Organic matter diagenesis in hadal setting: Insights from the pore-water geochemistry of the Mariana Trench sediments

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ARTICLE INFO
Keywords: Hadal sediments Organic matter diagenesis Aerobic respiration Denitrification

ABSTRACT
The diagenetic processes of organic matter (OM) in hadal sedimentary environments (> 6000 m water depth) are much less studied than those in other accessible environments. In this study, we quantify OM oxidation processes using pore-water geochemical measurements, fluxes, and diagenetic rate calculations in sediments along a depth transect from abyssal to hadal sites (5500–10257 m) in the Mariana Trench. The total benthic O2 consumption, and depth-integrated rates of nitrification and denitrification are positively correlated with water depth, indicating that OM diagenesis is enhanced in the deep sites of the hadal zone. The negative linear correlation between water depth and oxygen/nitrate penetration depths further supports this conclusion. In the abyssal sites, aerobic respiration dominates OM degradation, and anaerobic processes are negligible. In contrast, denitrification plays an important role in anaerobic OM degradation, and accounts for approximately 5% of the depth-integrated total OM mineralization at the deepest hadal site. Moreover, our results suggest that direct coupling between nitrification and denitrification is significant, and may define the turnover of N in hadal sediments. Although they are not without uncertainties, our results shed new light on the importance of denitrification in sedimentary diagenesis in the deepest part of the Earth’s ocean, and could have important implications for understanding the current state of biogeochemical cycles in the hadal zone.

1. Introduction

Hadal zones are mainly composed of trenches and troughs with depths greater than 6000 m. Although they only account for approximately 1–2% of the global marine benthic area, hadal zones constitute the deepest 45% of the deep ocean (Jameson et al., 2010). As they are located in tectonically active areas, they are commonly characterized by tectonically-triggered mass-wasting events that provide large amounts of sedimentary material from the adjacent margin to the hadal zone (Oguri et al., 2013; Bao et al., 2018). Therefore, hadal zones are considered as potential depo-centers of organic matter (OM) (Itou et al., 2000; Danovaro et al., 2003; Glud et al., 2013).

Quantifying the pathways and rates of OM degradation in sediments is essential for understanding global element cycles as it is directly or indirectly coupled to almost all biogeochemical processes (Froelich et al., 1979; Middelburg et al., 1993; Arndt et al., 2013). However, many of the previous studies on OM diagenesis focused on accessible environments, such as continental margin sediments (Chong et al., 2014; Pozzo et al., 2017) or lake sediments (Clayer et al., 2016), where the high OM input leads to high OM degradation rates. To date, only a few studies have discussed OM degradation in hadal sedimentary environments. For example, Glud et al. (2013) used an autonomous micro-profiling system to first access the benthic oxygen consumption rates in the sediments of the Challenger Deep at the Mariana Trench (MT), which is the deepest oceanic site on Earth. They demonstrated that hadal sediments possess higher organic carbon contents (1108 g m⁻² contrast to 887 g m⁻²) and intense OM diagenesis than the adjacent abyssal plains. Further studies quantified the benthic O2 consumption rates in hadal sediments of the Izu-Bonin, Tonga (Wenzhofer et al., 2016), Mussau, and New Britain Trenches (Luo et al., 2018), and revealed elevated OM diagenesis in the central trench. These previous studies solely focused on aerobic respiration in OM oxidation, and, while microbial and isotopic studies have indicated the activity of anaerobic diagenetic processes (such as denitrification) (Nunoura et al., 2013, 2018), no one has yet directly measured them.

In this paper, for the first time, we report a compilation of data, including dissolved oxygen (DO), nitrate (NO3⁻), ammonium (NH4⁺), and sulfate (SO4²⁻) in pore-water, and solid-phase data (TOC and TN) of hadal sediments, along a depth transect of the MT (5423–10257 m). Combining this new dataset with a one-dimensional reactive transport
equation, this study focuses on: 1) characterizing and differentiating the OM diagenesis pathways; 2) quantifying the rates of the reactions responsible for OM mineralization and nitrogen turnover in this extreme sediment environment.

2. Materials and methods

Three cruises to the southwestern part of the MT were conducted: 14 April-1 July 2016 (DY37) aboard the R/V Xiang Yang Hong 09, and 15 July-25 August 2016 (TS01) and 15 January-24 March 2017 (TS03) aboard the R/V Tan Suo Yi Hao. The sampling locations were concentrated in the southwestern part of the MT in areas of the Challenge Deep (Fig. 1). Sediment samples were collected using push-cores (PC) by the submersible Jiao Long, gravity cores (GC), a box corer (BC), and multiple cores (MUC) at three depth ranges of 5423–6010 m, 6980–7143 m, and 8638 m. Additionally, we utilized published pore-water data collected from the 10257 m-deep sedimentary column of the MT (Nunoura et al., 2018) (Fig. 1, Table 1). Overlying water was collected using an autonomous lander equipped with Niskin bottles and an SBE19 conductivity, temperature, and depth (CTD) sensor (Sea-Bird Electronics) to determine the basic properties of the bottom water, including its depth, temperature, and salinity. The lander was positioned 1.5 m above the sediment surface at areas near sites B05 and GT01. The bottom water (approximately 50 mL) was filtered and preserved following the method for pore-water samples (described in Section 2.1).

Upon recovery, the GCs were divided into 1-m segments, capped, and then transferred into the ship’s cold room. Each BC was visually inspected, and only unperturbed cores were used. Sub-cores of BC were collected using PVC tubes (9 cm inner diameter and 70 cm length, similar to the multiple corer tubes), which were manually inserted into the central BC zones, where the in-situ temperature is generally stable (Schulz, 2006). All sub-cores were immediately delivered to the ship’s cold room for further processing.

2.1. Dissolved oxygen measurements and pore-water sampling

To allow temperature equilibration, DO measurements were performed at least 5 h after core recovery. We drilled holes that were approximately 2 mm in diameter through the wall of the core liners with 2-cm intervals for PC and MUC, and 5-cm intervals for GC. The DO concentration was measured by inserting amperometric Clark-type

<table>
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<tr>
<th>Cruise</th>
<th>Site</th>
<th>Device</th>
<th>Core length</th>
<th>Water depth</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Salinity</th>
<th>Temperature</th>
<th>O₂</th>
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<td>N</td>
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* Data at AB11 site from Nunoura et al. (2018).
microelectrodes (Revsbech, 1989), which took measurements with an error of approximately 5%. Two-point calibration was performed with N2-purged (as a zero) and air-saturated seawater collected from a depth of 8000 m. Signals were amplified using a picocurrentmeter (Unisense, Denmark), and the values were recorded directly using the Profix software after electrode readings were steadied within 2 min. The O2 concentration of the overlying water was also measured using microelectrodes. Note that DO was only measured in cores from cruises DY37 and TS03, and data were not obtained for the BC cores as the microelectrodes were damaged during cruise TS01.

Following the measurement of O2 pore-water was extracted using Rhizons samplers (Seeberg-Elverfeldt et al., 2005), which were pre-soaked in 18.2 MΩ de-ionized water and connected to 50 mL evacuated disposable syringes with three-way Luer-lock stopcocks, and then simultaneously inserted into the core. A plank was inserted between each syringe housing and plunger to apply suction to the Rhizons. Approximately 30 mL of the extracted pore-water (1–2 h) was utilized for macronutrient and other analyses. One aliquot of each pore-water sample was added to 3–5 mL vials already filled with 0.2 mL of a 20% (m/v) Zn acetate solution for H2S analysis. A second aliquot was transferred into 3 mL vials and acidified with purified nitric acid to pH < 2, and stored at 4 °C for Fe3+ measurement. The NH4+ concentration of a third aliquot was directly measured within 2 h of pore-water sampling. The remaining samples were stored in 20–50 mL glass bottles and frozen so that nutrient (NO3−, NO2−) and other ion (SO42−, Cl−) analyses could be conducted after the cruises.

### 2.2. Pore-water and solid phases analyses

Pore-water NH4+ was analyzed onboard the vessels using a fluorospectrometer (LS55, PE) following the procedure reported by Holmes et al. (1999), with slight modifications. NO3− and NO2− were measured on-shore following photometric methods (Schnetger and Lehners, 2014). The analytical precision was better than 5%, and the detection limits (DL) were 0.2, 0.05, and 0.5 μmol L−1 for NH4+, NO3−, and NO2−, respectively. H2S was analyzed following the method described by Cline (1969). SO42− and Cl− were quantified after 100-fold dilution using an ion chromatograph (IC990, Dionex) equipped with a 4 × 250-mm AS19 analytical column, a 4-mm AER500 suppressor, and an AS-DV auto-sampler. We used 20 mM potassium hydroxide as the eluent with a flow rate of 0.6 mL min−1. The precision and accuracy were assessed by analyzing commercial nutrient standards (China Reference Material) at regular intervals. The analytical precision of SO42− was better than 4%, and the detection limit was 0.1 μmol L−1.

The water content was determined from the relative weight loss of known sediments after drying to a constant weight at 60 °C. The porosity (φ) was calculated from the weight of the freeze-dried sediment and water content, using a dry sediment density of 1.24 g cm−3 (Glud et al., 2013). After freeze-drying, sediment samples were ground and homogenized in an agate mortar. The sedimentary total carbon (TC) and total nitrogen (TN) contents were determined using an elemental analyzer. For measuring the total organic carbon (TOC) content, approximately 500 mg of sediment powder was first digested in 5 mL of 20% HCl for 24 h to remove any inorganic carbon. The residues were analyzed to determine their TOC contents. The weight percentages of total inorganic carbon (TIC) were calculated by subtracting the amount of TOC from that of TC. The average standard deviations of each measurement, determined by conducting multiple analyses of the same sample, were ± 0.02 and ± 0.005 wt% for TOC and TN, respectively.

### 2.3. Reaction transport modeling

To determine the net reaction rates from the measured reactive solute (O2, NO3−, NH4+, and SO42−) concentration profiles under steady-state conditions, the general one-dimensional diagenetic transport-reaction model was applied (Boudreau, 1997). The bioturbation and bioirrigation processes were neglected in our model as they are unlikely to be important in MT sediments owing to the low benthic macrofaunal abundance (Glud et al., 2013).

\[
\frac{d}{dx}(\varphi D_{sw} \frac{dC}{dx}) - \frac{d(\varphi \delta C)}{dx} + R_{net} = 0
\]

(1)

where C is the solute concentration in pore-water, ϕ is the sediment’s porosity, x is the depth (positive downward), D is the effective diffusion coefficient, δ is the sum of the groundwater advection, sediment burial, and compaction rates, and \( R_{net} \) is the net production rate (or consumption rate if \( R_{net} \) is negative) of a solute per unit of wet sediment volume. The effective diffusion coefficient in the sediment was calculated as \( D_{eff} = \varphi^2 D_{sw} \) (Ullman and Aller, 1982), where \( D_{sw} \) is the diffusion coefficient of the solute in water. A value of δ ~ 10⁻³ cm s⁻¹ was estimated by fitting Eq. (1) without the reaction term to the observed profiles of the non-reactive Cl− solute (data not shown). Such a low δ value corresponds to Peclot numbers (P) of 0.001–0.066 for the various solutes, indicating that the advection term in Eq. (1) can be neglected (Cleyet et al., 2016). According to these observations, Eq. (1) can be written as:

\[
\frac{d}{dx}(\varphi D_{sw} \frac{dC}{dx}) + R_{net} = 0
\]

(2)

The PROFILE (Berg et al., 1998) and REC (Rate Estimation from Concentrations) (Lettmann et al., 2012) computer codes were used to solve Eq. (2) for \( R_{net} \), with the concentration profiles of reactive solutes, measured ϕ values, and \( D_{sw} \) as input parameters. \( D_{sw} \) was obtained and adjusted to the in-situ bottom-water temperature (2 °C) using the Stokes–Einstein equation (Li and Gregory, 1974), giving \( D_{sw} \) values of 10.82 × 10⁻⁶, 9.65 × 10⁻⁶, 10.06 × 10⁻⁶, and 5.44 × 10⁻⁶ cm² s⁻¹ for O2, NO3−, NH4+, and SO42−, respectively. The Dirichlet condition was set as the boundary condition. The calculation domain was set to extend from the sediment surface to the maximum sampling depth (core length, Table 1). In a particular zone, the depth-integrated \( R_{net} \) (\( R_{net}^d \)) value was obtained from a \( R_{net} \) (solute) profile, as follows:

\[
R_{net}^d = \Delta x R_{net}
\]

(3)

where Δx(cm) denotes the thickness of this zone.

### 2.4. Reaction network and thermodynamic calculations

The main reactions considered in OM mineralization during the early diagenesis of the MT sediments were listed in Table 2. The modeled O2, NO3−, NH4+, and SO42− reaction rates were integrated over a sediment depth of 60 cm to allow comparisons between different sites. The integrated terminal electron-accepting processes were

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
<th>ΔG (kJ mol⁻¹ OM)</th>
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</thead>
<tbody>
<tr>
<td>[CH2O] + O2 → CO2 + H2O</td>
<td>Aerobic respiration</td>
<td>-503.51</td>
</tr>
<tr>
<td>5[CH2O] + 4NO3− → 2N2 + 4NO2− + CO2 + 5H2O</td>
<td>Denitrification</td>
<td>-452.69</td>
</tr>
<tr>
<td>2[CH2O] + SO42− → H2S + 2H2O</td>
<td>Sulfate reduction</td>
<td>-109.14</td>
</tr>
<tr>
<td>NH4+ + 2O2 → 2NO2− + H2O + 2H+</td>
<td>Nitrification</td>
<td>-67.81</td>
</tr>
<tr>
<td>H2S + 2O2 → SO42− + 2H+</td>
<td>Sulfide oxidation</td>
<td>-91.35</td>
</tr>
</tbody>
</table>
recalculated into carbon equivalents for the O$_2$, NO$_3^-$, and SO$_4^{2-}$ electron acceptor using idealized CH$_4$O stoichiometry for OM.

Standard-state energy yields ($\Delta G^0$) for various OM diagenesis pathways (Table 2) were calculated and corrected for temperature using Gibbs functions, $\Delta G^0 = \Delta H^0 - T \Delta S^0$, with the thermodynamic data of products and reactants for reactive solutes (O$_2$, NO$_3^-$, NH$_4^+$, and SO$_4^{2-}$) from Stumm and Morgan (2012). The in-situ Gibbs free-energy ($\Delta G$) per mole of reaction was calculated as:

$$\Delta G = \Delta G^0 + RT \ln Q$$

(4)

where $R$ is the gas constant, $T$ is the in-situ temperature in Kelvin, and $Q$ denotes the activity quotient of the reactants and products. The activity of the solutes was computed from the input of major ions at the in-situ pH and temperature using the Visual MINTEQ software with the specific ion interaction theory activity coefficient model; the activity coefficients of dissolved gases were set to 1.

3. Results

In this paper, [X] and (X) represent the concentration and content of species X in the aqueous and solid phase, respectively, and the errors are the standard deviations (SD).

3.1. Core descriptions

The retrieved core lengths ranged between 12 and 361 cm (Table 1). In general, the sediments of most sites can be divided into two parts (Supplementary Fig. 1): the upper sediments (0–30 cm) are dominated by homogenous, brown-silty-clay mud, and the lower parts of the cores are dominated by pale yellow-greyish sediment layers with brownish-black ranging from 1 to 4 cm in thickness.

3.2. Geochemical characteristics of bottom-water, pore-water, and solid phases

The geochemical characteristics of the bottom-water at various sampling sites are listed in Table 1. The bottom-water salinity is constant, with a value of 34.69 PSU at all sites. The temperature varies between 1.53 and 2.03 °C, and increased with increasing water depth; a higher temperature (2.03 °C) was detected at site GT01. All bottom-water is well-oxygenated, with oxygen concentrations exceeding 180 μmol L$^{-1}$.

The representative pore-water profiles of DO, NO$_3^-$, NH$_4^+$, and SO$_4^{2-}$ for the studied sites are shown in Fig. 2. [NO$_3^-$] is negligible at the sampled sites (< 0.4 μmol L$^{-1}$, data not shown). Based on the differences between the sampled water depths, we distinguish a third group of cores with similar chemical characteristics. The first group of “high-nitrate” profiles include sites with a depth of 5423–6010 m (abyssal sites, hereafter), characterized by a steady (site MC02; 32.32 ± 0.49 μmol L$^{-1}$) or slightly increasing (sites MC01, GC02, and GC03) NO$_3^-$ concentration with depth (from 32.67 to 33.95 μmol L$^{-1}$). The pore-water O$_2$ rapidly decreases from 190 to 96 μmol L$^{-1}$ within the upper 50 cm of the cores, and then declines more slowly as the depth increases, but is not exhausted at the maximum sampling depth of approximately 110 cm below seafloor (cmbsf). The second group includes four sites (B02, B05, B08, and B09 with a depth of 6980–7143 m, hereafter referred to as 7000-m sites) with distinct down-core NO$_3^-$ profiles. More precisely, below the sediment-water interface, [NO$_3^-$] increases slightly with depth, then decreases significantly as the depth continues to increase (from 31.5 μmol L$^{-1}$ in the overlying water to 34.5 μmol L$^{-1}$ at 6 cmbsf, then to 26.6 μmol L$^{-1}$ at 48 cmbsf at site B02). The third group includes sites GT01 and B10, with a depth of 8638 m (hereafter referred to as 8638-m sites), where [O$_2$] decreases exponentially with increasing depth, decreasing from 184.5 μmol L$^{-1}$ in the overlying water to below the detection limit within 80 cmbsf at site GT01. Moreover, [NO$_3^-$] also rapidly decreases from the bottom-water concentration (32.08 μmol L$^{-1}$) to almost-zero within 90 cmbsf at site GT01. The dissolved [SO$_4^{2-}$] remains almost constant with increasing depth, with a value of 27–28 mmol L$^{-1}$ at all sites. The concentration of H$_2$S is below the detection limit in all samples. The pore-water Fe$^{2+}$ concentrations are generally quite low (< 1.5 μmol L$^{-1}$) (Supplementary Fig. 2).

The variations in the TOC and TOC/TN weight ratios with depth are presented in Fig. 3. The TOC contents at the abyssal sites generally exhibit a gradual decline from the top of the core to the maximum sampled sediment depth, where they range from 0.48 to 0.09 wt%. In contrast, the profiles of TOC in the hadal sites are erratic without any clear trend, and range between 0.07 and 0.59 wt%. The TIC values are negligible at all sites (data not shown), which is reasonable as the hadal sediments are below the carbonate compensation depth (CCD) of 4500 m in the Pacific Ocean (Jamieson et al., 2010). At all sites, OM is characterized by TOC/TN weigh ratios ranging from 2.19 to 8.72, suggesting that it is mainly marine-derived (Meyers, 1994; Luo et al., 2017).

3.3. Modeled reaction rates of O$_2$ and NO$_3^-$

The O$_2$ and NO$_3^-$ concentration profiles calculated using the PROFILE code accurately fit the measured data ($r^2 > 0.95$ for O$_2$ and $r^2 > 0.90$ for NO$_3^-$, Fig. 4). In addition, the R$_{net}$ (O$_2$) and R$_{net}$ (NO$_3^-$) depth profiles generated by the PROFILE and REC codes exhibit comparable rate values and depth-intervals for the various consumption and production zones (Fig. 4). Hereafter, we will restrict our discussion to the results obtained using PROFILE as it is more user-friendly.

The R$_{net}$ (O$_2$) profiles show that O$_2$ diffuses into the sediment from the overlying water, with a flux of 35.34 ± 7.57 (n = 4) μmol m$^{-2}$ d$^{-1}$ for the abyssal sites and 81.38 (n = 1) μmol m$^{-2}$ d$^{-1}$ for site GT01 (Table 3). The R$_{net}$ (NO$_3^-$) profiles show a zone of net NO$_3^-$ production (0–45 cm) above a zone of net consumption (> 45 cm). They are clear variations in the values of R$_{net}$ (NO$_3^-$) between the sampling sites (Fig. 4). For example, the maximum values of R$_{net}$ (NO$_3^-$) at site AB11 reach 18.57 × 10$^{-3}$ mmol cm$^{-3}$ d$^{-1}$, but those at sites B05 and B10 are 2.94 × 10$^{-3}$ and 3.10 × 10$^{-3}$ mmol cm$^{-3}$ d$^{-1}$, respectively. The values of R$_{net}$ (SO$_4^{2-}$) are very low among the studied sites, with the exception of site GC02, where R$_{net}$ (SO$_4^{2-}$) is low but it is calculable, with a value of 1.64 × 10$^{-3}$ mmol cm$^{-3}$ d$^{-1}$. The estimated R$_{net}$ (NO$_3^-$) values in the NO$_3^-$ production/consumption zones amount to 0.98/0.16, 2.21/1.45, 2.54/1.45, and 3.93/3.71 μmol m$^{-2}$ d$^{-1}$ for the abyssal, 7000-m, 8638-m, and AB11 sites, respectively. Our calculation likely represents minimum rate values, as the code provides the net reaction rate rather than the gross rate, and we assume no nitritification below the transition depth of R$_{net}$ (NO$_3^-$) (Fig. 4) to transform the net rates into effective rates.

Based on the geochemical data, we calculated the Gibbs free-energy that could be exploited by different OM diagenesis processes in hadal sediments (Table 2). This allowed us to predict the extent to which denitrification and sulfate reduction are favorable under in-situ conditions. As the minimum energy requirement for microbial survival is approximately ~20 kJ per mole reaction (Schink, 1997), the energy available for OM diagenesis is sufficient.

4. Discussion

4.1. O$_2$ and NO$_3^-$ penetration depths within hadal sediments

The O$_2$ and NO$_3^-$ penetration depths in sediments may be useful indicators of the degree to which the O$_2$ and NO$_3^-$ consumption rates are oxidant (i.e., electron acceptor) or substrate (i.e., organic matter)-limited (Cai and Sayles, 1996; Hartnett and Devol, 2003; Fischer et al., 2009). When there is an abundant supply of OM, O$_2$ and NO$_3^-$ are rapidly consumed in pore-water, resulting highly limited penetration depths (from mm to less than 10 cm). Alternatively, with abundant
supplies of O$_2$ and NO$_3^-$ relative to OM, the amount and availability of OM limit the consumption of O$_2$ and NO$_3^-$, resulting in a large penetration depth. Therefore, the penetration depths of O$_2$ and NO$_3^-$ contain information about the pathways and magnitude of OM diagenesis.

At all sites, the sediment surface was well oxygenated and the O$_2$ penetration depth (OPD) exceeded the maximum sampling depth (108 cm), excluding site GT01, where the OPD is 80 cm (Fig. 2, Table 1). This suggests that O$_2$ consumption is limited by the amount of OM. The uppermost sediment at site GT01 may have been lost during the coring process, so caution should be taken against the over-interpretation of this value. However, our results still provide direct evidence that O$_2$ can be exhausted at a given depth in the MT sediment, which differs from the patterns observed in the previously explored sub-seafloor sediments of the oligotrophic regions, such as the South Pacific Gyre, where O$_2$ persists throughout the sediment sequence (D’Hondt et al., 2009; D’Hondt et al., 2015). While the O$_2$ concentration profile of site AB11 (10257 m) is unavailable, a maximum OPD of 85 cm can be derived, as O$_2$ is the preferred terminal electron acceptor in sediments, followed by NO$_3^-$ (Froelich et al., 1979; Canfield and Thamdrup, 2009). Taken together, the OPD exhibited an inverse correlation with water depth in the MT sediments, suggesting that there is a relatively adequate supply of OM at deep sites.

The nitrate penetration depth (NPD) in sediment is controlled by the combined result of NO$_3^-$ diffusion from the overlying seawater and several microbial mediated diagenetic processes, including nitrification and denitrification (Glud et al., 2009; Wankel et al., 2015). In organic-rich shelf sediments, NO$_3^-$ is generally consumed within a few centimeters or millimeters below the sediment-water interface (Chang and Devol, 2009; Kraal et al., 2012). However, in sediments underlying large oligotrophic ocean areas, the penetration of NO$_3^-$ is very deep, even exhibiting extensive accumulation well above the bottom seawater concentrations in some areas, indicating the predominance of aerobic ammonia oxidation in deep sediments (D’Hondt et al., 2009; Ziebis et al., 2012; D’Hondt et al., 2015; Wankel et al., 2015). In this study, applying a linear extrapolation of the [NO$_3^-$] profile provides minimum NPDs of 212 ± 16 (n = 4) and 125 cm (n = 1) at the 7000-

![Fig. 2](image-url)
m sites and 8638-m sites, respectively. Nunoura et al. (2018) reported a minimum NPD of 85 cm at site AB11 (10257 m). Considering these data, an evident trend of decreasing NPD with increasing depth was observed (Fig. 5), indicating high NO₃⁻ consumption rates at deeper sites.

4.2. Organic matter diagenesis in hadal sediments

The processes of OM diagenesis are related to the availability of electron acceptors, such as O₂, NO₃⁻, and SO₄²⁻, and their occurrence or absence in pore-water can provide valuable information on variations in the redox conditions of sediment columns. Therefore, these solutes have been widely used to decipher the various biogeochemical processes in sediments (Froelich et al., 1979; Middelburg et al., 1993; Soetaert et al., 1996; Clayer et al., 2016).

The values of \( \*R_{\text{net}}(\text{O}_2) \), \( \*R_{\text{net}}(\text{NO}_3^-) \), and \( \*R_{\text{net}}(\text{SO}_4^{2-}) \) reported in Table 3 are used to quantify the relative importance of the reactions responsible for OM oxidation in hadal sediments. Full details of the calculation process are given in the Appendix. Here, Fe is not considered as an oxidant as the concentration of Fe²⁺ is very low (< 1.5 μmol L⁻¹, Supplementary Fig. 2). Mn reduction is also neglected in our study as this process is only likely to be important in some manganese oxide-rich areas, such as the CCZ (Clarion-Clipperton Zone, Pacific Ocean) (Volz et al., 2018) or the Black Basin (Thamdrup et al., 2000). However, further studies on the dynamics of Mn²⁺ may be required to evaluate its potential effect on OM diagenesis. In brief, the total OM oxidation rate \( R_{\text{OM}} \) in sediments is the sum of aerobic respiration \( R_{\text{Ar}} \), denitrification \( R_{\text{den}} \), and sulfate reduction \( R_{\text{SR}} \). In this study, we attribute NO₃⁻ production to nitrification, and NO₃⁻ consumption to denitrification, as anammox, an alternative NO₃⁻ consumption pathway, may not be a major process in hadal sediments, according to molecular studies (Nunoura et al., 2018). Additionally, the calculation assumes that no reduced metabolites, such as Fe²⁺, NH₄⁺, and H₂S, diffuse up to the overlying water owing to their very low concentrations.

4.2.1. Total organic matter oxidation

The derived reaction rates in the MT sediments along the depth transect are listed in Table 3. The total OM oxidation rates in the MT sediments range between 27.19 and 118.82 μmol C m⁻² d⁻¹. One of the most prominent features is that the total OM oxidation rate increased with increasing water depth, which contrasts with the general perception that the rates of OM oxidation decline with increasing water depth (Glud, 2008). This reflects a greater supply of OM at deeper sites as the amounts of oxidant (i.e., O₂ and NO₃⁻) supplied from the overlying water are similar (Table 1). This is further indicated by the TOC depth profiles. While the TOC contents at the sediment surfaces (0–30 cm) of all sites are similar, the contents integrated downwards reflected significantly higher TOC contents at hadal sites than at the abyssal sites (Fig. 3). The high TOC contents and irregular depth profiles of the hadal sites are indicative of relatively rapid sediment deposition and burial, which may be due to the occasional tectonically-triggered sediment remobilization events (Itou et al., 2000; Oguri et al., 2013; Bao et al., 2018). The clear stratification of hadal sediments further suggests occasional sediment input (Supplementary Fig. 1).

4.2.2. O₂ fluxes and aerobic respiration

The calculated O₂ flux into the sediment at site GT01 (81.38 μmol m⁻² d⁻¹) is slightly lower than the previously reported values of 85 ± 38 μmol m⁻² d⁻¹ from a 6000-m water depth in the MT
(Glud et al., 2013). This difference may be due to the low sampling resolutions of the O2 data used in this study, as a coarse sampling resolution of several centimeters would underestimate the O2 flux (Fischer et al., 2009; Ziebis et al., 2012). Based on the data presented in this study, as well as previously reported data from the MT (Glud et al., 2013; Luo et al., 2018), a pronounced trend of increasing O2 fluxes toward deeper sites is observed (Fig. 5), indicating more intense O2 consumption at the deep sites than those in the shallow sites. It has been suggested that O2 consumption is the most important diagenetic process in deep-sea sediments (Canfield, 1993). Our data support this, and the O2 consumption rates account for > 90% of the total OM oxidation rate (Table 3). This is to be expected, given the oligotrophic conditions. One of the maximum O2 consumption zones was located in the upper portion of the sediment column at all sites (Fig. 4), rather than near the oxic-anoxic interface. This suggests that most O2 fluxes into the hadal sediments are used for the aerobic respiration of OM in the upper sedimentary package, rather than the oxidation of reduced compounds that are supplied by diffusion from the subsurface (Berg et al., 1998). Therefore, we propose that aerobic respiration dominates OM oxidation in the upper package of hadal sediments.

### 4.2.3. Anaerobic diagenesis and nitrogen redox in hadal sediments

Unlike aerobic respiration, knowledge of anaerobic diagenetic processes in hadal sediments is still limited. However, several studies have recently demonstrated that microbial functional genes involved in microbial nitrogen redox reactions, such as aerobic ammonia oxidation and anaerobic denitrification, are abundant in hadal sediments (Nunoura et al., 2013, 2018), suggesting the occurrence of both the production and reduction of NO3− in this extreme environment. The stable isotope analysis of nitrate has also presented important information regarding the co-occurrence of nitrification and denitrification (Nunoura et al., 2013, 2018). Here, we provide further

### Table 3

<table>
<thead>
<tr>
<th>Description</th>
<th>Unit</th>
<th>Abyssal sites</th>
<th>Hadal sites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5423-6010 m</td>
<td>6980-7143 m</td>
</tr>
<tr>
<td>O2 flux at SWI</td>
<td>μmol O2 m⁻² d⁻¹</td>
<td>−35.34 ± 7.57 (n = 4)</td>
<td>nd</td>
</tr>
<tr>
<td>NO3⁻ flux at SWI</td>
<td>μmol N m⁻² d⁻¹</td>
<td>−0.14 ± 0.28 (n = 4)</td>
<td>0.10 ± 0.23 (n = 4)</td>
</tr>
<tr>
<td>NH4⁺ flux at SWI</td>
<td>&lt; 0.01 (n = 4)</td>
<td>&lt; 0.01 (n = 4)</td>
<td>0.03 (n = 2)</td>
</tr>
<tr>
<td>*Rnet (NO3⁻) production</td>
<td></td>
<td>0.98 ± 0.56 (n = 4)</td>
<td>2.21 ± 0.82 (n = 4)</td>
</tr>
<tr>
<td>*Rnet (NO3⁻) consumption</td>
<td></td>
<td>−0.16 ± 0.07 (n = 4)</td>
<td>−1.45 ± 0.27 (n = 4)</td>
</tr>
<tr>
<td>*Rnet (SO4²⁻)</td>
<td>μmol SO4²⁻ m⁻² d⁻¹</td>
<td>−0.05 ± 0.04 (n = 2)</td>
<td>−0.03 ± 0.04 (n = 3)</td>
</tr>
<tr>
<td>*Rden</td>
<td>μmol C m⁻² d⁻¹</td>
<td>0.20</td>
<td>1.81</td>
</tr>
<tr>
<td>RDEN</td>
<td></td>
<td>0.10</td>
<td>0.06</td>
</tr>
<tr>
<td>Rama</td>
<td></td>
<td>26.89</td>
<td>nd</td>
</tr>
<tr>
<td>RCO2</td>
<td></td>
<td>27.19</td>
<td>nd</td>
</tr>
</tbody>
</table>

Fig. 4. Selected concentration profiles of DO and NO3⁻ (blank dot) and the consumption rates as a function of depth (red step curves). The fits (blank lines) were obtained using the PROFILE interpretation software. The green solid lines represent the REC model output. The positive values indicate solute production and negative values indicate solute consumption. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
geochemical evidence for dynamic nitrogen cycling in hadal sedimentary settings.

The model-determined denitrification rate is only 0.20 μmol C m⁻² d⁻¹ (n = 4) at the abyssal sites, while it increased to 4.64 μmol C m⁻² d⁻¹ at site AB11 (Table 3). Accordingly, there is a positive linear correlation between the modeled, depth-integrated denitrification rates and water depth (r² = 0.96, Fig. 5). Considering that the rates of benthic denitrification are most sensitive to the flux of OM and the bottom-water concentrations of O₂ and NO₃⁻ (Middelburg et al., 1996), the higher denitrification rate further demonstrates that there is a relatively abundant supply of OM in deeper sites. The sulfate reduction rates at all sites are very low (< 0.1 μmol C m⁻² d⁻¹), accounting for less than 0.5% of the total OM oxidation rate. This is similar to organic-poor open ocean sediments, where the rate of SO₄²⁻ reduction is also inappreciable (D’Hondt et al., 2002; Bowles et al., 2014). The low organic carbon content of hadal sediments might be the main factor limiting the use of SO₄²⁻ as an electron acceptor by microorganisms. Moreover, undetectable sulfate reduction is favorable for nitrogen metabolism (such as denitrification) because high sulfide concentrations strongly inhibit nitrification (Joye and Hollibaugh, 1995; Kraft et al., 2014; Hardison et al., 2015). The thermodynamic calculations further suggest that OM oxidation by denitrification is more favorable than sulfate reduction under hadal conditions (Table 2). Overall, diagenetic modeling indicated that denitrification is a significant process that dominates anaerobic OM oxidation in hadal sediments.

4.2.4. Nitrification

The NO₃⁻ rate profiles indicate positive NO₃⁻ production (nitrification) in the upper portions of the profiles, and production is coincident with the maximum subsurface NO₃⁻ (Fig. 2). Furthermore, the derived fluxes of NO₃⁻ indicate a clear upward flux into the overlying seawater and a downward flux to the denitrification zone at all hadal sites (Table 3). This demonstrates that the newly produced NO₃⁻ from nitrification contributes to the gross denitrification. Although the depth-integrated nitrification rates (0.98–3.93 μmol N m⁻² d⁻¹) are low, they are consistent with the values calculated for sediments in the eastern Clarion-Clipperton Zone of the Pacific Ocean (0.71–9.68 μmol N m⁻² d⁻¹) (Volz et al., 2018). As we had no high-resolution NO₃⁻ concentration profiles for the sediment-water interface and inevitable perturbation induced by box and gravity coring, we infer that these values represent the lower limits of the nitrification rates. However, the nitrification rates also exhibited a positive linear correlation with water depth (Fig. 5). The regulation of nitrification is ultimately dependent on the availability of O₂ and supply of NH₄⁺, which must be produced by OM mineralization (Jensen et al., 1994). At deep sites, the relatively high nitrification rates indicate enhanced OM diagenesis, as the supply of O₂ from the overlying seawater was sufficient (Glud et al., 2013). The very low concentrations of NH₄⁺ are likely the result of tight coupling between the NH₄⁺ production and consumption processes. Further work is required to verify this hypothesis.

Based on our calculation, the depth-integrated nitrification rates exceed denitrification at all hadal sites, reaching 2.21 to 1.45 μmol N m⁻² d⁻¹ at the 7000-m sites, 2.54 to 1.87 μmol N m⁻² d⁻¹ at the 8638-m sites, and 3.93 to 3.71 μmol N m⁻² d⁻¹ at site AB11, respectively. In other words, all NO₃⁻ consumption via denitrification in hadal sediment is supported by nitrification. Hence, we may conclude that hadal sediments could serve as a source of NO₃⁻ for overlying seawater, and the direct coupling between nitrification and denitrification is
significant and defines the N turnover in hadal sediments. Similar characteristics may be widespread in sediments underlying oligotrophic ocean areas, such as the oligotrophic North Atlantic (Ziebis et al., 2012; Wankel et al., 2015). Further studies of the dynamics of NO$_3^-$ in hadal sediments are required to evaluate its potential importance in hadal sedimentary diagenesis processes.

5. Conclusions

In this study, the geochemical characteristics of pore-water in sediments along a depth transect of the MT (water depths from 5500 to 10255 m) were used to explore the diagenesis activity of OM and nitrogen turnover in hadal sediments. Pore-water profiles and the applied transport-reaction model indicated that the intensity of benthic O$_2$ consumption, denitrification, and nitrification activity increase with water depth, indicating that OM diagenesis is intense at deeper sites in the hadal zone. Although aerobic respiration is the main pathway of OM diagenesis, the enhanced denitrification activity at deeper sites suggests that denitrification could play an important role in hadal sediment diagenesis. Moreover, our study demonstrates the occurrence of active nitrification and denitrification in hadal sediments, indicating that these sediments may serve as a NO$_3^-$ source for overlying seawater.

However, we are quite aware of the shortcomings and limitations of ex-situ sampling and analytical techniques, which have been discussed in several studies. Caveats or shortcomings related to models cannot be ignored, and the potential O$_2$ and NO$_3^-$ turnover associated with the little infauna activity was not included in this study. Nevertheless, our data suggest that denitrification is an important pathway of OM diagenesis in the Earth’s deepest seafloor sediments. Further work should target more hadal sites and different trench settings, which may provide complementary information regarding the role of denitrification in OM diagenesis in hadal setting.

Acknowledgements

We are thankful to the crews of the R/V Tan Suo Yi Hao for their help during the Expedition. We are also grateful to Dr. Jiwei Li, Shun Chen, Hanchao Xu, Kaiwen Ta, and Zixiao Guo for their help during subsampling and analysis of the samples. We thank Dr. Bonnie X Chang, University of Washington, and four reviewers for their helpful comments that have improved this manuscript. This study was financially supported by the National Key Research and Development Program of China (Grant No. 2016YFC0304900), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB06020000), and the National Natural Science Foundation of China (Grant No. 41576038).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dsr.2019.03.011.

APPENDIX

According to the reactions listed in Table 2, the total OM oxidation rate ($R_{OM}$, μmol C m\textsuperscript{-2} d\textsuperscript{-1}) can be taken as the sum of the amount of carbon oxidized by O$_2$, NO$_3^-$, and SO$_4^{2-}$:

$$R_{OM} = R_{AR} + R_{DEN} + R_{SR}$$

(A1)

where $R_{AR}$ is the rate of OM oxidation by O$_2$ (μmol C m\textsuperscript{-2} d\textsuperscript{-1}), $R_{DEN}$ is the rate of OM oxidation by denitrification (μmol C m\textsuperscript{-2} d\textsuperscript{-1}), and $R_{SR}$ is the rate of OM oxidation by sulfate (μmol C m\textsuperscript{-2} d\textsuperscript{-1}). We define the ammonium production rates ($R_{NH4^+}$) as:

$$R_{NH4^+} = aR_{AR} + aR_{DEN} + aR_{SR}$$

(A2)

where $a = 16/106$, which is the average Redfield ratio for marine plankton: $\text{(CH}_2\text{O)}_{106}\text{(NH}_3\text{)}_{16}\text{(H}_3\text{PO}_4\text{)}$. As O$_2$ can oxidize OM and reduced inorganic species (i.e., NH$_4^+$, or H$_2$S), the equation for O$_2$ flux ($F_{O2}$) can be written as:

$$F_{O2} = R_{AR} + 2R_{NH4^+-F_{NH4^+}} + 2R_{H2S}$$

(A3)

where $2(R_{NH4^+}-F_{NH4^+})$ is the total NH$_4^+$ oxidation, i.e., the total ammonium production ($R_{NH4^+}$) minus the NH$_4^+$ flux ($F_{NH4^+}$) (NH$_4^+$ oxidation is multiplied by two because 2 mol of O$_2$ are required to oxidize 1 mol of NH$_4^+$ to NO$_3^-$), and $R_{H2S}$ is the amount of sulfide oxidation with a coefficient of two, because 2 mol O$_2$ are required to oxidize 1 mol of H$_2$S to SO$_4^{2-}$. We assume that all H$_2$S is oxidized to SO$_4^{2-}$ as no H$_2$S was measured in this study, thus, $R_{H2S} = R_{SR}$. We also assume that no NH$_4^+$ escapes the sediment by diffusion ($F_{NH4^+} = 0$). This is a reasonable assumption, because the NH$_4^+$ flux is very low (Table 3). Therefore, equation (A3) can then be simplified to:

$$F_{O2} = R_{AR} + 2R_{NH4^+} + 2R_{SR}$$

(A4)

giving a system of three Eqs. (A1, A2, and A4), which can be solved to determine the unknown rates ($R_{OM}$ and $R_{AR}$).

References


