT}}/\text{IRM}_{300\text{mT}}$ ),  $\text{IRM}_{1,000\text{mT}}$  (SIRM) relative to  $k$  ( $\text{SIRM}/k$ ; Nowaczyk et al., 2013; Snowball & Thompson, 1990), and the S-ratio ( $\text{IRM}_{300\text{mT}}/\text{IRM}_{1,000\text{mT}}$ ; Stober & Thompson, 1979). The potential for gyroremanent magnetization (GRM;

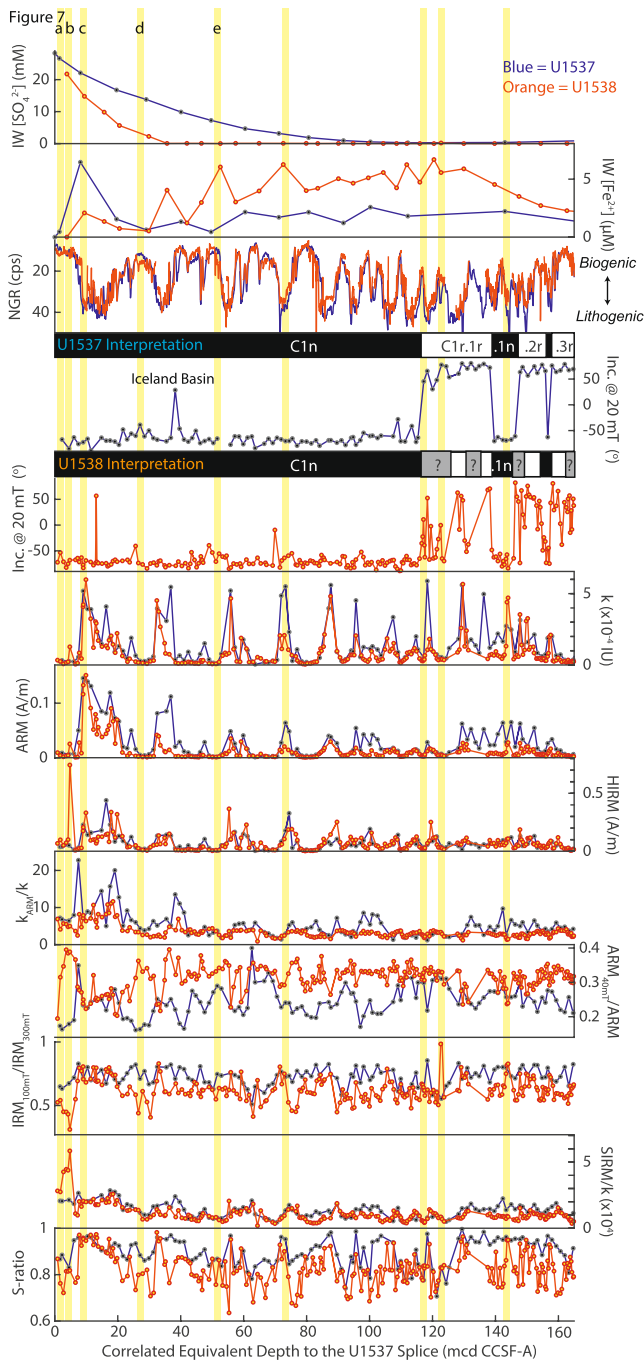


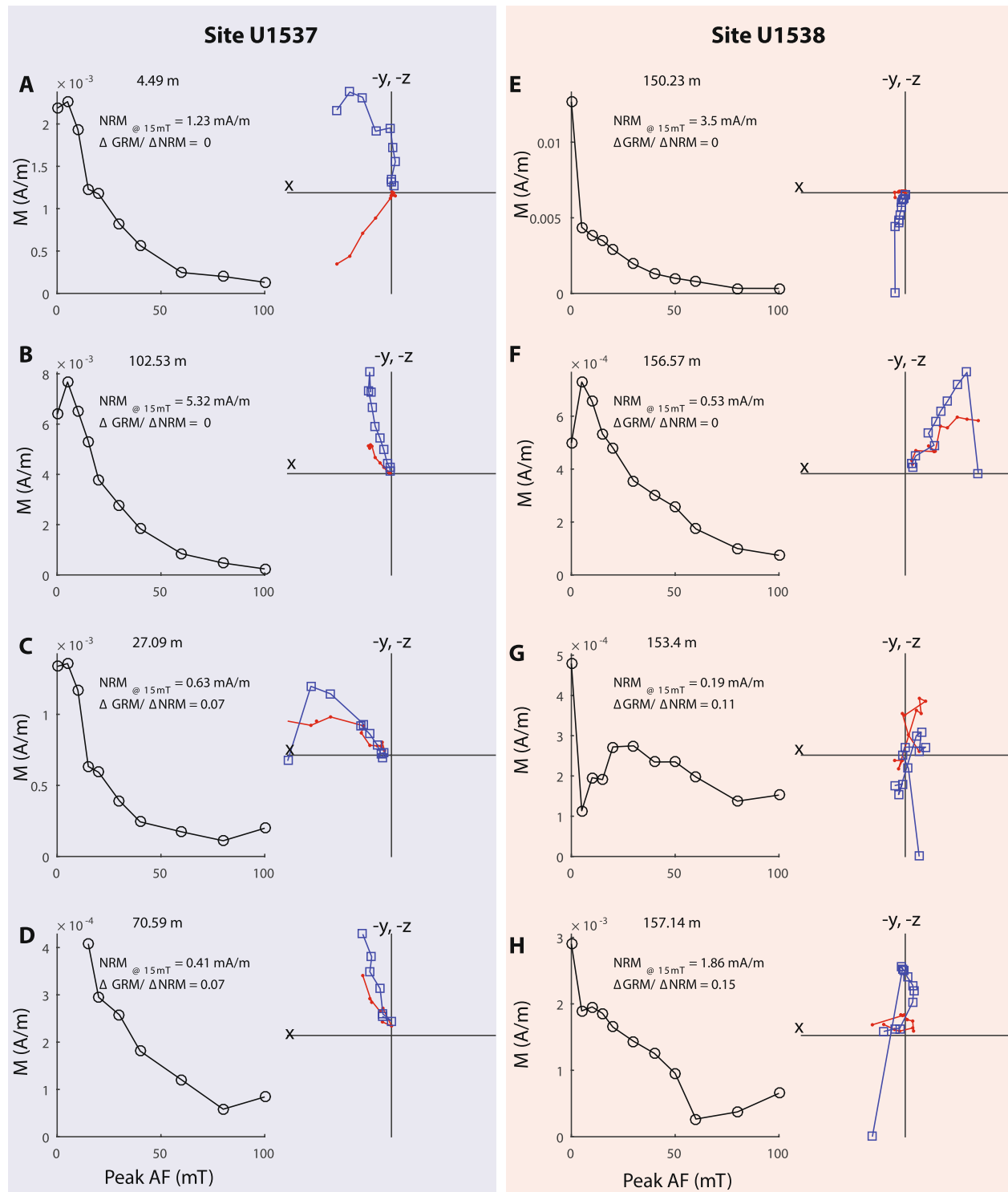
Figure 4.

Stephenson, 1993), the acquisition of magnetic remanence in the plane perpendicular to the last applied AF, is discussed using the  $\Delta\text{GRM}/\Delta\text{NRM}$  parameter (Fu et al., 2008). The parameter is slightly modified and calculated as  $(\text{NRM}_{@100\text{mT}} - \text{NRM}_{\text{Minimum}})/(\text{NRM}_{\text{Maximum}} - \text{NRM}_{\text{Minimum}})$ , as the initial magnetization for sediments with normal magnetization is reduced due to the presence of the nearly antiparallel drill string overprint (see Richter et al., 2007; Weber et al., 2021c, 2021d).

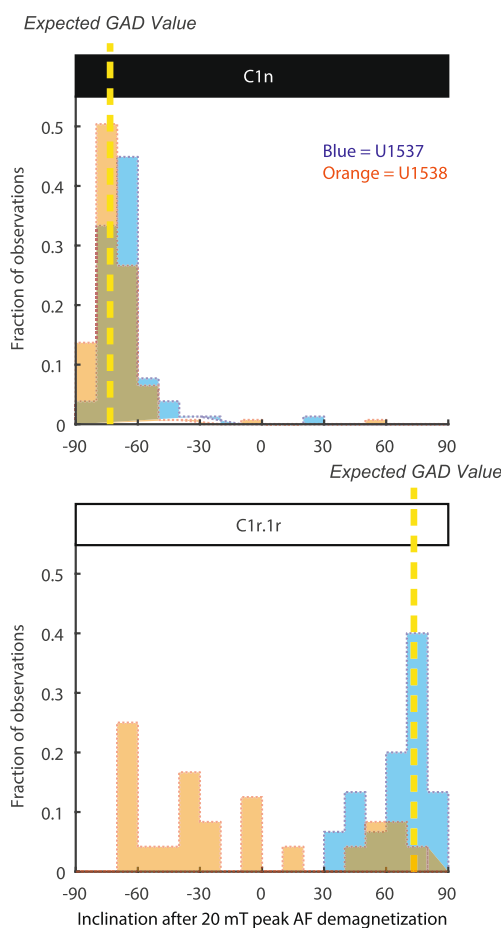
Next, cubes were subsampled and dried sediments were immobilized in an etched borosilicate glass vial with  $\text{K}_2\text{SiO}_3$ . To investigate the relationship between coercivity and unblocking/alteration temperatures, IRMs were imparted on three axes and were thermally demagnetized at sequentially higher temperatures (Lowrie, 1990). First, a 1,000 mT IRM was imparted along the Z axis. A 300 mT IRM was then imparted along the X axis, and finally a 100 mT IRM was imparted along the Y axis (IRM strengths were selected based on IRMs imparted for initial cube measurements). Specimens were heated in air for 30 min from 100 to 700 at 50°C intervals, cooled to room temperature in a zero field, and measured. For each axis, we calculated the magnetization fraction remaining from the initial magnetization on that axis at 450°C as a proxy for variability in unblocking/alteration temperatures.

Additional rock magnetic measurements were made on a subset of these cubes at the Institute for Rock Magnetism, University of Minnesota. Field cooled (FC), zero field cooled (ZFC), low temperature cycling of room temperature saturation IRM (LTC-SIRM), and alternating current (AC) susceptibility at 1, 10, and 100 Hz were measured on a Quantum Designs Magnetic Properties Measurement System using a 2.5 T field and minimum temperatures of 10 K (see Bilardello & Jackson, 2013). Hysteresis loops, DC demagnetization curves (DCDs), and first-order reversal curves (FORCs) were measured using a Lakeshore 8600 vibrating sample magnetometer. We calculate several parameters from these measurements to capture their variability, including  $\delta T_v$  for FC and ZFC curves  $(\text{LTSIRM}_{80\text{K}} - \text{LTSIRM}_{150\text{K}}/\text{LTSIRM}_{80\text{K}})$ , where LTSIRM is the FC or ZFC low temperature saturation IRM; Moskowitz et al., 1993),  $\delta\text{RTSIRM}$  (change in magnetization before and after LTC-RTSIRM, normalized by the initial RTSIRM), frequency dependent AC susceptibility  $(X_{\text{FD}} = (X_{1\text{Hz}} - X_{100\text{Hz}})/X_{1\text{Hz}})$ , coercivity of remanence ( $H_{\text{cr}}$ ), and hysteresis loop parameters (e.g.,  $M_r/M_s$ ; Day et al., 1977). FORC diagrams (Pike et al., 1999; Roberts et al., 2000) were generated using FORCinel v. 3.06 (Harrison & Feinberg, 2008; Harrison et al., 2018) and VARIFORC smoothing (Egli, 2013).

**Figure 4.** Summary of discrete cube measurements. Discrete cube measurements for Site U1537 (blue) and U1538 (orange) made after the expedition in the context of the interstitial water geochemistry and lithostratigraphy. U1538 data transferred to the U1537 splice depth scale following the correlation of Bailey et al. (2022). Data include: inclination after 20 mT alternating field (AF) demagnetization. Concentration dependent parameters: magnetic susceptibility ( $k$ ), anhysteretic remanent magnetization (ARM) and HIRM. Concentration independent ratios sensitive to magnetic domain state and mineralogy: anhysteretic susceptibility to  $k$  ( $k_{\text{ARM}}/k$ ), ARM after 40 mT AF demagnetization to the original ARM ( $\text{ARM}_{40\text{mT}}/\text{ARM}$ ), isothermal remanent magnetization (IRM) acquired at 100 mT to the IRM acquired at 300 mT ( $\text{IRM}_{100\text{mT}}/\text{IRM}_{300\text{mT}}$ ), saturation IRM acquired at 1,000 mT to  $k$  ( $\text{SIRM}/k$ ), and the IRM acquired in a 300 mT backfield to the SIRM ( $S$ -ratio). Yellow bars highlight correlative depth intervals investigated with more detailed rock magnetic measurements (Figures 7 and 8), with the letters indicating specimens with the most comprehensive analyses reported in Figure 7 and additional samples including  $H_{\text{cr}}$  in Figures 8a and 8b.



**Figure 5.** Example alternating field (AF) demagnetization and orthogonal projection plots for well-defined and poorly defined magnetization. Data from Site U1537 (a–d) and Site U1538 (e–h) with sample depth corresponding to the U1537 equivalent depth plotted in Figure 4. Data  $\leq 15$  mT peak AF were all collected onboard the JOIDES Resolution. Blue open squares represent data projected into the vertical plane, while red closed circles represent data projected in the horizontal plane.



**Figure 6.** Inclinations histograms. Distributions of inclinations at Site U1537 (blue) and U1538 (orange) during normal polarity Chron C1n and reverse polarity Chron C1r.1r. The expected values based on a geocentric axial dipole for each plot are indicated with a vertical dashed yellow line.

### 3. Results

#### 3.1. Magnetic Properties

Site U1538 NRM intensities are often weak, particularly below the  $\text{SO}_4^{2-}$  reduction zone, and are increasingly noisy at higher AF demagnetization steps. In Figure 4, we therefore plot the inclination measured after 20 mT peak AF demagnetization determined post-cruise. These data are largely consistent with the 15 mT peak AF demagnetization data generated shipboard, and are determined following sufficient demagnetization to remove the nearly vertical drill string overprint (Reilly et al., 2021; Weber et al., 2021c, 2021d).

These weak and noisy magnetization at higher AF steps limited our ability to quantify the influence of GRM, such as using the  $\Delta\text{GRM}/\Delta\text{NRM}$  parameter of Fu et al. (2008). About 2% of values calculated for Site U1537 in the upper 165 mcd have  $\Delta\text{GRM}/\Delta\text{NRM}$  values greater than 0.05 (maximum value = 0.11), while 13% of values calculated for Site U1538 exceed this threshold (maximum value 0.23). However, most of these  $>0.05$   $\Delta\text{GRM}/\Delta\text{NRM}$  values are found in samples from weakly magnetized biogenic lithofacies with NRM intensities  $<0.002$  A/m at Site U1537 and  $<0.004$  A/m at Site U1538. We use demagnetization and orthogonal projection plots (Zijderveld, 1967) in Figure 5 to illustrate examples of demagnetization behavior along with their  $\Delta\text{GRM}/\Delta\text{NRM}$  values. For Site U1537, slight intensity increases at high AF steps that lead to  $\Delta\text{GRM}/\Delta\text{NRM}$  values  $>0.5$  with no acquisition along the  $x$  or  $y$ -axis makes it difficult to know if they can be attributed to GRM or to noisy unstable magnetization (Figures 5c and 5d; cf. Figure 3 in Reilly et al., 2021). Some samples from Site U1538 with higher  $\Delta\text{GRM}/\Delta\text{NRM}$  values have systematic acquisition at high AF steps consistent with a GRM (Figure 5h), while others with similar  $\Delta\text{GRM}/\Delta\text{NRM}$  values have noisy demagnetization behavior, possibly with multiple components, that are challenging to interpret (Figure 5g). Thus, while Site U1538  $\Delta\text{GRM}/\Delta\text{NRM}$  values indicate the potential for greater GRM compared to Site U1537, the underlying explanation is likely a combined influence of GRM and weak unstable magnetization.

The Site U1538 directional data can be further evaluated by a more direct comparison to Site U1537 through the depth transformation of Bailey et al. (2022) to a Site U1537 correlated equivalent depth (ced) (Figures 2 and 3). This comparison shows a mixture of what could be considered normal, intermediate, and reverse polarity directions in C1r.1r. These directions are inconsistent with known stable polarity during C1r.1r and inconsistent with geocentric axial dipole predicted values (Figures 4 and 6).

Concentration dependent parameters measured on the cubes, such as  $k$  and ARM, are consistent with shipboard  $k$  measurements and indicate that there are often lower concentrations of ferrimagnetic minerals at Site U1538 with respect to Site U1537. In Scotia Sea sediments,  $k$  varies strongly on glacial-interglacial timescales, with peaks at Site U1537 during the last 800 kyr corresponding to glacial intervals (Weber et al., 2022). In contrast, HIRM values are fairly similar at the two sites, which suggests the presence of similar high coercivity mineral concentrations that saturate in fields greater than 300 mT. This may not be surprising if the concentrations reflect the degree of dissolution during reductive diagenesis, as it is often observed that hematite is more resistant to dissolution than magnetite (Dillon & Bleil, 2006; Garming et al., 2005; J. Liu et al., 2004; Poulton et al., 2004; Reilly et al., 2020; Yamazaki et al., 2003). However, we also note a few anomalously high HIRM values in the U1538 stratigraphy without corresponding increases in other concentration dependent parameters, which are reminiscent of horizons with increased authigenic iron sulfide preservation that saturate above 300 mT, such as 3C pyrrhotite (Reilly et al., 2020).

Concentration independent parameters also have differences between Sites U1537 and U1538. This is well captured in ratios that track variability within the range of ferrimagnetic coercivities, such as  $\text{ARM}_{40\text{mT}}/\text{ARM}$  and

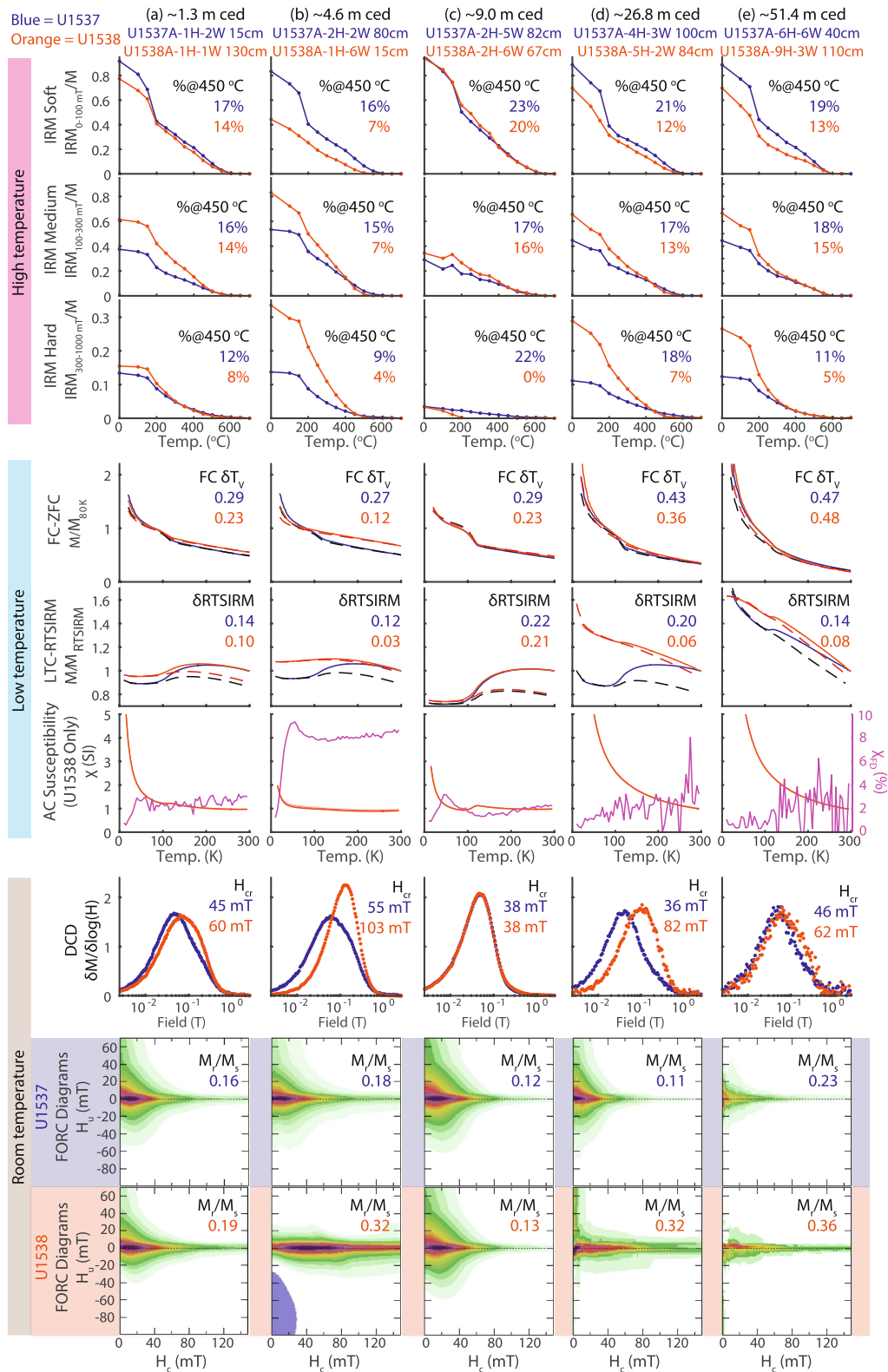


Figure 7.

$IRM_{100mT}/IRM_{300mT}$  (Figure 4). The values of both parameters diverge at the two sites in the upper part of the core in the Holocene interglacial interval (low  $k$ , low NGR; 0 to  $\sim 7$  m ced) and then return to similar values during the last glacial interval (high  $k$ , high NGR;  $\sim 7$ –19 m ced). Below the last glacial interval ( $> \sim 19$  m ced), the values diverge again, with  $ARM_{40mT}/ARM$  at Site U1538 remaining fairly constant and high in glacial and interglacial intervals alike (high and low NGR intervals), while U1537 values are generally lower and more variable. The anomalous rock magnetic properties of the Holocene sediments at Site U1538 are unique compared to those before the last glacial interval, with high  $SIRM/k$  values not observed elsewhere, which could be associated with a transient authigenic mineral horizon around the depth of iron reduction characterized by minerals that contribute to the HIRM. S-ratios likely in part reflect preferential magnetite dissolution relative to hematite, as observed in the concentration dependent data (i.e., HIRM is similar at the two sites, while ARM, IRM, and  $k$  are reduced at Site U1538).

### 3.2. Detailed Rock Magnetic Measurements

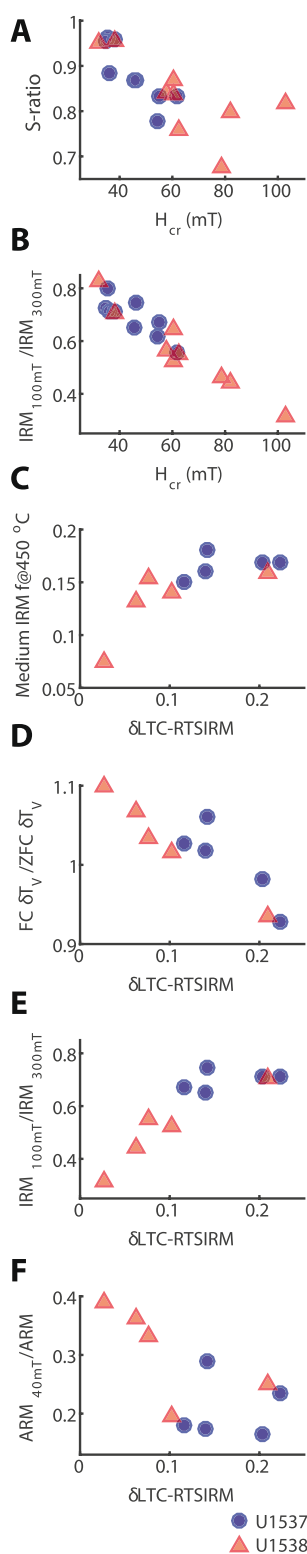
Detailed rock magnetic data (Figure 7) were collected for select intervals around the depths of modern sulfate reduction to understand magnetic mineralogy variations responsible for the patterns evident from higher resolution data in Figure 4 and to better understand the modern diagenetic environment. The relationship between the higher resolution data collected on the cubes and these additional parameters are summarized in Figure 8. Horizons were chosen to represent (a) the uppermost cube sample taken at each site  $\sim 1.3$  m ced; (b) the equivalent cube samples around the Holocene  $SIRM/k$  peak noted in Figure 4  $\sim 4.6$  m ced; (c) equivalent cube samples from the last glacial period  $\sim 9.0$  m ced; and (d–e) two equivalent intervals below the  $SO_4^{2-}$  reduction depths in U1538  $\sim 26.8$  and 51.4 m ced. In general, the uppermost sample from each site (Figure 7a) and in the last glacial maximum (Figure 7c) are similar and may be representative of the magnetic properties of the detrital assemblage during interglacial and glacial times, respectively.

Unblocking or alteration temperatures of a three-axis IRM are suppressed at Site U1538 relative to U1537, with less magnetization remaining in all samples and along in soft, medium and hard components by  $450^\circ\text{C}$ . The differences between the fraction remaining at  $450^\circ\text{C}$  between the two sites are greatest in the  $\sim 4.6$  m ced interval (Figure 7b) and  $\sim 26.8$  m ced interval (Figure 7d). These lower unblocking or alteration temperatures are also associated with suppressed Verwey transitions ( $T_v$  in FC and ZFC; and  $\delta LTC$ -RTSIRM), with a strong correlation for U1538 samples with  $\delta LTC$ -RTSIRM below  $\sim 0.1$  (Figure 8c). The lowest unblocking or alteration temperatures and most suppressed Verwey transitions are in the U1538  $\sim 4.6$  m ced sample, which are also characterized by anomalous magnetic properties including high  $SIRM/k$ , HIRM,  $X_{FD}$ , and  $H_{cr}$ , suggesting relatively high superparamagnetic and high coercivity mineral concentrations (Figures 4 and 7b). FORC diagrams for Site U1537 are consistent with typical observations of detrital magnetic mineral assemblages. Some of the Site U1538 assemblages are similar to their counterparts at Site U1537 (Figures 7a and 7c), while others include an additional component with higher coercivity along the  $H_c$  axis and skewed to more negative values along the  $H_u$  axis that is not recognized in their counterpart samples at Site U1537 (Figures 7b, 7d, and 7e). This signature is consistent with assemblages that include authigenic iron sulfide phases described elsewhere (Roberts et al., 2018). Overall, there appears to be a strong relationship between coercivity parameters and order-disorder transitions, with U1538 samples generally biased toward higher ferrimagnetic coercivities, more suppressed Verwey transitions, and lower unblocking/alteration temperatures (Figures 7 and 8).

## 4. Discussion

Despite having similar lithology and stratigraphy, Sites U1537 and U1538 have different magnetic properties. Given the close proximity and similarity of sediment transport pathways to Dove and Pirie Basins, it is unlikely that provenance can explain much of these differences. We argue that the differences are most likely the result of differences in the degree of magnetic mineral diagenesis—both in the dissolution of the primary detrital magnetic

**Figure 7.** Summary of detailed rock magnetic investigations. Specimens from U1537 (blue) and U1538 (orange) selected from correlative depth intervals were subject to thermal demagnetization of a three-axis 1,000, 300, and 100 mT isothermal remanent magnetization (Lowrie, 1990; normalized to total vector length before thermal demagnetization), FC-ZFC, LTC-RTSIRM, alternating current (AC) susceptibility and frequency dependent AC susceptibility ( $X$  and  $X_{FD}$ ; U1538 only), direct current demagnetization curves (plotted as the change in magnetization relative to the change in the logarithm of the applied field), and first-order reversal curve diagrams. Columns (a–e) correspond to samples highlighted in Figure 4. Parameters are defined in the methods section.



**Figure 8.** Comparison of detailed rock magnetic properties. Bi-plots of selected rock magnetic parameters to improve interpretation of discrete cube data presented in Figure 4 through comparison to and between the detailed rock magnetic analyses presented in Figure 7. Blue circles are U1537 and orange triangles are U1538.

assemblage and growth of authigenic remanence-bearing iron sulfide minerals. Differences in the growth and preservation of authigenic minerals at the two sites are the most probable explanation for why the U1537 polarity stratigraphy is reliable (Reilly et al., 2021), whereas the U1538 polarity stratigraphy is not. Rock magnetic anomalies at Site U1538 can be described as having (a) suppressed Verwey transitions, (b) lowered unblocking or alteration temperatures, (c) higher ferrimagnetic coercivities, (d) FORC diagrams with distributions skewed to more negative  $H_u$  values, and (e) greater superparamagnetic mineral content as indicated by  $X_{FD}$  (Figures 4, 7, and 8). These differences between the two sites are all consistent with greater dominance of magnetite (detrital) at Site U1537 and increased influence of remanence-bearing iron sulfides (authigenic) at Site U1538 (Hornig, 2018; Roberts et al., 2011, 2018).

Focusing on the upper ~50 m ced depths at both sites (<80 mbsf on the U1538 actual coring depth), we propose that at least two generations of these authigenic minerals exist. The first formed at shallower depths at Site U1538, above the zone of modern  $SO_4^{2-}$  reduction in the low- $k$  and low-NGR Holocene diatom ooze (Figure 4). This interval features some of the most anomalous rock-magnetic properties observed here, but the anomaly appears to be limited to the Holocene and is not found elsewhere in the stratigraphic record—glacial or interglacial (Figure 4). A few thinner horizons with anomalous HIRM and SIRM/ $k$  deeper down core at Site U1538 may exist, but they are rare and, if forming as discrete horizons, may not have been reliably captured in our magnetic data sets due to our ~1.5 m sampling resolution. These high coercivity layers could represent a transient authigenic mineral horizon that forms at a modern redox gradient and is not necessarily well preserved in the stratigraphy, such as well-documented Mn oxide layers (Froelich et al., 1979) or authigenic magnetic minerals (Reilly et al., 2020) that form at different redox horizons. These minerals seem to be limited to Holocene horizons. We do not see any sign of them in the more terrigenous silty clay of the last glacial interval or biogenic ooze of the last interglacial at ~25 m ced (Figures 4 and 7), which suggests either (a) that their formation, but not preservation, is related to a non-steady state diagenetic process that had a greater influence when the biogenic sediment supply was higher in interglacial times, or (b) that this diagenetic signal may be hidden in glacial silty-clay sediments at our study sites because terrigenous inputs are high enough during these times to dilute its influence on bulk magnetic properties.

We propose that a second generation of magnetic minerals forms at greater depths below the  $SO_4^{2-}$  reduction interval (>~46 mbsf), where  $Fe^{2+}$  is enriched in porewaters at Site U1538. Previous studies have demonstrated that this type of geochemical environment, although not predicted based on traditional early diagenetic models (e.g., Froelich et al., 1979), is associated with ferrimagnetic iron sulfide enrichment when found at shallower depths (Amiel et al., 2020; Reilly et al., 2020). Here, we find that below these depths, ferrimagnetic coercivity diverges between Sites U1537 and U1538, which persist in interglacial and glacial intervals alike (Figure 4). The higher coercivities at Site U1538 captured by  $ARM_{40mT}/ARM$  and  $IRM_{100mT}/IRM_{300mT}$  have a clear relationship with lower unblocking or alteration temperatures and suppressed Verwey transitions (Figure 8), consistent with these coercivity changes being driven by not just changes in magnetic domain state but also by magnetic mineralogy.

This modern diagenetic environment provides insight into diagenetic processes that likely occurred over the Pleistocene at Site U1538. Thus, in this

framework, ferrimagnetic iron sulfide formation below the base of the  $\text{SO}_4^{2-}$  reduction zone at around 46 mbsf ( $\sim 33$  m ced) at Site U1538 (Figure 2) would represent a horizon where a CRM is acquired in the modern geomagnetic field in sediments that contain an ancient DRM. The depth of this horizon and preservation of these ferrimagnetic iron sulfides likely varies through time as environmental and oceanographic conditions change, but its presence provides a plausible explanation for why the most recent magnetic reversal (the Matuyama-Brunhes) occurs where we expect it to be at Site U1537 (Reilly et al., 2021; Weber et al., 2022), while it is displaced lower by  $\sim 16$ – $22$  m at Site U1538 in sediments that have no apparent deformation or other complications (Weber et al., 2021d).

## 5. Conclusions

Scotia Sea IODP Sites U1537 and U1538 have similar lithostratigraphic but different rock magnetic properties and porewater geochemistry profiles. These observations offer new insights into why Site U1537 has a reliable magnetic polarity signal, but the Site U1538 magnetic polarity stratigraphy is complicated by a poorly defined signal and an apparent  $\sim 16$ – $22$  m apparent downward displacement of the most recent geomagnetic reversal (the Matuyama-Brunhes) relative to Site U1537. Rock magnetic property differences suggest at least two ferrimagnetic iron sulfide formation generations at Site U1538. The first generation formed at relatively shallow depths at Site U1538 and seems to be limited to Holocene biogenic diatom oozes. The magnetic signature of these minerals is not as apparent lower in the stratigraphy, which suggests that this generation may be transient in nature near a modern redox boundary and that it is not well preserved in the stratigraphy. The second generation traced by anomalous magnetic mineralogy at Site U1538 relative to Site U1537, formed deeper, at around the 46 m depth of  $\text{SO}_4^{2-}$  reduction at Site U1538 in the modern and is present below these depths in both diatom-rich interglacial and terrigenous silty-clay glacial sediments. The depth of this horizon is dictated by the porewater geochemistry and may migrate with time as organic carbon supply, sedimentation rate, or other environmental factors vary.

We propose that the presence of  $\text{Fe}^{2+}$  in porewaters below the  $\text{SO}_4^{2-}$  reduction zone at Site U1538, but not at Site U1537, creates a geochemical environment favorable for the formation and preservation of authigenic ferrimagnetic iron sulfides that can acquire a CRM at these depths. This geochemical setting can explain the  $>10$  m downward displacement of the Matuyama-Brunhes boundary at Site U1538, where the relative strength of the deep-acquired CRM is similar to or greater than the primary DRM. Where tight stratigraphic control is not available, assessment of porewater geochemistry at other sites globally can provide means to assess the potential of this deep CRM mechanism.

## Data Availability Statement

All shipboard generated data can be accessed through the IODP LIMS database (Weber et al., 2021b, 2021c, 2021d; <https://web.iodp.tamu.edu/LORE/>). Magnetic data are available through the MagIC database (Reilly et al., 2024a; Weber et al., 2019). Additional data and rock magnetic data files are available through the Zenodo database (Reilly et al., 2024b).

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