ABSTRACT

The spatial distribution, mineralogy, and origin of manganese enrichments surrounding a large gas hydrate and cold seep field (Mississippi Canyon 118, Gulf of Mexico) are investigated in this study, to better constrain their biogeochemical context in deep-sea sediments and to assess how gas hydrates may alter such records. Manganese depth profiles from 10 sediment cores, documented using centimetre-scale X-ray fluorescence core scanning, display highly-enriched 1 to 10 cm thick layers. These manganese-rich layers are more numerous, but of lower concentration, in close proximity to the field, and show no consistent relationship with sedimentology (clay vs. carbonate content) or the established chronostratigraphic framework at the site. X-ray diffraction and sequential dissolution procedures indicate that the manganese enrichments are authigenic carbonates, which formed along a palaeo redox boundary during periods of prolonged steady-state conditions. The hypothesis that spatial heterogeneity of this manganese record is linked to the nearby gas hydrate and cold seep field, by influencing redox conditions and/or sedimentation processes, is investigated here. Results are consistent with more frequent interruption of steady-state sedimentation in closer proximity to the salt-tectonic induced bathymetric mound, which contains the active cold seeps and gas hydrate deposits. Thus, spatial mapping of manganese enrichment horizons provides a tool to reconstruct sedimentation surrounding these volatile sea bed features, yielding a measure of past activity of gas hydrates and cold seeps.

INTRODUCTION

Marine gas hydrates have received much attention due in part to the vast amount of carbon contained within these deposits (Kvenvolden, 1988; Dickens, 2001; Milkov, 2004), and their potential linkages to slope destabilization and past climate events (Nisbet, 1990; Paull et al., 1996, 2003; Haq, 1998; Maslin et al., 1998, 2004; Mienert et al., 2005). These aspects have motivated detailed biogeochemical and geophysical investigations of modern gas hydrates (Sassen et al., 2004; Castellini et al., 2006; McGee, 2006; Brunner, 2007; Lapham et al., 2008, 2010; McGee et al., 2009; Macelloni et al., 2012, 2013; Simonetti et al., 2013; Feng et al., 2014; Martens et al., 2016), and the development of palaeoceanographic proxy approaches to assess the stability of hydrates in Earth’s past (Dickens et al., 1995; Dickens, 2003). Unique opportunities to understand marine gas hydrates are provided by integrated studies that seek to link modern and palaeo-perspectives, through the investigation of detailed stratigraphic, sedimentological and geochemical records surrounding present-day gas hydrates (Castellini et al., 2006; Brunner, 2007; Ingram et al., 2010, 2013).

Late Quaternary sedimentation and detailed geochemical records are considered in this study, through an analysis of deep-sea cores recovered from the first National Gas Hydrate Seafloor Observatory (McGee, 2006), located on the northern Gulf of Mexico slope within offshore Federal Lease Block Mississippi Canyon 118 (MC118). A special emphasis is placed on the genesis and interpretation of anomalous Mn enrichments (‘Mn-layers’) that occur at the MC118 site – documented for the first time
in this study. These Mn-rich layers are investigated for their potential to reconstruct sedimentation and biogeochemical changes at the site, including linkages to the gas hydrate field. The Mn enrichments are revealed in exceptional detail through high-resolution elemental analysis (centimetre-scale) using X-ray fluorescence (XRF) scanning techniques (Richter et al., 2006), applied to a network of 10 deep-sea sediment cores across the MC118 site. The Mn-layers are further characterized via chemical dissolution/extraction procedures and X-ray diffraction (XRD) analysis. This suite of analytical approaches allows a detailed assessment of the spatial distribution of the Mn-layers at the MC118 site, determination of their mineral composition, and evaluation of possible linkages to past redox cycling and/or sedimentation processes. Interpretation of the Mn record is aided by a well-established stratigraphic framework, which includes previous chronostratigraphic (Ingram et al., 2010) and sedimentological (Ingram et al., 2013) studies of the same suite of cores.

Based on the analyses outlined above it is postulated that the Mn-layers at MC118 record the duration of steady-state redox conditions, along a palaeo-redox boundary between oxic and post-oxic sediments, and that movement of this boundary is linked to the gas hydrate and cold seep field through its influence on sedimentation. As will be shown, the distribution and concentration of Mn within the discrete Mn-layers is consistent with more frequent interruption of steady-state conditions closer to the field. This observation reveals a potential new method to evaluate past redox/sedimentation conditions across a wide range of time scales, through detailed characterization of solid-phase Mn profiles, by employing XRF scanning to ‘map’ movement of past redox boundaries. In addition, results presented here indicate that the MC118 field has influenced sea floor morphology and sedimentation, but has not contributed to a catastrophic slope failure during the last 14 000 years, consistent with prior studies (Ingram et al., 2010).

The MC118 site

The offshore MC118 site includes a large sea floor mound with active cold seeps and gas hydrates (Fig. 1), and is the focus of ongoing geophysical and geochemical monitoring (McGee, 2006; Brunner, 2007; Lapham et al., 2008, 2010; McGee et al., 2009; Macelloni et al., 2012, 2013; Simonetti et al., 2013). The field itself is centred at

![Fig. 1. (A) Bathymetric map of the study area (Block MC118) with labelled contours (light blue) in metres water depth (base map courtesy of Ken Sleeper) with inset digital elevation and bathymetry map (top left; NOAA geophysical data centre image) of the Gulf of Mexico Region. Bathymetry provided by the Gulf of Mexico Hydrate Research Consortium (modified after Sleeper et al., 2006). The location of the MC118 offshore federal lease block is indicated by the red box in the inset map. The extent of the studied gas hydrate-cold seep field is outlined by the dashed line and is characterized by an area with gas vents, sea floor pockmark features, petroleum seepage, shallow faults, carbonate hardgrounds and gas hydrate deposits. (B) Bathymetric map of the study site with the location of cores collected during cruises on the R/V Hatteras and R/V Pelican; base map image is courtesy of the Gulf of Mexico Hydrate Research Consortium. Cores are indicated as vertical magenta lines, with core identification (above) and water depth (in metres) below the core symbol. The edge of the gas hydrate-cold seep field is outlined by a thin dashed white line, black lines connecting cores indicate transects taken by the R/V Hatteras (‘Hatteras Transect’) and R/V Pelican (‘Pelican Transect’). The colour bar on the far right indicates water depth (metres below sea level).](image-url)
28.8523°N and 88.4920°W and lies at approximately 890 m water depth completely within the offshore federal lease block (Fig. 1). Regionally, the northern Gulf of Mexico slope, including this study site, is influenced by salt diapirism beneath the sea floor (Diegel et al., 1990; Jackson, 1995; Galloway et al., 2000). The field is underlain by a salt diapir 200 to 300 m below the sea floor (mbsf), which contributes to the formation of the sea floor mound itself (Sassen et al., 2006; Sleeper et al., 2006). Moreover, the cold-seep mound is the epicentre for the migration and release of hydrocarbons from the sea floor. This supply of hydrocarbons (natural gas and petroleum) supports active biological seep communities (Sassen et al., 2006) and microbial chemolithotrophy in the vicinity of the active seep. The upward migrating hydrocarbons are rapidly cycled and oxidized in shallow sediments, also documented at similar sites in the Gulf of Mexico (Castellini et al., 2006). While intense redox cycling occurs immediately over the MC118 mound, it decreases markedly in sediments outside the field (Lapham et al., 2008). This is important, as the cores used in the present study are positioned mostly outside the area with active seeps, with the exception of Core PEL-15 (Fig. 1). Visible outcroppings of gas hydrates, faulted carbonate ‘hardgrounds’, authigenic carbonates and pockmark features are present in places across ca 1 km² of the sea floor in the vicinity of the mound (Sassen et al., 2006; Sleeper et al., 2006; Feng et al., 2014).

Marine gas hydrates are a major feature at this research site, and worldwide they represent a massive reservoir of light hydrocarbons (Milkov, 2004). The vast majority of this carbon occurs in shallow deep-sea sediments along continental slopes (Ginsburg, 1988), such as at MC118. In the Gulf of Mexico, gas hydrates often form alongside cold seeps and supply hydrocarbons to the sea floor, driving substantial changes in both pore-water and sediment chemistry through various redox processes (Sassen et al., 2004, 2006; Paull et al., 2005; Castellini et al., 2006). The present work documents authigenic Mn in deep-sea sediments complicated by nearby gas hydrates and cold seeps, and the cores investigated in this study reflect ambient sea floor conditions as well as those influenced by the mound (Fig. 1).

**MATERIAL AND METHODS**

**Core collection and processing**

A total of 10 gravity cores were collected from surface ships, five on board the R/V *Hatteras* in August, 2007 and five by the R/V *Pelican* in April, 2008 (Sleeper & Lutken, 2008; Ingram et al., 2010; Fig. 1). Cores were transported to and processed at a shore-based laboratory at the University of North Carolina, Chapel Hill, where they were prepared for geochemical analyses (see Ingram et al., 2010, for detailed description of coring and processing methods).

**X-ray fluorescence (XRF) core scanning**

Cores were analysed using an Avaatech-XRF scanner (2nd generation) with a rhodium target X-ray source, and a Canberra X-PIPS detector. Continuous down-core XRF scanning was conducted at a resolution of 1 cm along the archive-half split core surface (Richter et al., 2006; Ingram et al., 2010). Manganese was scanned using a 10 kV acceleration voltage, 1000 mA, with a cellulose filter, and 90 sec measurement time, with duplicate scans every 10 cm, which yielded highly reproducible results (Table 1). The XRF scanning ‘count’ data are calibrated (least-squares linear fits; Table 1) to Mn concentration data for selected cores (HAT-03, PEL-04, PEL-07; 54 samples), using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES; SGS Laboratory method ICP-AES 40B, see Table 1 for error analysis).

**Reductive and acidification dissolutions**

Five Mn-rich layers were sampled from Core PEL-07 to operationally determine the mineral phases associated with the Mn enrichment. Sediment from each depth interval (Mn-layer) was first pulverized into 100-mesh powder. The procedure from Chun et al. (2010) was then followed with detailed description of coring and processing methods.

| Cores | XRF CV | ICP-ES CV | Core | XRF CV |
|-------|--------|-----------|------|--------|
| HAT-01 | 0.098  | NA        | PEL-02 | 0.116 |
| HAT-02 | 0.137  | NA        | PEL-15 | 0.129 |
| HAT-03 | 0.035  | 0.008     | PEL-04 | 0.066 |
| HAT-04 | 0.12   | NA        | PEL-08 | 0.106 |

**Table 1. XRF-ICP Mn Calibration Data: Calibration equations (least-squares linear fits) relating concentration from ICP-AES method to counts from X-ray fluorescence method, Pearson correlation coefficients (r² value) and number of samples used for calibration. Average coefficient of variation (CV) ratios for Mn XRF counts (XRF CV) are based on duplicate scans analysed every ca 10 cm, and select duplicates from ICP-ES sent to SGS Labs (SGS Laboratory method ICP-AES 40B). Average errors (CV) for XRF counts of Mn are slightly higher than other elements previously measured (Ingram et al., 2010), likely a result of lower concentration of Mn in these marine sediments.**
used to remove oxides and oxyhydroxides by reductive dissolution, followed by an acid dissolution step (sodium acetate, pH = 3.96) to remove carbonates, with the remaining residue comprising ‘insoluble’ clays and/or fine-grained silicates. Manganese and Ti concentrations were measured after each step, using ICP-AES (SGS Laboratory method ICP-AES 40B) on the same split sample from each fraction of the procedure, allowing estimation of: (1) untreated (total Mn), (2) Mn oxide, (3) Mn carbonate, and (4) insoluble residue, which represents the unreactive aluminosilicates (clay content) and/or silicates (Schenau et al., 2002; Chun et al., 2010).

Manganese enrichment factors (EF), EF = (metal/Ti)\text{sample}/(metal/Ti)\text{crust} were calculated to normalize Mn to Ti, a conservative detrital input. ‘Excess’ Mn (authigenic) was calculated using the following equation \[\text{Mn excess} = \text{Mn}_{\text{total}} - (\text{Ti})_{\text{sample}} \times (\text{Mn/Ti})_{\text{crust}}\] from Chun et al. (2010), and the bulk crustal Mn/Ti ratio (mol/mol) of 0.156 from Rudnick & Gao (2003). Enrichment factors and excess Mn calculations are a means to correct for inadvertent loss of mass during the sequential extraction procedures. These values are used to better constrain the fraction of Mn contained in carbonates versus oxides (Table 2).

**Table 2.** Mn concentrations from ICP-AES determined for sediment samples from authigenic Mn-layers within Core PEL-07. Sediment samples were selected from 5 depths, and subjected to a two-step chemical dissolution to first remove oxides/oxyhydroxides, and then carbonates (see Material and Methods). Mn enrichment factor (Mn-EF) and ‘excess’ Mn (E. Mn) is also determined for each layer (see Methods; Chun et al., 2010), and is not applicable (NA) for insoluble clay, as ‘excess’ Mn is defined as the amount which exceeds the siliciclastic fraction, predominantly clay here. The insoluble (clay) fraction is the remaining material after dissolutions and is fine-grained, consisting of clay with minor silts possible.

| Core  | Depth | Dissolution | Mn (p.p.m.) | Ti (p.p.m.) | Mn EF | E. Mn (p.p.m.) | Composition | Mn (p.p.m.) | % Total (from p.p.m.) |
|-------|-------|-------------|-------------|-------------|-------|----------------|-------------|-------------|---------------------|
| PEL-07 | 130   | Untreated   | 2800        | 2900        | 5.393 | 2347           | Oxyhydroxides | 160         | 5.71                |
| PEL-07 | 130   | Step 1      | 2640        | 3100        | 4.756 | 2156           | Carbonates   | 2373        | 84.75               |
| PEL-07 | 130   | Step 2      | 267         | 3600        | 0.414 | NA             | Insoluble (Clay) | 267       | 9.54                |
| PEL-07 | 189   | Untreated   | 1990        | 2800        | 3.969 | 1553           | Oxyhydroxides | 60          | 3.02                |
| PEL-07 | 189   | Step 1      | 1930        | 3100        | 3.477 | 1446           | Carbonates   | 1674        | 84.12               |
| PEL-07 | 189   | Step 2      | 256         | 3300        | 0.433 | NA             | Insoluble (Clay) | 256       | 12.86               |
| PEL-07 | 212   | Untreated   | 1670        | 2800        | 3.331 | 1233           | Oxyhydroxides | 90          | 5.39                |
| PEL-07 | 212   | Step 1      | 1580        | 2900        | 3.043 | 1128           | Carbonates   | 1331        | 79.7                |
| PEL-07 | 212   | Step 2      | 249         | 2900        | 0.48  | NA             | Insoluble (Clay) | 249       | 14.91               |
| PEL-07 | 577   | Untreated   | 1610        | 2700        | 3.33  | 1189           | Oxyhydroxides | 0           | 0                   |
| PEL-07 | 577   | Step 1      | 1610        | 2800        | 3.212 | 1173           | Carbonates   | 1239        | 76.96               |
| PEL-07 | 577   | Step 2      | 371         | 3200        | 0.648 | NA             | Insoluble (Clay) | 371       | 23.04               |
| PEL-07 | 599   | Untreated   | 2350        | 2700        | 4.861 | 1929           | Oxyhydroxides | 180         | 7.66                |
| PEL-07 | 599   | Step 1      | 2170        | 2700        | 4.489 | 1749           | Carbonates   | 1753        | 74.6                |
| PEL-07 | 599   | Step 2      | 417         | 2700        | 0.863 | NA             | Insoluble (Clay) | 417       | 17.74               |
| PEL-07 | Avg.  | Untreated   | 2084        | 2800        | 4.187 | 1647           | Oxyhydroxides | 98          | 4.36                |
| PEL-07 | Avg.  | Step 1      | 1986        | 2900        | 3.799 | 1534           | Carbonates   | 1674        | 80.02               |
| PEL-07 | Avg.  | Step 2      | 312         | 3100        | 0.555 | NA             | Insoluble (Clay) | 312       | 15.62               |

**RESULTS**

**Stratigraphy and XRF scanning results**

Ten shallow gravity cores collected around the MC118 field comprise 38.6 m of total recovered sediment (Fig. 2), and reveal a detailed Mn record documented by centimetre-scale XRF core scans. The occurrence of Mn-layers is described in the context of the previously established chronostratigraphy at the site. Detailed sedimentological, stratigraphic and chronostratigraphic information can be found in Ingram et al. (2010, 2013) (For the chronostratigraphic framework, see figs 3–6 in Ingram...
et al., 2010). Additionally, the previously established stratigraphy is also provided here for visual context of the sedimentological units (Fig. 2).

Shallow sediments of Unit I are informally broken into Units IA and IB to better describe the occurrence of Mn-layers within the larger stratigraphic Unit I (Fig. 2). Sediments of Unit IA are late Holocene in age (ca 2300 calendar years BP to present) calcareous nannofossil silty clays, and are laterally discontinuous across the study area. Sediments of underlying Unit IB are also calcareous nannofossil silty clays, but are more nannofossil-rich than the overlying Unit IA. Across all studied cores, the more calcareous Unit IB is generally thicker than Unit IA (Fig. 2), and accumulated over a longer time period (ca 2300 to 9500 calendar years BP). Sediments of Unit IB are also lighter in colour and exhibit fewer sedimentary structures (Ingram et al., 2010).

With these sedimentological units defined, the occurrence of Mn-layers is presented in stratigraphic context (Figs 2 and 3). The shallowest Unit IA exhibits very few Mn-layers, with some exceptions. Core HAT-04 displays a shallow Mn-layer completely within Unit IA, and to a lesser extent PEL-04 shows an increased Mn concentration at the top of the core (Fig. 3). With the exception of core HAT-04, all other recovered cores lack discernable Mn-layers within this shallowest stratigraphic interval. Unit IB below also contains few authigenic Mn-layers, with one notable exception, Core HAT-03, which displays two nearly synchronous layers at the base of the unit with Mn content well above ‘background’ levels (Fig. 3).

Unit II beneath the shallower carbonate-rich interval (Fig. 2) is a mottled, hemipelagic nannofossil silty clay (Ingram et al., 2010). Sediments here are markedly more clay rich with substantially lower carbonate content. This unit appears visually darker with sedimentary structures that are disturbed by burrows in places. Sediments are early Holocene to late Pleistocene in age ranging from 9500 to 14 000 calendar years from the top to the base of the unit (Fig. 2). This interval contains more Mn-layers than any other unit (at least 15 identified layers) with highly pronounced layers in Cores HAT-01, -05 and PEL-02 (Fig. 3). XRF scans of these same three cores also display less numerous Mn-layers, and in places exhibit only one or two, while cores that contain many layers generally yield lower concentrations for the individual layers. Calibration of XRF data indicates these ‘more numerous’ layers are ca 1000 p.p.m. Mn less concentrated than the single or double highly discrete layers (Fig. 3).

A continuation of clay-rich sediments comprises Unit III, a well-laminated hemipelagic nannofossil silty clay, which is differentiated from overlying sediments by numerous red-brown layers (Fig. 2). Sediments of this lowermost unit are chemically and lithologically similar to the unit above, yet with slightly higher lithogenic inputs (Ingram et al., 2013). The top of this unit is marked by a prominent red-brown band (‘red band’),

**Fig. 2.** Stratigraphic correlation of marine sediments over the MC118 site. Cores are arranged by increasing distance (left to right) away from the field. Dates obtained via AMS radiocarbon analysis of planktonic foraminifera (red, Ka) and foraminiferal biostratigraphic boundaries (dark blue, Y/Z ca 10 Ka and Y1/Y2 ca 15 Ka) are shown alongside their stratigraphic position; all reported ages are in calibrated calendar years BP. Three stratigraphic units are identified as follows: Unit I (light blue) = massive nannofossil calcareous silty clay; Unit II (light green) = mottled nannofossil clay; Unit III (grey) = laminated nannofossil clay containing reddish-brown nannofossil clay layers (red lines); for detailed stratigraphic description see Ingram et al. (2010). The distinct ca 5-cm thick reddish clay layer (‘red band’) contains highly ‘reworked’ (pre-Quaternary) nannofossils and defines the top of Unit III.
Manganese enrichments

also observed by previous investigators (Lutken et al., 2006; Brunner, 2007; Sleeper & Lutken, 2008; Ingram et al., 2010). This marker bed is coincident with reworked pre-Quaternary nannofossils deposited during Melt Water Pulse 1A (MWP-1A; Marchitto & Wei, 1995), and is dated between 14 000 and 15 000 calendar years BP (Ingram et al., 2010). The unit lacks a defined base, and thus extends to the greatest depth recovered. Based on accumulation rates and radiocarbon dating (Ingram et al., 2010), sediments are latest Pleistocene in age and certainly older than the MWP-1A reworked nannofossil horizon, which defines the top of the unit (Fig. 2).

Manganese profiles spanning units II and III may appear correlative, such as in Cores PEL-04, -08 and -07, yet upon close examination, Mn layers are not chronostratigraphically equivalent (PEL-04, PEL-07 and -08; Fig. 3). It is also apparent that Unit III mostly lacks the highly concentrated Mn-layers, with one exception in Core PEL-08 (near the top of the unit; Fig. 3), yet recovery of this unit was incomplete using shallow gravity coring. The Pelican transect recovered more of Unit III than the previous cruise and yields several metres of late Pleistocene-aged sediments in some cores. While this unit lacks the discrete highly concentrated Mn-layers, it does display many ‘minor’ layers (Fig. 3).

Mn-layer mineralogy

A multi-step reductive dissolution and acid digestion procedure was used to operationally determine probable mineral phases associated with the authigenic Mn (Fig. 4; Table 2). From five sediment samples taken within the Mn-layers, just over 80 percentage of the total Mn content is comprised of Mn-rich calcite (Ca-Mn(CO₃)₂) and/or rhodochrosite (MnCO₃) (Table 2). Manganese oxides account for slightly less than 10 percent, and the ‘insoluble’ clay fraction accounts for ca 10% (Table 2). Thus,
Mn within the concentrated layers is predominantly associated with carbonates, followed by aluminosilicates and minor amounts of oxides. Some change in concentration may be an artefact of the total change in sample mass associated with dissolution of carbonates. This is a concern for sediments with very high carbonate content, however, the samples investigated here (selected for sequential dissolution in PEL-07) are from clay-rich Units II and III with less than 13 wt.% CaCO₃ on average. To more rigorously address this issue, Mn enrichment factors and ‘excess’ Mn are also calculated (Table 2). Manganese enrichment and ‘excess’ Mn (defined as the non-clay fraction) are largely associated with carbonates and not oxides (Table 2). This is shown by determining the percentage of ‘excess’ Mn in each respective fraction (oxide versus carbonate) where the clay fraction has already been removed (via calculation of ‘excess’ Mn). The following expression:

\[
\left(\frac{\text{untreated excess} - \text{carbonate excess}}{\text{untreated excess}}\right) \times 100
\]

yields only 6.8% of Mn as potentially associated with oxides or oxyhydroxides, based on the average of all five layers (Table 2). Hence, ‘excess’ Mn from within the Mn-layers is dominantly associated with carbonates (over 90% on average).

Six untreated samples were also analysed using XRD (PEL-07-layer1, PEL-07-layer2, PEL-07-layer3, PEL-07-layer4, PEL-07-layer5 and PEL-04 at 5 cm depth; Fig. 5). All six XRD diffraction results show the existence of the following phases but in different proportions: quartz, calcite, feldspar, dolomite, rhodochrosite and clay minerals. Manganese is present as carbonate or Mn-Fe carbonate, which may form a complete solid solution (Fig. 5). Manganese carbonate in most samples has a \(d_{104}\) peak at \(2.82\) Å, except sample PEL-07-layer 4 that has a value of \(2.87\) Å. The \(d_{104}\) peak for the pure Mn end member (rhodochrosite) is 2.84 Å, and that for the pure Fe end member (siderite) is 2.79 Å. The \(d_{104}\) of the samples indicates a Mn-rich (>50% Mn) carbonate. One acid treated sample taken from PEL-07 (Mn-layer3; Fig. 5B) yielded no carbonates in the diffraction pattern; this result indicates that the dissolution procedure used here and by Chun et al. (2010) effectively removes Mn-carbonate minerals.

To summarize, the X-Ray diffraction and reductive dissolution/acidification results reveal that Mn within the
Mn-layers is largely contained in the carbonate phase. Given sample heterogeneity, preferred orientation and different proportions of mineral phases, intensities of the rhodochrosite d_{104} peak is not expected to exactly correlate with the XRF/ICP-AES derived Mn concentration – for example, Mn-layer3 is not the most concentrated based on the XRF profile (Figs 4 and 5). However, Mn-layers 1, 2 and 3 exhibit larger rhodochrosite peaks than Mn-layers 4 and 5 (Fig. 5), which is generally consistent with Mn concentrations from XRF and ICP-AES (Fig. 4; Table 2).

INTERPRETATION AND DISCUSSION

Manganese carbonate layers at MC118

A detailed deep-sea sedimentary record is documented at MC118 in an effort to better understand accumulation of highly enriched Mn-layers and possible mechanisms for their formation. Foremost, it is clear that Mn-layers occur in sediments of different age and generally do not follow lithostratigraphic or chronostratigraphic trends. Hence, their characterization as authigenic deposits, which formed in situ through redox processes (Figs 2 and 3), representing diageneric palaeo-redox horizons. Multi-step chemical dissolution procedures combined with XRD analyses confirms that the Mn-layers are primarily carbonates.

The documentation of such a highly detailed spatio-temporal record of recurring authigenic Mn carbonate layers as observed at MC118 is somewhat unique considering water depth and proximity to the seabed with nearby cold seeps (Canfield et al., 1993; Chun et al., 2010). However, Mn enrichments are often observed in ancient marine sediments or mudstones, along with other elements associated with authigenic deposits, and have been linked to changes in past climate or oceanographic conditions (Dickens & Owen, 1994; Schenau et al., 2002; Tribovillard et al., 2006). The MC118 results indicate that substantial variability in Mn enrichment is present in Recent (Late Pleistocene-Holocene) deep-sea sediments over a relatively small area of the sea floor (ca 2 km^2; Fig. 1). This has important implications for interpreting chemostratigraphic records from similar deep-sea depositional environments, as it implies that modern and ancient sedimentary Mn records may reflect localized conditions from depositional heterogeneity, rather than more widespread regional or ‘global’ events. Thus, subtle variation in depositional or redox environments in deep-marine continental slope sediments may drive noticeable differences in the accumulation of authigenic minerals. The MC118 record shows that authigenic Mn can vary considerably within continental slope sediments over a small area of the sea floor, and suggest linkages to the local gas-hydrate and cold-seep field. This includes sea
Biogeochemistry of the Mn-carbonate layers

Nearly all of the Mn-layers occur at depths well below expected oxygenated pore waters for this depositional setting, consistent with a Mn-carbonate phase preserved in post-oxic sediments. Previous studies have demonstrated that oxygen depletion occurs within 5 cm of the sea floor for similar settings such as the western Gulf of Mexico Shelf (Hu et al., 2011) and the Mississippi Canyon region (Diaz & Trefry, 2006). More recent studies have reported Mn-enrichments (oxides) within 10 cm of the sea floor at similar water depths and close to the MC118 site (Brooks et al., 2015; Hastings et al., 2016). In contrast, most Mn layers at MC118 are found more than a metre below the sea floor, thus they are considered much too deep for active formation of Mn-oxides, which develop near the oxygen depletion depth (Burdige & Gieskes, 1983; Kalthorn & Emerson, 1984; Heggie et al., 1986; Aller, 1990, 1994; Shaw et al., 1990; Reimers et al., 1992). However, it should also be noted that Mn carbonates can develop a protective crust around oxides formed earlier, thereby diminishing their dissolution within post-oxic pore waters (Burdige, 1993). This protective crust may account for the small fraction (under 10%) of Mn-oxide observed in some layers (Table 2).

Repeated Mn cycling (the ‘Mn pump’; Sageman & Lyons, 2003) can concentrate dissolved Mn within alkaline pore waters to form Mn-rich carbonates. Thus, Mn enrichment may form along palaeo-redox boundaries, related to the carbonate-Mn pump, where dissolved Mn concentrated in pore waters leads to precipitation of Mn-carbonate minerals under sufficiently alkaline conditions. Mn-oxide dissolution may occur contemporaneously with formation of Mn-carbonates just beneath an active redox front, followed by subsequent burial and preservation of the palaeo-redox boundary (Pedersen & Price, 1982; Burdige, 2006). The rapid burial of highly concentrated Mn-oxides into deeper dysoxic/anoxic and alkaline pore waters, due to a (pulsed) increase in sedimentation rate, would also promote the preservation of Mn-carbonate layers. More generally, sedimentation can influence redox processes through erosion and/or deposition.

Other factors that drive the movement of the Mn-redox boundary include, but are not limited to, (1) changes in organic carbon delivery and reactivity, (2) bottom water oxygen content, or (3) intensity of bioturbation/bioirrigation. All of the above factors influence preservation of ‘relict’ Mn-peaks (Burdige, 2006). Most of these factors are not explicitly constrained in this study, although previous efforts quantify sedimentation rates, and organic matter accumulation/composition (Ingram et al., 2013). There is a shift towards more reactive organic matter (Type II) within the shallow Holocene sediments, which is expected to drive the redox boundary upwards, yet this is also balanced by slower sedimentation rates (Ingram et al., 2010). Regardless, there are too many discrete Mn-layers to explain with one stepwise change in sedimentation. Furthermore, while organic matter accumulation is variable with time (Ingram et al., 2013), it should be more uniform spatially in a deep-sea setting – unless it is also influenced by the presence of the seeps. Thus, dynamic sedimentation associated with the mound is hypothesized as a more viable driver to explain spatio-temporal trends of the Mn-peaks across the network of MC118 cores, which suggest the field’s influence.

Mapping Mn-carbonate layers: a tool to delineate palaeo-redox conditions

The analysis presented here suggests that the high-resolution Mn record at MC118 primarily reflects the duration of steady-state conditions and the frequency with which they are interrupted, through changes in sedimentation that are driven by local effects from the presence of the elevated bathymetric mound. Relatively more stable sedimentation is expected for core sites farther away from the area of active cold seepage and gas hydrate formation (centred over the bathymetric mound). Such distal sites should be characterized by prolonged periods of steady-state conditions, and hence a more stable palaeo-redox boundary along which more concentrated Mn-layers can form. Conversely, frequent interruption of steady-state conditions is expected in closer proximity to or downslope from the field yielding less-concentrated and more-numerous Mn-layers (Fig. 2). The distribution of Mn-layers at the site is consistent with this hypothesis, as only one or two very-concentrated authigenic Mn-layers (Cores HAT-01, HAT-05 and PEL-02) are observed at locations distal from the field, while a greater abundance of less-concentrated layers are observed closer to the field (Core HAT-03 and HAT-04, Fig. 3).

Authigenic Mn enrichments are well-documented in marine sediments (Burdige, 1993, 2006), however, it is the remarkable detail of the MC118 record in both time and space that makes this study unique, and reveals past movement of the palaeo-redox boundary at various core sites. This record is made possible through the application of high-resolution XRF scanning techniques. The integration of such spatio-temporal data with quantitative biogeochemical models for Mn-cycling should provide a powerful new tool for evaluating redox cycling and/or sedimentation events over a wide range of time scales, for example, quantification of the duration of steady state
Conclusions

The results presented here demonstrate that multiple discrete Mn-layers observed at MC118 are authigenic deposits, preserved as carbonates and formed within shallow sediments along a transient palaeo-redox boundary. The Mn-layers occur independently from established lithostratigraphic and chronostratigraphic horizons at the site, and results from sequential extraction procedures, along with XRD analysis, reveal that layers are mostly rhodochrosite (MnCO₃). It is not known if the Mn-layers formed initially in shallow sediments as oxides/oxyhydroxides or as carbonates, however, they are presently carbonate minerals preserved within post-oxic conditions. The spatio-temporal heterogeneity of this Mn record is linked to the MC118 gas-hydrate and cold-seep field, including the related salt diapirism beneath the mound. This sea floor feature and associated release of hydrocarbons in turn influenced palaeo-redox cycling and/or sedimentation processes that impacted the duration of steady-state conditions in the past. Thus, the concentrations and frequency of Mn-layers across the site is a fingerprint of the palaeo-redox boundary and its spatial expression with time. While numerous factors drive changes in redox conditions, it is suggested that variability in sedimentation rate, caused by the presence of the sea floor mound, is a viable mechanism to explain the complexity of the Mn record.

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References

Aller, R.C. (1990) Bioturbation and manganese cycling at the sediment-water interface. Philos. Trans. R. Soc. London, 331, 51–68.

Aller, R.C. (1994) The sedimentary cycle in Long Island Sound: its role as intermediate oxidant and the influence of bioturbation, O₂, and Corg flux on diagenetic reaction balances. J. Mar. Resour., 52, 259–295.

Brooks, G.R., Larson, R.A., Schwing, P.T., Romero, I., Moore, C., Reichart, G.-J., Jilbert, T., Chanton, J.P., Hastings, D.W., Overholt, W.A., Marks, K.P., Kostka, J.E., Holmes, C.W. and Hollander, D. (2015) Sedimentation pulse in the NE Gulf of Mexico following the 2010 DWH blowout. PLoS ONE, 10, 1–24, e0132341.

Brunner, C.A. (2007) Stratigraphy and Palaeoenvironment of Shallow Sediments from MC118. Proceedings of the Annual Meeting of the Gulf of Mexico Hydrate Research Consortium, October 10–11, 2007, Oxford, Mississippi.

Burdige, D.J. (1993) The biogeochemistry of manganese and iron reduction in marine sediments. Earth Sci. Rev., 35, 249–284.

Burdige, D.J. (2006) Geochemistry of Marine Sediments. Princeton University Press, Princeton, NJ, 609 pp.

Burdige, D.J. and Gieskes, J.M. (1983) A pore water/solid phase diagenetic model for manganese in marine sediment. Am. J. Sci., 283, 29–47.

Canfield, D.E., Thamdrup, B. and Hansen, J.W. (1993) The anaerobic degradation of organic matter in Danish coastal sediments: Fe reduction, Mn reduction, and sulfate reduction. Geochim. Cosmochim. Acta, 57, 3867–3883.

Castellini, D.G., Dickens, G.D., Snyder, G.T. and Ruppel, C.D. (2006) Barium cycling in shallow sediments above active mud volcanoes in the Gulf of Mexico. Chem. Geol., 226, 1–30.

Chun, C.O.J., Delaney, M.L. and Zachos, J.C. (2010) Palaeoredox changes across the Palaeocene-Eocene thermal maximum, Walvis Ridge (ODP Sites 1262, 1263, and 1266): evidence from Mn and U enrichment factors. Paleoceanography, 25, 1–13.

Diaz, R.J. and Trefry, J.H. (2006) Comparison of sediment profile image data with profiles of oxygen and Eh from sediment cores. J. Mar. Syst., 62, 164–172.

Dickens, G.R. (2001) The potential volume of oceanic methane hydrates with variable external conditions. Org. Geochem., 32, 1179–1193.

Dickens, G.R. (2003) Rethinking the global carbon cycle with a large dynamic and microbially mediated gas hydrate capacitor. Earth Planet. Sci. Lett., 213, 169–183.

Dickens, G.R. and Owen, R.M. (1994) Late Miocene-Early Pliocene manganese redirection in the central Indian Ocean.
expansion of the intermediate water oxygen minimum zone. *Paleoceanography*, 9, 169–181. doi:10.1029/93PA02699.

Dickens, G.R., O’Neil, J.R., Rea, D.K. and Owen, R.M. (1995) Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Palaeocene. *Paleoceanography*, 10, 965–971.

Diegel, F.A., Karlo, J.F., Schuster, D.C., Shoup, R.C. and Tauvers, R.C. (1995) Cenozoic structural evolution and tectono-stratigraphic framework of the northern Gulf Coast continental margin. In: *Salt Tectonics: A Global Perspective* (Eds M.P.A. Jackson, D.G. Roberts and S. Snelson), *Am. Assoc. Petrol. Geol. Mem.*., 65, 109–151.

Feng, D., Birgel, D., Peckmann, J., Roberts, H.H., Joyce, S.B., Sassen, R., Liu, X.-L., Hinricks, K.-U. and Chen, D. (2014) Time integrated variation of sources of fluids and seepage dynamics archived in authigenic carbonates from Gulf of Mexico Gas Hydrate Seafloor Observatory. *Chem. Geol.*, 385, 129–139.

Finney, B.P., Lyle, M.W. and Heath, G.R. (1988) Sedimentation at MANOP site H (eastern Equatorial Pacific) over the past 400,000 years: climatically induced redox variations and their effects on transient metal cycling. *Paleoceanography*, 3, 169–189.

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hrtman, B. and Maynard, V. (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta*, 43, 1075–1090.

Galloway, W.E., Ganey-Curry, P.E., Li, X. and Buffler, R.T. (2000) Cenozoic depositional history of the Gulf of Mexico basin. *Am. Assoc. Petrol. Geol. Bull.*, 84, 1743–1774.

Ginsburg, G.D. (1998) Gas hydrate accumulation in deep-water marine sediments. In: *Gas Hydrates: Relevance to World Margin Stability and Climate Change* (Eds J.P. Henriet and J. Mienert), *Geol. Soc. London. Spec. Publ.*, 137, 51–62.

Haq, B.U. (1998) Natural gas hydrates: searching for the long-term climatic and slope-stability records. In: *Gas Hydrates: Relevance to World Margin Stability and Climate Change* (Eds J.P. Henriet and J. Mienert), *Geol. Soc. London. Spec. Publ.*, 137, 303–318.

Hastings, D.W., Schwing, P.T., Brooks, G.R., Larson, R.A., Morford, J.L., Roeder, T., Quinn, K.A., Bartlett, T., Romero, I.C. and Hollander, D.J. (2016) Changes in sediment redox conditions following the BP DWH blowout event. *Deep-Sea Res. II*, 129, 167–178.

Heggie, D.T., Kahn, D. and Fischer, K. (1986) Trace metals in metalliferous sediments, MANOP site M: interfacial pore water profiles. *Earth Planet. Sci. Lett.*, 80, 106–116.

Hu, X., Cai, W.J., Wang, Y., Guo, X. and Lou, S. (2011) Geochemical environments of continental shelf-upper slope sediments in the northern Gulf of Mexico. *Palaeogeoogr. Palaeoclimatol. Palaeoecol.*, 312, 265–277.

Ingram, W.C., Meyers, S.R., Brunner, C.B. and Martens, C.S. (2010) Late Pleistocene-Holocene sedimentation surrounding an active seafloor gas-hydrate and cold-seep field on the Northern Gulf of Mexico Slope. *Mar. Geol.*, 278, 43–53.

Ingram, W.C., Meyers, S.R. and Martens, C.S. (2013) Controls on sedimentary Geochemistry and organic carbon burial at a large gas-hydrate and cold-seep field on the northern Gulf of Mexico Slope. *Mar. Pet. Geol.*, 46, 190–200.

Jackson, M.P.A. (1995) Retrospective Salt Tectonics. In: *Salt Tectonics: A Global Perspective* (Eds M.P.A. Jackson, D.G. Roberts and S. Snelson), *Am. Assoc. Petrol. Geol. Mem.*, 65, 1–28.

Kalhorn, S. and Emerson, S. (1984) The oxidation state of manganese in surface sediments of the deep sea. *Geochim. Cosmochim. Acta*, 48, 897–902.

Kvenvolden, K.A. (1988) Methane Hydrate – a major reservoir of carbon in the shallow geosphere? *Chem. Geol.*, 71, 41–51.

Lapham, L.L., Chanton, J.P., Martens, C.S., Sleeper, K. and Woolsey, J.R. (2008) Microbial activity in surficial sediments overlying acoustic wipeout zones at a Gulf of Mexico cold seep. *Geochim. Geophys. Geosyst.*, 9, 1–17.

Lapham, L.L., Chanton, J.P., Chapman, R. and Martens, C.S. (2010) Methane under-saturated fluids in deep-sea sediments: implications for gas hydrate stability and rates of dissolution. *Earth Planet. Sci. Lett.*, 298, 275–285. doi:10.1016/j.epsl.2010.07.016.

Lutken, C.B., Brunner, C.A., Lapham, L.L., Chanton, J.P., Rogers, R., Sassen, R., Dearman, J., Lynch, L., Kuykendall, J. and Lowrie, A. (2006) *Analyses of Core Samples from the Mississippi Canyon 118, Paper OTC 18208 Offshore Technology Conference*, American Association of Petroleum Geologist, May 1–4, 2006, Houston, TX.

Macelloni, L., Simonetti, A., Knapp, J.H., Knap, C.C., Lutken, C.B. and Lapham, L.L. (2012) Multiple resolution seismic imaging of a shallow hydrocarbon plumbing system, Woolsey Mound, Northern Gulf of Mexico. *Mar. Pet. Geol.*, 38, 128–142.

Macelloni, L., Brunner, C.A., Caruso, S., Lutken, C.B., D’Emidio, M. and Lapham, L.L. (2013) Spatial distribution of seafloor bio-geological and geochemical proxies of fluid regime and evolution of a carbonate/hydrates mound, northern Gulf of Mexico. *Deep Sea Res. Part I*, 74, 25–38.

Marchitto, T.M. and Wei, K.Y. (1995) History of the Laurentide meltwater flow to the Gulf of Mexico during the last glaciation, as revealed by reworked calcareous nanofossils. *Geology*, 23, 779–782.

Martens, C.S., Medlovitz, H.P., Seim, H., Lapham, L. and D’Emidio, M. (2016) Sustained in situ measurements of dissolved oxygen, methane and water transport processes in the benthic boundary layer at MC118 northern Gulf of Mexico. *Deep-Sea Res. II*, 129, 41–52.
Maslin, M., Mikkelsen, N., Vilela, C. and Haq, B. (1998) Sealevel and gas-hydrate-controlled catastrophic sediment failures of the Amazon Fan. *Geology*, 26, 1107–1110.

Maslin, M., Owen, M., Day, S. and Long, D. (2004) Linking continental-slope failures and climate change: testing the clathrate gun hypothesis. *Geology*, 32, 53–56.

McGee, T. (2006) A seafloor observatory to monitor gas hydrates in the Gulf of Mexico. *Lead. Edge.*, 25, 644–647.

McGee, T., Lutken, C., Rogers, R., Brunner, C., Dearman, J., Lynch, F. and Woolsey, R. (2009) Can fractures in soft sediments host significant quantities of gas hydrates? *Geol. Soc. London. Spec. Publ.*, 319, 29–49.

Mienert, J., Vanneste, M., Bunz, S., Andreassen, K., McGee, T., Lutken, C., Rogers, R., Brunner, C., Dearman, J., Milkov, A.V. (2004) Global estimates of hydrate-bound gas in continental-slope failures and climate change: testing the clathrate gun hypothesis. *Geology*, 32, 53–56.

Milkov, A.V. (2004) Global estimates of hydrate-bound gas in marine sediments: how much is really out there? *Earth Sci. Rev.*, 66, 183–197.

Nisbet, E.G. (1990) The end of the ice-age. *Can. J. Earth Sci.*, 27, 148–157.

Pauli, C.K., Buelow, W.J., Ussler, W., III and Borowski, W.S. (1996) Increased continental-margin slumping frequency during sea-level lowstands above gas-hydrate-bearing sediments. *Geology*, 24, 143–146.

Pauli, C.K., Brewer, P.G., Ussler, W., III, Peltzer, E.T., Rehder, G. and Clague, D. (2003) An experiment demonstrating that marine slumping is a mechanism to transfer methane from gas-hydrate deposits into the upper ocean and atmosphere. *Geo-Mar. Lett.*, 22, 198–203.

Pauli, C.K., Ussler, W., Lorenson, T.D., Winters, W. and Dougherty, J.A. (2005) Geochemical constraints on the distribution of gas hydrates in the Gulf of Mexico. *Geo-Mar. Lett.*, 25, 273–280.

Pedersen, T.P. and Price, N.B. (1982) The geochemistry of manganese carbonate in Panama Basin sediments. *Geochem. Cosmochim. Acta.*, 46, 59–68.

Price, B.A. (1998) Equatorial Pacific Sediments: A Chemical Approach to Ocean History. PhD Diss. Scripps Institute of Oceanography, UCSD, San Diego, CA, 364 pp.

Reimers, C.E., Jahnke, R.A. and McCorkle, D.C. (1992) Carbon fluxes and burial rates over the continental slope and rise off central California with implications for the global carbon cycle. *Global Biogeochem. Cycles.*, 6, 199–224.

Richter, T.O., Van Der Gaast, S., Koster, B., Vaars, A., Gieles, R., De Stigter, H.C., De Haas, H. and Van Weering, T.C.E. (2006) The Avaatech XRF Core Scanner: technical description and applications to NE Atlantic sediments. In: *New ways of Looking at Sediment Core and Core Data* (Ed. R.G. Rothwell), pp. 39–50. Geological Society Special Publication, London.

Rudnick, R.L. and Gao, S. (2003) Composition of the continental crust. In: *Treatise on Geochemistry* (Eds D.H. Heinrich and K.T. Karl), pp. 1–64. Pergamon, Oxford, UK.

Sageman, B.B. and Lyons, T.W. (2003) Geochemistry of fine-grained sediments and sedimentary rocks. In: *Treatise on Geochemistry*, Vol. 7 (Ed. F. MacKenzie), pp. 115–158. Elsevier, New York, NY.

Sassen, R., Roberts, H.H., Carney, R., Milkov, A.V., DeFreitas, D.A., Lanoil, B. and Zhang, C.L. (2004) Free hydrocarbon gas, gas hydrate, and authigenic minerals in chemosynthetic communities of the northern Gulf of Mexico continental slope: relation to microbial processes. *Chem. Geol.*, 205, 195–217.

Sassen, R., Roberts, H.H., Jung, W., Lutken, C.B., DeFreitas, D.A., Sweet, S.T. and Guinasso, N.L. Jr (2006) The Mississippi Canyon 118 Gas Hydrate Site: A Complex Natural System Paper OTC 18132, Offshore Technology Conference, May 1–4, Houston, TX.

Schenau, S.J., Reichart, G.J. and De Lange, G.J. (2002) Oxygen minimum zone controlled Mn redistribution in Arabian Sea sediments during the late Quaternary. *Paleoceanography*, 17, 1058. doi:10.1029/2000PA000621.

Shaw, T.J., Gieskes, J.M. and Jahnke, R.A. (1990) Early diagenesis in differing depositional environments: the response of transitional metals in pore water. *Geochem. Cosmochim. Acta.*, 54, 1233–1246.

Simonetti, A., Knapp, J.H., Sleeper, K., Lutken, C.B., Macelloni, L. and Knapp, C.C. (2013) Spatial distribution of gas hydrates from high-resolution seismic and core data, Woolsey Mound, Northern Gulf of Mexico. *Mar. Pet. Geol.*, 44, 21–33.

Sleeper, K.A. and Lutken, C. (2008) Activities Report for Cruise GOM1-08-MC118 Aboard the R/V Pelican Sampling and Deployment Cruise Mississippi Canyon Federal Lease Block 118 Northern Gulf of Mexico April 22–28, 2008. The Center for Marine Resources and Environmental Technology and the Seabed Technology Research Center, University of Mississippi. Available at: http://www.olemiss.edu/depts/mmri/programs/ppt_list.html.

Sleeper, K.A., Lowrie, A., Bosman, A., Macelloni, L. and Swann, C.T. (2006) Bathymetric Mapping and High Resolution Seismic Profiling by AUV in MC 118 (Gulf of Mexico). Paper OTC 18133, Offshore Technology Conference, Houston, TX.

Tribovillard, N., Algeo, T.J., Lyons, T. and Armelle, R. (2006) Trace metals as palaeoredox and palaeoproduction proxies: an update. *Chem. Geol.*, 232, 12–32.