https://doi.org/10.5194/cp-2019-70
Preprint. Discussion started: 20 June 2019

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Millennial-scale variations of sedimentary oxygenation in the western subtropical North Pacific and its links to the North Atlantic climate

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Key Points

1. History of sedimentary oxygenation processes at mid-depths in the western subtropical North Pacific since the Last Glacial is reconstructed using sediment-bound geochemical proxies.

2. Redox-sensitive proxies reveal millennial-scale variations in sedimentary oxygenation that correlated closely to changes in the North Pacific Intermediate Water.

3. A millennial-scale out-of-phase relationship between deglacial ventilation in the western subtropical North Pacific and the formation of North Atlantic Deep Water is suggested.

https://doi.org/10.5194/cp-2019-70
Preprint. Discussion started: 20 June 2019

4. A larger CO_2 storage at mid-depths of the North Pacific corresponds to the termination of atmospheric CO_2 rise during the Bölling-Alleröd interval.

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Abstract

Lower glacial atmospheric CO_2 concentrations have been attributed to carbon sequestration in deep oceans. However, potential roles of voluminous subtropical North Pacific in modulating atmospheric CO_2 levels on millennial timescale are poorly constrained. Further, an increase in respired CO_2 concentration in the glacial deep ocean due to biological pump generally is coeval with less oxygenation in the subsurface layer. This link thus offers a chance to visit oceanic ventilation and the coeval export productivity based on redox-controlled sedimentary geochemical parameters. Here we investigate a suite of sediment geochemical proxies to understand the sedimentary oxygenation variations in the subtropical North Pacific (core CSH1) over the last 50 thousand years (ka). Our results suggest that sedimentary oxygenation at mid-depths of the subtropical North Pacific intensifies during the episodes of late glacial (50-25 ka), Last Glacial Maximum (LGM) and also the interval after 8.5 ka, especially pronounced for the North Atlantic millennial-scale abrupt cold events of the Younger Dryas, Heinrich Stadial (HS) 1 and 2. On the other hand, oxygen-depleted seawater is found during the Bölling - Alleröd (B/A) and Preboreal. Our findings of enhanced sedimentary oxygenation in the subtropical North Pacific is aligned with intensified formation of North Pacific Intermediate Water (NPIW) during cold spells, while the ameliorated sedimentary oxygenation seems to be linked with the intensified Kuroshio Current since 8.5 ka. In our results, diminished sedimentary oxygenation during the B/A indicates an enhanced CO_2 sequestration at mid-depth waters, along with slight increase in atmospheric CO_2 concentration. Mechanistically, we speculate that these millennial-scale changes were linked to the strength of North Atlantic Deep Water, leading to intensification of NPIW formation and enhanced abyss flushing during deglacial cold and warm intervals, respectively. Enhanced formation of NPIW seem to be driven by the perturbation of sea ice formation and sea surface salinity oscillation in high latitude North Pacific through atmospheric and oceanic teleconnection. During the B/A, decreased sedimentary oxygenation likely resulted from an upward penetration of aged deep water into the intermediate-depth in the North Pacific, corresponding to a

resumption of Atlantic Meridional Overturning Circulation.

Keywords: sedimentary oxygenation; millennial timescale; North Pacific Intermediate Water; Atlantic Meridional Overturning Circulation; subtropical North Pacific

https://doi.org/10.5194/cp-2019-70
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1. Introduction

The sluggish ocean ventilation depletes dissolved oxygen in the sediment-water interface and facilitates the storage of respired carbon, which in turn plays a role in regulating sedimentary oxygen, potentially linking to atmospheric CO_2 changes on orbital and millennial timescales (Jaccard and Galbraith, 2012; Lu et al., 2016; Sigman and Boyle, 2000). The reconstruction of past sedimentary oxygenation is therefore crucial for understanding changes in export productivity and the renewal rate of deep ocean circulation (Nameroff et al., 2004). Previous studies from high-latitude North Pacific margins and subarctic Pacific have identified drastic variations in export productivity and marine oxygen levels at glacial-interglacial timescales using diverse proxies such as trace elements (Cartapanis et al., 2011; Chang et al., 2014; Jaccard et al., 2009; Zou et al., 2012), benthic foraminiferal assemblages (Ohkushi et al., 2016; Ohkushi et al., 2013; Shibahara et al., 2007)and nitrogen isotopic composition ($\delta^{15}N$) of organic matter (Chang et al., 2014; Galbraith et al., 2004; Riethdorf et al., 2016) in cored sediments. These studies further suggested that both North Pacific Intermediate Water (NPIW) and export of organic carbon regulate the sedimentary oxygenation variation during the last glaciation and Holocene in the northeast North Pacific. By contrast, little information exists on millennial-scale oxygenation changes to date in the western subtropical North Pacific.

The modern NPIW is mainly sourced from the NW Pacific marginal seas (Shcherbina et al., 2003; Talley, 1993; You et al., 2000), and then it spreads into subtropical North Pacific at intermediate depths of 300 to 800 m (Talley, 1993). The pathway and circulation of NPIW have been identified byYou (2003), who suggested that cabbeling is the principle mechanism responsible for transforming subpolar source waters into subtropical NPIW along the subarctic-tropical frontal zone. More specifically, You et al. (2003) argued that a lower subpolar input of about 2Sv is sufficient for subtropical ventilation. Benthic foraminiferal $\delta^{13}C$ data from the North Pacific suggested enhanced ventilation at water depths of < 2000 m during the last glacial period(Keigwin, 1998; Matsumoto et al., 2002). Furthermore, on the basis of both radiocarbon data and modeling results, Okazaki et al. (2010) provided further

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insight into the formation of deep water in the North Pacific during early deglaciation. Enhanced NPIW penetration is further explored using numerical model simulations (Chikamoto et al., 2012; Gong et al., 2019; Okazaki et al., 2010). The downstream effects of intensified GNPIW can be seen in the record of $\delta^{13}C$ of *Cibicides wuellerstorfi* in core PN-3 from the middle Okinawa Trough (OT), whereas lower deglacial $\delta^{13}C$ values were attributed to enhanced OC accumulation rates due to higher surface productivity by Wahyudi and Minagawa (1997).

The Okinawa Trough is separated from the Philippine Sea by the Ryukyu Islands and is an important channel of the northern extension of the Kuroshio in the western subtropical North Pacific (Figure 1). Surface hydrographic characteristics of the OT over glacial-interglacial cycles are largely influenced by the Kuroshio and East China Sea Coastal Water (Shi et al., 2014); the latter is related to the strength of summer East Asian monsoon (EAM) sourced from the western tropical Pacific. Modern physical oceanographic investigations showed that intermediate waters in the OT are mainly derived from horizontal advection and mixture of NPIW and South China Sea Intermediate Water (Nakamura et al., 2013). These waters intrude into the OT through two ways (Nakamura et al., 2013): (i) deeper part of the Kuroshio enters the OT through the channel east of Taiwan (sill depth 775 m) and (ii) through the Kerama Gap (sill depth 1100 m). In the northern OT, the occupied subsurface water mainly flows through the Kerama Gap through horizontal advection from the Philippine Sea (Nakamura et al., 2013). Recently, Nishina et al. (2016) found that an overflow through the Kerama Gap controls the modern deep-water ventilation in the southern OT.

Both surface hydrography and deep ventilation in the OT varied greatly since the last glaciation. During the last glacials, the mainstream of the Kuroshio likely migrated to the east of the Ryukyu Islands or and also became weaker due to lower sea levels (Shi et al., 2014; Ujiié and Ujiié, 1999; Ujiié et al., 2003) and the hypothetical emergence of a Ryukyu-Taiwan land bridge (Ujiié and Ujiié, 1999). In a recent study, based on the Mg/Ca-derived temperatures in surface and thermocline waters and planktic foraminiferal indicators of water masses from two sediment cores

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located in the northern and southern OT, Ujiié et al. (2016) further argued that the hydrological conditions of North Pacific Subtropical Gyre since MIS 7 is modulated by the interaction between the Kuroshio and the NPIW. Besides the Kuroshio, the flux of East Asian rivers to the East China Sea (ECS), which is related to the summer EAM and the sea level oscillation coupled with topography are also regulating the surface hydrography in the Okinawa Trough (Chang et al., 2009; Kubota et al., 2010; Sun et al., 2005; Yu et al., 2009).

Based on benthic foraminiferal assemblages, previous studies have implied a reduced oxygenation in deep waters of the middle and southern OT during the last deglacial period (Jian et al., 1996; Li et al., 2005), but a strong ventilation during the Last Glacial Maximum (LGM) and the Holocene (Jian et al., 1996; Kao et al., 2005). High sedimentary $\delta^{15}N$ values, an indicator of increased denitrification in the subsurface water column, also occurred during the late deglaciation in the middle OT(Kao et al., 2008). Inconsistent with these results, Dou et al. (2015) suggested an oxic depositional environment during the last deglaciation in the southern OT based on weak positive cerium anomalies. Furthermore, Kao et al. (2006) concluded a reduced ventilation of deepwater in the OT during the LGM due to the reduction of KC inflow using a 3-D ocean model. Yet, the patterns and reasons that caused sedimentary oxygenation in the OT thus remain unclear.

2. Paleo-redox proxies

Sedimentary redox condition is the balance between the rate of oxygen supply from the overlying bottom water and the rate of oxygen removal from pore water (Jaccard et al., 2016), processes that are closely related to the advection of submarine ocean circulation and organic matter respiration, respectively. Contrasting geochemical behaviors of redox-sensitive trace metals (Mn, Mo, U, etc.) have been extensively used to reconstruct bottom water and sedimentary oxygen changes (Algeo, 2004; Algeo and Lyons, 2006; Crusius et al., 1996; Dean et al., 1997; Tribovillard et al., 2006; Zou et al., 2012), as their concentrations respond to redox condition of the depositional environment (Morford and Emerson, 1999).

In general, enrichment of Mn with higher speciation states (Mn (III) and Mn (IV))

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in the form of Mn-oxide coatings is observed in marine sediments, when oxic condition prevails into great sediment depths as a result of low organic matter degradation rates and well-ventilated bottom water (Burdige, 1993). In reducing conditions, Mn is released as dissolved Mn (II) species into the pore water and thus its concentration is usually low in suboxic (O_2 and HS^- absent) and anoxic (HS^- present) sediments. In addition, when Mn enrichment occurs in oxic sediments as solid phase Mn oxyhydroxides, it may lead to co-precipitation of other elements, such as Mo (Nameroff et al., 2002).

The elements Mo and U behave conservatively in oxygenated seawater, but are preferentially enriched in oxygen-depleted water. However, these two trace metals behave differently in several ways. Molybdenum can be enriched in both oxic sediments, such as the near surface manganese-rich horizons in continental margin environments (Shimmield and Price, 1986) and in anoxic sediments (Nameroff et al., 2002). Under anoxic conditions, Mo can be reduced either from the +6 oxidation state to insoluble MoS_2, though this process is known to occur only under extremely reducing conditions, such as hydrothermal and/or diagenesis (Dahl et al., 2010; Helz et al., 1996) or be converted to particle-reactive thiomolybdates (Vorlicek and Helz, 2002). Zheng et al. (2000) suggested two critical thresholds for Mo scavenging from seawater: 0.1μM hydrogen sulfide (H_2S) for Fe-S-Mo co-precipitation and 100 μM H_2S for Mo scavenging as Mo-S or as particle-bound Mo without Fe. Although Crusius et al. (1996) noted insignificant enrichment of sedimentary Mo under suboxic conditions, Scott et al. (2008) argued that burial flux of Mo is not so low in suboxic environments. Excess concentration of Mo (Mo_{excess}) in sediments thus suggests the accumulation of sediments either in anoxic (H_2S occurrence) or well oxygenated conditions (if Mo_{excess} is in association with Mn-oxides).

In general, U is enriched in anoxic sediments (>1 μM H_2S), but not in oxic sediments (>10 μM O_2) (Nameroff et al., 2002). Accumulation of U depends on the content of reactive organic matter (Sundby et al., 2004) and U precipitates as uraninite (UO_2) during the conversion of Fe (III) to Fe (II) in suboxic conditions (Morford and Emerson, 1999; Zheng et al., 2002). One of the primary removal mechanisms for U

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from the ocean is via diffusion across the sediment-water interface of reducing sediments (Klinkhammer and Palmer, 1991). Under suboxic conditions, soluble U (VI) is reduced to insoluble U (IV), but free sulfide is not required for U precipitation(McManus et al., 2005).Jaccard et al. (2009) suggested that the presence of excess concentration of U (U_{excess}) in the absence of Mo enrichment is indicative of a suboxic, but not sulfidic condition, within the diffusional range of the sediment-water interface. The felsic volcanic is also a primary source of uranium (Maithani and Srinivasan, 2011). Therefore, the potential input of uranium from active volcanic sources around the northwestern Pacific to the adjacent sediments should not be neglected.

In this study, we investigate a suite of redox-sensitive elements and the ratio of Mo/Mn along with productivity proxies from a sediment core retrieved from the northern OT to reconstruct the sedimentary oxygenation in the western subtropical North Pacific over the last 50ka. Based on that, we propose that multiple factors, such as NPIW ventilation, the strength of the Kuroshio Current and export productivity, control the bottom sedimentary oxygenation in the OT on millennial time scales since the last glacial.

3. Oceanographic setting

The OT resulted from the collision of the Philippine and Eurasian plates and initially opened at the middle Miocene (Sibuet et al., 1987). Since that time, the OT has been a depositional center in the ECS and receives large sediment supplies from nearby rivers (Chang et al., 2009). At present, water depth in the axial part of the OT deepens from 500 m in the north to ~2700 m in the south.

Surface hydrographic characteristics of the OT are mainly controlled by the warmer, more saline Kuroshio water and cooler, less saline Changjiang Diluted Water, and the modern flow-path of the former is influenced by the bathymetry of the OT (Figure 1a). The Kuroshio Current originates from the North Equatorial Current and flows into the ECS from the Philippine Sea through the Suao-Yonaguni Depression. In the northern OT, Tsushima Warm Current (TWC), a branch of the Kuroshio, flows into the Japan Sea through the shallow Tsushima Strait. Volume transport of the

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Kuroshio varies seasonally due to the influence of the EAM with a maximum of 24 Sv (1 Sv = 10^6 m^3 /s) in summer and a minimum of 20 Sv in autumn across the east of Taiwan (Qu and Lukas, 2003).

Figures 2a and b show the lower sea surface salinity (SSS) zone in summer in the ECS migrates toward the east of OT, indicating enhanced impact of the Changjiang discharge associated with summer EAM. The mean annual discharge of the Changjiang is 0.028 Sv and ~80% of its total discharge is supplied to the ECS (Ichikawa and Beardsley, 2002). In situ observational data of surface hydrography along the ship track from Taiwan Strait to Korea Strait and around the entrance of the Tsushima Strait in the northern part of the ECS show a lower SSS in summer and a negative correlation between the Changjiang discharge and SSS in July (Delcroix and Murtugudde, 2002). Lower SSS in summer than that in winter suggests stronger effects of summer EAM on surface hydrography over the Kuroshio Current (Sun et al., 2005). Consistently, previous studies from the Okinawa Trough reported such close relationship between summer EAM and SSS back to the late Pleistocene (Chang et al., 2009; Clemens et al., 2018; Kubota et al., 2010; Sun et al., 2005).

Despite the effects of EAM and the Kuroshio, evidence of geochemical tracers (temperature, salinity, oxygen, nutrients and radiocarbon-$\Delta^{14}C$)collected during the World Ocean Circulation Experiment (WOCE) Expeditions in the Pacific (transects P24 and P03) favors the presence of low saline, nutrient-enriched intermediate and deep waters (Talley, 2007). Dissolved oxygen content is <100 µM at water depths of below 600 m in the OT along WOCE transects PC03 and PC24 (Talley, 2007). Modern oceanographic observations at the Kerama Gap reveal that upwelling in the OT is associated with the inflow of NPIW and studies using box model predicted that overflow through the Kerama Gap is responsible for upwelling (3.8–7.6 × 10^{-6}m s^{-1}) (Nakamura et al., 2013; Nishina et al., 2016).

4. Materials and methods

4.1. Chronostratigraphy of core CSH1

A 17.3 m long sediment core CSH1 (31° 13.7' N, 128° 43.4' E; water depth: 703 m) was collected from the northern OT, close to the main stream of TWC (Figure 1b)

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and within the depth of NPIW (Figure 1c) using a piston corer during *Xiangyanghong*09 Cruise in 1998. This location is thus enabling us to reconstruct millennial changes in the properties of TWC and NPIW. The expedition was carried out by the First Institute of Oceanography, Ministry of Natural Resources of China. Core CSH1 mainly consists of clayey silt and silt with occurrence of plant debris at some depth intervals (Ge et al., 2007) (Figure 3a). In addition, three layers of volcanic ash were observed at depths of 74−106 cm, 782−794 cm, 1570−1602 cm and these three intervals can be correlated with well-known ash layers, Kikai-Akahoya (K-Ah; 7.3 ka), Aira-Tanzawa (AT; 29.24 ka) and Aso-4 (roughly around MIS 5a) (Machida, 1999), respectively. The core was split and sub-sampled at every 4 cm interval and then stored in China Ocean Sample Repository at 4 °C until analysis.

Previously, some paleoceanographic studies have been conducted and a set of data have been investigated for core CSH1, including the contents of planktic foraminifers as well as their carbon ($\delta^{13}C$) and oxygen isotope ($\delta^{18}O$) compositions (Shi et al., 2014), pollen (Chen et al., 2006), paleomagnetism (Ge et al., 2007) and $CaCO_3$ (Wu et al., 2004). An age model for this core has been constructed by using ten Accelerator Mass Spectrometry (AMS) ^{14}C dates and six oxygen isotope ($\delta^{18}O$) age control points. The whole 17.3 m core contains *ca.* 88 ka-long record of continuous sedimentation (Shi et al., 2014).

It is noteworthy that previous age control points with constant radiocarbon reservoir throughout core CSH1 are used to reveal orbital-scale Kuroshio variations (Shi et al., 2014), but insufficient to investigate millennial-scale climatic events. On the basis of original age model, a higher abundance of *Neogloboquadrina pachyderma* (*dextral*) that occurred during warmer intervals, such as the B/A, has been challenging to explain reasonably. On the other hand, paired measurements of $^{14}C/^{12}C$ and ^{230}Th ages from Hulu Cave stalagmites suggest magnetic field change has greatly contributed to high atmospheric $^{14}C/^{12}C$ values at HS4 and the YD (Cheng et al., 2018). Thus a constant reservoir age assumed when calibrating foraminiferal radiocarbon dates using CALIB 6 software and the Marine13 calibration dataset (Reimer et al., 2013)for Core CSH1 may cause large chronological uncertainties.

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Here, we therefore recalibrated the radiocarbon dates using CALIB 7.04 software with Marine 13 calibration dataset (Reimer et al., 2013). Moreover, on the basis of significant correlation between planktic foraminiferal $\delta^{18}O$ and Chinese stalagmite $\delta^{18}O$ (Cheng et al., 2016), a proxy of summer EAM related to SSS of ECS, we re-established the age model for core CSH1 (Figures 3b-d). Overall, the new chronological framework is similar tothe one previously reported by Shi et al. (2014), but with more dates. In order to compare with published results associated with ventilation changes in the North Pacific, here we mainly report the history of sedimentary oxygenation in the northern OT since the last glacial. Linear sedimentation rate varied between 10 and 60 cm/ka. The age control points were shown in Table 2.

4.2. Chemical analyses

Sediment subsamples for geochemical analyses were freeze-dried and ground to a fine powder with an agate mortar and pestle. Based on the age model, 85 subsamples from core CSH1 with time resolution of about 200 years (4 cm interval) were selected for detailed geochemical analyses of major and minor elements and total contents of carbon (TC), organic carbon (TOC) and nitrogen (TN). The pretreatment of sediment and other analytical methods have been reported elsewhere (Zou et al., 2012)

TC and TN were determined with an elemental analyzer (EA; Vario EL III, Elementar Analysen systeme GmbH) in the Key Laboratory of Marine Sediment and Environment Geology, First Institute of Oceanography, Ministry of Natural Resources of China, Qingdao. Carbonate was removed from sediments by adding 1M HCl to the homogenized sediments for total organic carbon (TOC) analysis using the same equipment. The content of calcium carbonate ($CaCO_3$) was calculated using the equation:

$$CaCO_3 = (TC-TOC) \times 8.33$$

where 8.33 is the ratio between the molecular weight of carbonate and the atomic weight of carbon. National reference material (GSD-9), blank sample and replicated samples were used to control the analytical process. The relative standard deviation of

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the GSD-9 for TC, TN and TOC is ≤ 3.4%.

About 0.5 g of sediment powder was digested in double distilled HF:HNO_3 (3:1), followed by concentrated $HClO_4$, and then re-dissolved in 5% HNO_3. Selected major and minor elements such as aluminum (Al) and manganese (Mn) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Thermo Scientific iCAP 6000, Thermo Fisher Scientific), as detailed elsewhere (Zou et al., 2012). In addition, Mo and U were analyzed with inductively coupled plasma mass spectrometry (ICP-MS; Thermo Scientific XSERIES 2, Thermo Fisher Scientific), as described in Zou et al. (2012). Precision for most elements in the reference material GSD-9 is ≤ 5% relative standard deviation. The excess fractions of U and Mo were estimated by normalization to Al:

Excess fraction = $\text{total}_{\text{element}}$— $(\text{element}/\text{Al}_{\text{average shale}} \times \text{Al})$,with $\text{U}/\text{Al}_{\text{average shale}} = 0.307\times10^{-6}$ and $\text{Mo}/\text{Al}_{\text{average shale}} = 0.295\times10^{-6}$ (Li and Schoonmaker, 2014).

In addition, given the different geochemical behaviors of Mn and Mo and co-precipitation and adsorption processes associated with the redox cycling of Mn, we calculated the ratio of Mo to Mn, given that higher Mo/Mn ratio indicates lower oxygen content in the depositional environment and vice versa. In combination with the concentration of excess uranium, we infer the history of sedimentary oxygenation in the subtropical North Pacific since the last glaciation.

5. Results

5.1. TOC, TN, and $CaCO_3$

TN content shows a larger variation compared to TOC (Figure 4b), but it still strongly correlates with TOC ($r = 0.74$, $p<0.01$) throughout the entire core. Concentration of TOC ranges from 0.5 to 2.1% and it shows higher values with stable trends during the last glacial phase (MIS 3) (Figure 4c). Molar ratios of TOC/TN vary around 10, with higher ratios at the transition into the LGM (Figure 4d), corresponding to higher linear sedimentation rate (Figure 4a). The content of $CaCO_3$ varies from 8.8 to 35% (Figure 4e) and it mostly shows higher values with increasing trends during the last deglaciation. Conversely, the content of $CaCO_3$ is low and exhibits decreasing trends during late MIS 3 and the LGM (Figure 4e).

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Both TOC and $CaCO_3$ are widely used as proxies for the reconstruction of past export productivity (Rühlemann et al., 1999). Molar C/N ratios of >10 (Figure 4c) suggest that terrigenous organic sources significantly contribute to the TOC concentration in core CSH1. The TOC content therefore may be not a reliable proxy for the reconstruction of surface water export productivity during times of the LGM and late deglaciation, when maxima in C/N ratios co-occur with decoupled trends between $CaCO_3$ and TOC concentrations. In addition, the negative correlation coefficient ($r = -0.85$, $p<0.01$) between Al and $CaCO_3$ in sediments throughout core CSH1 confirms the biogenic origin of $CaCO_3$ against terrigenous Al (Figure 4f). Moreover, a detailed comparison between $CaCO_3$ concentrations and the previously published foraminiferal fragmentation ratio (Wu et al., 2004) clearly shows, apart from a small portion within the LGM, no clear co-variation. This suggests that $CaCO_3$ changes are primarily driven by variations in carbonate primary production, and not overprinted by secondary processes, such as carbonate dissolution through changes in the lysocline depth. On the other hand, terrigenous dilution generally decreases the content of $CaCO_3$. The increasing trend of $CaCO_3$ associated with high sedimentation rate (Figures 4a, e) indicates a substantial increase in export productivity during the last deglacial interval. Thus, we can confidently use $CaCO_3$ content as productivity proxy to a first order approximation.

5.2. Redox-sensitive Elements

Figure 4 shows time series of selected redox-sensitive elements (RSEs) and proxies derived from them. Mn shows higher concentrations during the LGM and HS1 (16–22.5ka) and middle-late Holocene, but lower concentrations during the last deglacial and Preboreal periods (15.8–9.5ka) (Figure 4g). Generally, concentrations of excess Mo and excess U (Figures 4j, l) show coherent patterns with those of Mo and U (Figures 4i, k), but both are out-of-phase with Mn over the last glacial period (Figure 4h). It should be noted that pronounced variations in U concentration since 8.5 ka is related to the occurrence of discrete volcanic materials. A negative correlation between Mn and Mo_{excess} during the last glaciation and the Holocene, and the strong positive correlation between them during the LGM and HS1 (Figures 5a and 5b) further corroborate the complicated geochemical behavior of Mn and Mo. A strong positive correlation between Mo_{excess} and Mn (Figure 5b) seems to be attributed to co-precipitation of Mo by Mn-oxyhydroxide under oxygenated conditions. Here, we use Mo/Mn ratio, instead of excess Mo concentration to reconstruct variations in sedimentary redox state. Overall, the Mo/Mn ratio shows similar downcore pattern to that of Mo_{excess} with higher values during the last deglaciation, but lower values during the LGM and HS1. A strong correlation between Mo/Mn ratio and excess U concentration (Figure 5c) further corroborates the integrity of Mo/Mn as an indicator of sedimentary oxygenation changes.

Rapidly decreasing Mo/Mn ratio indicates an oxygenated sedimentary environment since ~8 ka (Figure 4h). Both higher Mo/Mn ratios and excess U concentration, together with lower Mn concentrations suggest an oxygen-deficient sedimentary environment during the late deglacial period (15.8–9.5 ka), whereas lower values during the LGM, HS1 and HS2 indicate relatively better oxygenated sedimentary condition. A decreasing trend in Mo/Mn ratio and excess U concentration from 50 ka to 25 ka also suggest higher sedimentary oxygen levels.

6.Discussion

6.1. Constraining paleoredox conditions in the Okinawa Trough

In general, three different terms, hypoxia, suboxia and anoxia, are widely used to describe the degree of oxygen depletion in the marine environment (Hofmann et al., 2011). Generally, redox states in waters can be classified as oxic (>89 μmol /L O_2), suboxic (~8.9-89 μmol/LO_2), anoxic–nonsulfidic (<89 μmol/L O_2, 0 μmol/L H_2S), and anoxic– sulfidic or euxinic (0 ml O_2/L, >0 μmol/L H_2S) (Savrda and Bottjer, 1991).

Proxies associated with RSEs, such as sedimentary Mo concentration (Lyons et al., 2009; Scott et al., 2008) have been used to constrain the degree of oxygenation in seawater. Algeo and Tribovillard (2009) proposed that open-ocean systems with suboxic waters tend to yield U_{excess} enrichment relative to Mo_{excess} and to result in sediment $(Mo/U)_{excess}$ ratio less than that of seawater (7.5-7.9). Under increasingly reducing and occasionally sulfidic conditions, the accumulation of Mo_{excess} increase

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relative to that of U_{excess} leading the $(Mo/U)_{excess}$ ratio either is equal to or exceeds with that of seawater. Furthermore, Scott and Lyons (2012) suggested a non-euxinic condition with the presence of sulfide in pore waters, when Mo concentrations range from> 2 ppm, the crustal average to < 25 ppm, a threshold concentration for euxinic condition. Given that the Okinawa Trough is located in weakly restricted basin settings, we use these two above mentioned proxies to evaluate the degree of oxygenation in sediments.

Both bulk Mo concentration (1.2-9.5 ppm) and excess (Mo/U) ratio (0.2-5.7) in core CSH1 suggest that oxygen-depleted conditions may have prevailed in the deep water of the northern OT over the last 50 ka. However, increased excess Mo concentration with enhanced Mo/U ratio during the last termination (18-9 ka) indicate a stronger reducing condition compared to the Holocene and the last glacial period, though Mo concentration is less than 25 ppm, a threshold for euxinic deposition proposed by Scott and Lyons (2012).

The relative abundance of benthic foraminiferal species that thrive in different oxygen concentrations also have been widely used to reconstruct the variations in bottom water ventilation, such as enhanced abundance *of Bulimina aculeata*, *Uvigerina peregrina and Chilostomella oolina* found under oxygen-depleted conditions in the central and southern OT during the last deglaciation (Jian et al., 1996; Li et al., 2005). An oxygenated bottom water condition is also indicated by abundant benthic foraminifera species *Cibicidoides hyalina* and *Globocassidulina subglobosa* (Jian et al., 1996; Li et al., 2005) and high benthic $\delta^{13}C$ values (Wahyudi and Minagawa, 1997) in cores E017 (water depth 1826 m) , 225 (water depth 1575 m) and PN-3 (water depth 1058 m) from the middle and southern OT (Figures 1 and 3) during the postglacial period. The inferred ventilation pattern from benthic foraminiferal assemblages is consistent with the one inferred from RSEs in this study (Figure 4). Although we did not carry out benthic foraminiferal species analyses for our core CSH1, it is reasonable to infer based on RSEs that the deepwater in the northern OT was also in a prominent oxygen-poor condition during the late deglacial interval. A clear link thus can be built between the ventilation of deep water and the

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sedimentary oxygenation in the OT. In brief, our proxy records of RSEs in core CSH1 show oxygen-rich conditions during the last glaciation and middle and late Holocene (since 8.5 ka) intervals, but oxygen-poor conditions during the late deglacial period.

6.2. Causes for sedimentary oxygenation variations

As discussed above, the pattern of RSEs in core CSH1 suggest that drastic changes in sedimentary oxygenation occurred on orbital and millennial timescales over the last glaciation in the Okinawa Trough. In general, four factors can regulate the redox condition in the deep water column: (i) O_2 solubility, (ii) export productivity and subsequent degradation of organic matter, (iii) vertical mixing, and (iv) lateral provision of oxygen through intermediate and deeper water masses (Ivanochko and Pedersen, 2004; Jaccard and Galbraith, 2012). In the OT, the oxygen deficiency during the late deglacial period can be caused either by one and/or a combination of more than one of these factors. In order to uncover the mechanisms responsible for sedimentary oxygenation variations in the basin-wide OT, we compare our proxy records of sedimentary oxygenation (U_{excess} concentration and Mo/Mn ratio) and export productivity ($CaCO_3$) with benthic foraminifera $\delta^{13}C$, a proxy for water mass, in core PC23A (Rella et al., 2012), abundance of benthic foraminifera in the NE Pacific, an indicator of anoxic condition (Cannariato and Kennett, 1999), abundance of *Pulleniatina obliquiloculata*, an indicator of the Kuroshio strength (Shi et al., 2014) (Figure 6).

6.2.1. Effects of regional ocean temperature on deglacial deoxygenation

Warming ocean temperatures lead to lower oxygen solubility. In the geological past, solubility effects connected to temperature changes of the water column thought to enhance or even trigger hypoxia (Praetorius et al., 2015). For instance, Shi et al. (2014) reported an increase in SST of around 4°C (~21°Cto ~24.6°C) during the last deglaciation in core CSH1. Based on thermal solubility effects, a hypothetical warming of 1°C at our site would reduce oxygen concentrations by about 8 μM (Benson and Krause, 1984), which could drive a drastic drop of oxygen concentration by <30 μM in subsurface water of the OT. Therefore, we assume that the late deglacial hypoxia in the OT underwent a similar increase in ocean temperatures.

However, given the semi-quantitative nature of our data about oxygenation changes, which seemingly exceed an amplitude of >30 μM, we suggest that other factors, in particular processes like local changes in export productivity, regional influences such as vertical mixing due to changes of the Kuroshio Current, as well as far-field effects all may have played some decisive roles in shaping the oxygenation history of the OT.

6.2.2. Links between deglacial primary productivity and sedimentary deoxygenation

Previous studies have suggested the occurrence of high primary productivity in the entire OT during the last deglacial period (Chang et al., 2009; Jian et al., 1996; Kao et al., 2008; Li et al., 2017; Shao et al., 2016; Wahyudi and Minagawa, 1997). Such an increase in export production was due to favorable conditions for bloom development, which were likely induced by warm temperatures and maxima in nutrient availability, the latter being mainly sourced from increased discharge of the Changjiang River, erosion of material from the ongoing flooding of the shallow continental shelf in the ECS, and upwelling of Kuroshio Intermediate Water (Chang et al., 2009; Li et al., 2017; Shao et al., 2016; Wahyudi and Minagawa, 1997). On the basis of sedimentary reactive phosphorus concentration, Li et al. (2017) concluded that export productivity increased during warm episodes but decreased during cold spells on millennial timescales over the last 91 ka in the OT. Gradually increasing concentrations of $CaCO_3$ in core CSH1 during the deglaciation (Figure 6a) and little changes in foraminiferal fragmentation ratios (Wu et al., 2004), are indicative of high export productivity in the northern OT. Accordingly, our data indicate that an increase in export productivity, which was previously reported from the middle and southern OT during the last deglaciation, and thus was a pervasive, synchronous phenomenon of entire study region at the outermost extension of the ECS.

As a consequence, high export productivity lowers oxygen concentrations in deeper waters, due to subsurface consumption of oxygen by remineralization of organic matter. Similar events of high export productivity have been extensively reported in the entire North Pacific due to increased nutrient supply, high SST, reduced sea ice cover, etc. (Crusius et al., 2004; Dean et al., 1997; Jaccard and

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Galbraith, 2012; Kohfeld and Chase, 2011). In most of these cases, the increases in productivity were likely also responsible for oxygen depletion in mid-depth waters, due to exceptionally high oxygen consumption. However, the productivity changes during the deglacial interval, very specifically $CaCO_3$, are not fully consistent with the trends of excess U and Mo/Mn ratio (Figure 4). The sedimentary oxygenation thus cannot be determined by export productivity alone.

6.2.3 Effects of the Kuroshio dynamics on sedimentary oxygenation

The Kuroshio Current, one of the main drivers of vertical mixing, has been identified as the key factor in controlling modern deep ventilation in the Okinawa Trough (Kao et al., 2006). However, the flow path of the Kuroshio in the Okinawa Trough during the glacial interval remains a matter of debate. Planktic foraminiferal assemblages in sediment cores from inside and outside the Okinawa Trough indicated that the Kuroshio have migrated to the east of the Ryukyu Islands during the LGM (Ujiié and Ujiié, 1999). Subsequently, Kao et al. (2006) based on modeling results suggested that the Kuroshio still enters into the Okinawa Trough, but the volume transport was reduced by 43% compared to the present-day transport and the outlet of Kuroshio switches from the Tokara Strait to the Kerama Gap at -80 and -135m lowered sea level. Combined with sea surface temperature (SST) records and ocean model results, Lee et al. (2013) argued that there was little effect of deglacial sea-level change on the path of the Kuroshio, which still exited the Okinawa Trough from the Tokara Strait during the glacial period. Because the main stream of the Kuroshio Current is at a water depth of ~150 m, the SST records are insufficient to decipher past changes of the Kuroshio (Ujiié et al., 2016).On the other hand, low abundances of *P. obliquiloculata* in core CSH1 in the northern OT (Figure 6e) indicate that the main flow path of the Kuroshio may have migrated to the east of the Ryukyu Island (Shi et al., 2014). Such a flow change would have been caused by the proposed block of the Ryukyu-Taiwan land bridge by low sea level (Ujiié and Ujiié, 1999) and an overall reduced Kuroshio intensity (Kao et al., 2006), effectively suppressing the effect of the Kuroshio on deep ventilation in the OT. Our RSEs data show that oxygenated sedimentary conditions were dominant in the northern OT throughout the last glacial

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period (Figures 6a, b, c, d). The Kuroshio thus likely had a weak or even no effect on the renewal of oxygen to the sedimentary environment during the last glacial period.

On the other hand, the gradually increasing abundance of *P.obliquiloculata* (Figure 6e) from 15 ka onwards indicates an intensified Kuroshio Current. Matsumoto et al. (2002) suggested that the influence of the present Kuroshio can reach to the bottom depth of the permanent thermocline, which is approximately at 1000 m water depth. However, as mentioned above, the effect of Kuroshio on the sedimentary oxygenation was likely very limited during glacial period and only gradually increasing throughout the last glacial termination. Therefore, while its effect on our observed deglacial variation in oxygenation may provide a slowly changing background condition in vertical mixing effects on the sedimentary oxygenation in the OT, it cannot account for the first order, rapid oxygenation changes that we observe between 18 and 9 ka, including indications for millennial-scale variations (Figure 6).

Better oxygenated sedimentary conditions since 8.5 ka coincided with intensified Kuroshio (Shi et al., 2014; Ujiié et al., 2003), as indicated by rapidly increased SST and *P. obliquiloculata* abundance in core CSH1 (Figure 6e). The re-entrance of the Kuroshio into the OT (Shi et al., 2014) with rising eustatic sea level likely enhanced the vertical mixing and exchange between bottom and surface waters, ventilating the deep water in the OT. Previous comparative studies based on epibenthic $\delta^{13}C$ values indicated well-ventilated deep water feeding both inside the OT and outside off the Ryukyu Islands during the Holocene (Kubota et al., 2010; Wahyudi and Minagawa, 1997). In summary, during the Holocene our observed enhanced sedimentary oxygenation regime is mainly related to the intensified Kuroshio, while the effect of the Kuroshio on OT oxygenation was limited before 15 ka.

6.2.4. Effects of GNPIW on sedimentary oxygenation

Relatively stronger oxygenated Glacial North Pacific Intermediate Water (GNPIW), coined by (Matsumoto et al., 2002), has been widely documented in the Bering Sea (Itaki et al., 2012; Kim et al., 2011; Rella et al., 2012), the Okhotsk Sea (Itaki et al., 2008; Okazaki et al., 2014; Okazaki et al., 2006; Wang and Wang, 2008; Wu et al., 2014), off east Japan (Shibahara et al., 2007), the eastern North Pacific

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(Cartapanis et al., 2011; Ohkushi et al., 2013) and western subarctic Pacific (Keigwin, 1998; Matsumoto et al., 2002). The intensified ventilation of GNPIW is firstly attributable to the displacement of formation source region to the Bering Sea (Ohkushi et al., 2003) and then is further confirmed by Horikawa et al. (2010). Under such conditions, the invasion of well-ventilated GNPIW into the OT through the Kerama Gap would have replenished the water column oxygen in the OT, although the penetration depth of GNPIW remains under debate(Jaccard and Galbraith, 2013; Okazaki et al., 2010; Rae et al., 2014). Both a gradual decrease in excess U concentration and an increase in Mo/Mn ratio during the last glacial period (25-50 ka) validate such inference, suggesting pronounced effects of intensified GNPIW in the OT.

During HS1, a stronger formation of GNPIW was recorded in the North Pacific by a variety of studies. On the basis of paired benthic-planktic (B-P) ^{14}C data and model simulations, Okazaki et al. (2010) suggested that NPIW penetrated into a water depth of ~2500 to 3000 m during HS1. In contrast, Max et al. (2014) argued against deep water formation in the North Pacific and showed that GNPIW was well-ventilated only to intermediate water depths (< 1400 m). Various mid- and high-latitude North Pacific records of B-P ^{14}C age offsets at the intermediate water depth (<600–2000 m) showed an active production of GNPIW during HS1 (Max et al., 2014; Sagawa and Ikehara, 2008). Moreover, Kubota et al. (2010) reported increased subsurface water temperatures related to enhanced GNPIW contributions during HS1 at a water depth of 1166m (GH08, and young deep water was observed in the northern South China Sea during HS1 (Wan and Jian, 2014).

All these multiple lines of evidence imply the presence of well-ventilated intermediate water in the upper 2000 m of the North Pacific during HS1. At this point, the effect of a strong GNPIW likely reached the South China Sea (Wan and Jian, 2014; Zheng et al., 2016), further to the south the Okinawa Trough. The pathway of GNPIW from numerical model simulations(Zheng et al., 2016) was similar to modern observations (You, 2003). Thus, a persistent, cause and effect relation has been established between GNPIW ventilation, the oxygen concentration of OT deepwater

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and sediment redox state during HS1. In addition, our data also suggested a similarly enhanced ventilation in HS2 (Figure 6) that must also be attributed to intensified GNPIW.

Hypoxic conditions during Bölling-Alleröd (B/A) have been also widely observed in the mid- and high-latitude North Pacific (Jaccard and Galbraith, 2012; Praetorius et al., 2015). Our data, both excess U concentrations and Mo/Mn ratio recorded in core CSH1 (Figures 6b-d), further reveal the expansion of oxygen-depletion at mid-depth waters down to the subtropical NW Pacific during the late deglacial period. Based on high relative abundances of radiolarian species, indicators of upper intermediate water ventilation in core PC-23A, Itaki et al. (2012) suggested that a presence of well-ventilated waters was limited to the upper intermediate layer (200–500 m) in the Bering Sea during warm periods, such as the B/A and Preboreal. Higher B-P foraminiferal ^{14}C ages, together with increased intermediate water temperature and salinity recorded in core GH02-1030 (off East Japan) supported a weakened formation of NPIW during the B/A (Sagawa and Ikehara, 2008).These lines of evidence indicate that the boundary between GNPIW and North Pacific Deep Water shoaled during the B/A, in comparison to HS1. Based on a comparison of two benthic foraminiferal oxygen and carbon isotope records from off northern Japan and the southern Ryukyu Island, Kubota et al. (2010) found a stronger influence of Pacific Deep Water on intermediate-water temperature and ventilation at their southern than the northern locations, although both sites are located at similar water depths (1166 m and 1212 m, respectively). Higher excess U concentration and low Mo/Mn ratio in our core CSH1 during the B/A and Preboreal suggest reduced sedimentary oxygenation, consistent with reduced ventilation of GNPIW, contributing to the subsurface water suboxia in the OT.

During the YD, Mo/Mn ratio and excess U show a slightly decreased oxygen condition in the northern OT. In contrast, benthic foraminiferal $\delta^{18}O$ and $\delta^{13}C$ values in a sediment core collected from the Oyashio region suggested a strengthened formation and ventilation of GNPIW during the YD (Ohkushi et al., 2016). This pattern possibly indicates a time-dependent, varying contribution of distal GNPIW to

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the deglacial OT oxygenation history, and we presume a more pronounced contribution of organic matter degradation due to high export productivity during this period, as suggested by increasing $CaCO_3$ content.

6.3. Subtropical North Pacific ventilation links to North Atlantic Climate

Our RSEs data show a substantial millennial variability in intermediate water ventilation in the subtropical North Pacific. Notably, both enhanced ventilation during HS1 and HS2 and oxygen-poor condition during the B/A respectively correspond to the collapse and resumption of Atlantic meridional overturning circulation (AMOC) (Bohm et al., 2015; McManus et al., 2004) (Figure 7 d). This is consistent with the results of various modeling simulations (Chikamoto et al., 2012; Menviel et al., 2014; Okazaki et al., 2010; Saenko et al., 2004), although these models had different scenarios and causes for the observed effects in GNPIW formation, and ventilation ages derived from B-P^{14}C (Freeman et al., 2015; Max et al., 2014; Okazaki et al., 2012). These lines of evidence reveal a persistent link between the ventilation of North Pacific and the North Atlantic climate. Such links have also been corroborated by using proxy data and modeling experiment between AMOC and East Asian monsoon during the 8.2 ka event (Liu et al., 2013), the Holocene (Wang et al., 2005) and 34–60 ka (Sun et al., 2012). The mechanism linking East Asia with North Atlantic has been attributed to an atmospheric teleconnection, such as the position and strength of Westerly Jet and Mongolia-Siberian High (Porter and Zhisheng, 1995). However, the mechanism behind such oceanic ventilation seesaw pattern between the North Atlantic and North Pacific is still unclear.

Increased NPIW formation of HS1 may have been caused by enhanced salinity-driven vertical mixing through higher meridional water mass transport from the subtropical Pacific. Previous studies have proposed that intermediate water formation in the North Pacific hinged on a basin-wide increase in sea surface salinity driven by changes in strength of the summer EAM and the moisture transport from the Atlantic to the Pacific (Emile-Geay et al., 2003). Several modeling studies found that freshwater forcing in the North Atlantic could cause a widespread surface salinification in the subtropical Pacific Ocean (Menviel et al., 2014; Okazaki et al., 2010; Saenko et al., 2004). This idea has been tested by proxy data (Rodríguez-Sanz et al., 2013; Sagawa and Ikehara, 2008), which indicated a weakened summer EAM and reduced transport of moisture from Atlantic to Pacific through Panama Isthmus owing to the southward displacement of ITCZ caused by a weakening of AMOC. Along with this process, as predicted through a general circulation modeling, a strengthened Pacific Meridional Overturning Circulation would have transported more warm and salty subtropical water into the high-latitude North Pacific (Okazaki et al., 2010). In accordance with comprehensive Mg/Ca ratio-based salinity reconstructions, however, Riethdorf et al. (2013) found no clear evidence for such higher salinity patterns in the subarctic northwest Pacific during HS1.

On the other hand, a weakened AMOC would deepen the wintertime Aleutian Low (Okumura et al., 2009), which is closely related to the sea ice formation in the marginal seas of the subarctic Pacific (Cavalieri and Parkinson, 1987). Intense brine rejection, accompanied by expanded sea ice formation, would have enhanced the NPIW formation. Recently our modeling-derived evidence suggests enhanced sea ice coverage in the southern Okhotsk Sea and off East Kamchatka Peninsula (Gong et al., 2019). In addition, higher advection of low-salinity water via the Alaskan Stream to the subarctic NW Pacific was probably enhanced during HS1, related to a shift of the Aleutian Low pressure system over the North Pacific, which could also increase sea ice formation, brine rejection and thereafter intermediate water ventilation (Riethdorf et al., 2013).

During the late deglaciation, ameliorating global climate conditions, such as warming Northern Hemisphere, and a strengthened Asian summer monsoon, are a result of changes in insolation forcing, greenhouse gases concentrations, and variable strengths of the AMOC (Clark et al., 2012; Liu et al., 2009). During the B/A, a decrease in sea ice extent and duration, as well as reduced advection of Alaska Stream waters were indicated by combined reconstructions of SST and mixed layer temperatures from the subarctic Pacific (Riethdorf et al., 2013). At that time, the rising eustatic sea level (Spratt and Lisiecki, 2016) would have supported the intrusion of Alaska Stream into the Bering Sea by deepening and opening glacial

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closed straits of the Aleutian Islands chain, while reducing the advection of the Alaska Stream to the subarctic Pacific gyre (Riethdorf et al., 2013). In this scenario, saltier and more stratified surface water conditions would have inhibited brine rejection and subsequent formation and ventilation of NPIW (Lam et al., 2013), leading to a reorganization of the Pacific water mass, closely coupled to the collapse and resumption modes of the AMOC during these two intervals.

6.4 Increased storage of CO_2 at mid-depth water in the North Pacific at the B/A

One of the striking features of RSEs data is higher Mo/Mn ratios and excess U concentrations at the B/A, indicating a substantial oxygen-poor condition in the subtropical North Pacific, coinciding with the termination of atmospheric CO_2 concentration rise (Marcott et al., 2014) (Figure 7a). As described above, it can be related to the upwelling of nutrient- and CO_2-rich Pacific Deep Water due to resumption of AMOC and enhanced export production. Although here we are unable to distinguish these two reasons from each other, boron isotope data measured on surface-dwelling foraminifera in core MD01-2416 situated in the western subarctic North Pacific did reveal a decrease in near-surface pH and an increase in pCO_2 at this time (Gray et al., 2018). That is to say, subarctic North Pacific is a source of relatively high atmospheric CO_2 concentration at the B/A. Here we cannot conclude that the same processes could have occurred in the subtropical North Pacific due to the lack of well-known drivers to draw out of the old carbon in the deep sea into the atmosphere. However, an expansion of oxygen-depletion zone in the entire North Pacific suggest an increase in respired carbon storage at intermediate-depth in the subtropical North Pacific, which likely stalls the rise of atmospheric CO_2. Our results support the findings by Galbraith et al. (2007) and are consistent with the hypothesis of deglacial flushing of respired carbon dioxide from an isolated, deep ocean reservoir(Marchitto et al., 2007; Sigman and Boyle, 2000). Given the sizeable volume of the North Pacific, potentially, once the respired carbon could be emitted to the atmosphere in stages, which would play an important role in propelling the Earth out of the last ice age (Jaccard and Galbraith, 2018).

7. Conclusions

Our geochemical results revealed substantial changes in intermediate water redox conditions in the northern Okinawa Trough over the last 50kaon orbital and millennial timescales in the past. The sedimentary oxygenation variability presented here provides key evidence for the impact of ventilation of NPIW on the sedimentary oxygenation in the subtropical North Pacific and highlights the major role of Atlantic Meridional Overturning Circulation in regulating the variations in sedimentary oxygenation in the Okinawa Trough through ventilation of NPIW. Combined with other published records, we also suggest an expansion of oxygen-depleted zone and accumulation of respired carbon at the mid-depth waters of the North Pacific at the B/A, coinciding with the termination of atmospheric CO_2 rise. Once the release of the sequestered carbon into the atmosphere in stages, it would be helpful to maintain high atmospheric CO_2 levels during the deglaciation and to propel the earth out of the glacial climate.

Data availability. All raw data are available to all interested researchers upon request.

Author Contributions. J.J.Z. and X.F.S. conceived the study. A.M.Z. performed geochemical analyses of bulk sediments. J.J.Z., X.F.S. K.S. and X.G. led the write up of the manuscript. All other authors provided comments on the manuscript and contributed to the final version of the manuscript.

Competing interests: The authors declare no competing interests.

Acknowledgements

Financial support was provided by the National Program on Global Change and Air-Sea Interaction (GASI-GEOGE-04), by the National Natural Science Foundation of China (Grant Nos.: 41476056, 41876065, 41420104005, 41206059, and U1606401) and by the Basic Scientific Fund for National Public Research Institutes of China (No.2016Q09) and International Cooperative Projects in Polar Study (201613)and Taishan Scholars Program of Shandong.This study is a contribution to the bilateral

Sino-German collaboration project (funding through BMBF grant 03F0704A – SIGEPAX). XG, LLJ, GL, RT thank the bilateral Sino-German collaboration NOPAWAC project (BMBF grant No. 03F0785A).LLJ and RT acknowledge financial support through the national Helmholtz REKLIM Initiative. We would like to thank the anonymous reviewers, who helped to improve the quality of this manuscript. The data used in this study are available from the authors upon request (zoujianjun@fio.org.cn).

References

Algeo, T. J.: Can marine anoxic events draw down the trace element inventory of seawater?, Geology, 32, 1057-1060, 2004.

Algeo, T. J. and Lyons, T. W.: Mo-total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions, Paleoceanography, 21, PA1016, doi: 1010.1029/2004pa001112, 2006.

Algeo, T. J. and Tribovillard, N.: Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation, Chemical Geology, 268, 211-225, 2009.

Benson, B. B. and Krause, D.: The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere, Limnology and Oceanography, 29, 620-632, 1984.

Bohm, E., Lippold, J., Gutjahr, M., Frank, M., Blaser, P., Antz, B., Fohlmeister, J., Frank, N., Andersen, M. B., and Deininger, M.: Strong and deep Atlantic meridional overturning circulation during the last glacial cycle, Nature, 517, 73-76, 2015.

Burdige, D. J.: The biogeochemistry of manganese and iron reduction in marine sediments, Earth-Science Reviews, 35, 249-284, 1993.

Cannariato, K. G. and Kennett, J. P.: Climatically related millennial-scale fluctuations in strength of California margin oxygen-minimum zone during the past 60 k.y, Geology, 27, 975-978, 1999.

Cartapanis, O., Tachikawa, K., and Bard, E.: Northeastern Pacific oxygen minimum zone variability over the past 70 kyr: Impact of biological production and oceanic ventilation, Paleoceanography, 26, PA4208, doi: 4210.1029/2011PA002126, 2011.

Cavalieri, D. J. and Parkinson, C. L.: On the relationship between atmospheric circulation and the fluctuations in the sea ice extents of the bering and okhotsk seas, Journal of Geophysical Research-Oceans, 92, 7141-7162, 1987.

Chang, A. S., Pedersen, T. F., and Hendy, I. L.: Effects of productivity, glaciation, and ventilation on late Quaternary sedimentary redox and trace element accumulation on the Vancouver Island margin, western Canada, Paleoceanography, 29, doi: 10.1002/2013PA002581, 2014.

Chang, Y.-P., Chen, M.-T., Yokoyama, Y., Matsuzaki, H., Thompson, W. G., Kao, S.-J., and Kawahata, H.: Monsoon hydrography and productivity changes in the East China Sea during the past 100,000 years: Okinawa Trough evidence (MD012404), Paleoceanography, 24, PA3208, doi: 3210.1029/2007PA001577, 2009.

Chen, J., Zhang, D., Zhang, W., and Li, T.: The paleoclimatic change since the last galciation in the north of Okinawa Trough based on the spore-pollen records, Acta Oceanologica Sinica, 28, 85-91, 2006 (in Chinese with English Abstract).

Cheng, H., Edwards, R. L., Sinha, A., Spötl, C., Yi, L., Chen, S., Kelly, M., Kathayat, G., Wang, X., Li, X., Kong, X., Wang, Y., Ning, Y., and Zhang, H.: The Asian monsoon over the past 640,000 years and ice age terminations, Nature, 534, 640-646, 2016.

Cheng, H., Edwards, R. L., Southon, J., Matsumoto, K., Feinberg, J. M., Sinha, A., Zhou, W., Li, H., Li, X., Xu, Y., Chen, S., Tan, M., Wang, Q., Wang, Y., and Ning, Y.: Atmospheric 14C/12C changes during the last glacial period from Hulu Cave, Science, 362, 1293-1297, 2018.

Chikamoto, M. O., Menviel, L., Abe-Ouchi, A., Ohgaito, R., Timmermann, A., Okazaki, Y., Harada, N., Oka, A., and Mouchet, A.: Variability in North Pacific intermediate and deep water ventilation during Heinrich events in two coupled climate models, Deep Sea Research Part II: Topical Studies in Oceanography, 61-64, 114-126, 2012.

Clark, P. U., Shakun, J. D., Baker, P. A., Bartlein, P. J., Brewer, S., Brook, E., Carlson, A. E., Cheng, H., Kaufman, D. S., Liu, Z., Marchitto, T. M., Mix, A. C., Morrill, C., Otto-Bliesner, B. L., Pahnke, K., Russell, J. M., Whitlock, C., Adkins, J. F., Blois, J. L., Clark, J., Colman, S. M., Curry, W. B., Flower, B. P., He, F., Johnson, T. C., Lynch-Stieglitz, J., Markgraf, V., McManus, J., Mitrovica, J. X., Moreno, P. I., and Williams, J. W.: Global climate evolution during the last deglaciation, Proceedings of the National Academy of Sciences of the United States of America, 109, E1134-E1142, 2012.

Clemens, S. C., Holbourn, A., Kubota, Y., Lee, K. E., Liu, Z., Chen, G., Nelson, A., and Fox-Kemper, B.: Precession-band variance missing from East Asian monsoon runoff, Nature Communications, 9, 3364, doi: 3310.1038/s41467-41018-05814-41460, 2018.

Crusius, J., Calvert, S., Pedersen, T., and Sage, D.: Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition, Earth and Planetary Science Letters, 145, 65-78, 1996.

Crusius, J., Pedersen, T. F., Kienast, S., Keigwin, L., and Labeyrie, L.: Influence of northwest Pacific productivity on North Pacific Intermediate Water oxygen concentrations during the Boiling-Allerod interval (14.7-12.9 ka), Geology, 32, 633-636, 2004.

Dahl, T. W., Anbar, A. D., Gordon, G. W., Rosing, M. T., Frei, R., and Canfield, D. E.: The behavior of molybdenum and its isotopes across the chemocline and in the sediments of sulfidic Lake Cadagno, Switzerland, Geochimica et Cosmochimica Acta, 74, 144-163, 2010.

Dean, W. E., Gardner, J. V., and Piper, D. Z.: Inorganic geochemical indicators of glacial-interglacial changes in productivity and anoxia on the California continental margin, Geochimica et Cosmochimica Acta, 61, 4507-4518, 1997.

Delcroix, T. and Murtugudde, R.: Sea surface salinity changes in the East China Sea during 1997–2001: Influence of the Yangtze River, Journal of Geophysical Research: Oceans, 107, 8008, doi:8010.1029/2001JC000893, 2002.

Dou, Y., Yang, S., Li, C., Shi, X., Liu, J., and Bi, L.: Deepwater redox changes in the southern Okinawa Trough since the last glacial maximum, Progress in Oceanography, 135, 77-90, 2015.

Emile-Geay, J., Cane, M. A., Naik, N., Seager, R., Clement, A. C., and van Geen, A.: Warren revisited: Atmospheric freshwater fluxes and “Why is no deep water formed in the North Pacific”, Journal of Geophysical Research: Oceans, 108, 3178, 2003.

Freeman, E., Skinner, L. C., Tisserand, A., Dokken, T., Timmermann, A., Menviel, L., and Friedrich, T.: An Atlantic–Pacific ventilation seesaw across the last deglaciation, Earth and Planetary Science Letters, 424, 237-244, 2015.

https://doi.org/10.5194/cp-2019-70
Preprint. Discussion started: 20 June 2019

Galbraith, E. D., Jaccard, S. L., Pedersen, T. F., Sigman, D. M., Haug, G. H., Cook, M., Southon, J. R., and Francois, R.: Carbon dioxide release from the North Pacific abyss during the last deglaciation, Nature, 449, 890-893, 2007.

Galbraith, E. D., Kienast, M., Pedersen, T. F., and Calvert, S. E.: Glacial-interglacial modulation of the marine nitrogen cycle by high-latitude O2 supply to the global thermocline, Paleoceanography, 19, PA4007, doi:4010.1029/2003PA001000, 2004.

Ge, S., Shi, X., Wu, Y., Lee, T., Xiong, Y., and Saito, Y.: Rock magnetic property of gravity core CSH1 from the northern Okinawa Trough and the effect of early diagenesis, Acta Oceanologica Sinica, 26, 54-65, 2007.

Gong, X., Lembke-Jene, L., Lohmann, G., Knorr, G., Tiedemann, R., Zou, J. J., and Shi, X. F.: Enhanced North Pacific deep-ocean stratification by stronger intermediate water formation during Heinrich Stadial 1, Nature Communications, 10, 656, doi:610.1038/s41467-41019-08606-41462, 2019.

Gray, W. R., Rae, J. W. B., Wills, R. C. J., Shevenell, A. E., Taylor, B., Burke, A., Foster, G. L., and Lear, C. H.: Deglacial upwelling, productivity and CO2 outgassing in the North Pacific Ocean, Nature Geoscience, 11, 340-344, 2018.

Helz, G. R., Miller, C. V., Charnock, J. M., Mosselmans, J. F. W., Pattrick, R. A. D., Garner, C. D., and Vaughan, D. J.: Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence, Geochimica et Cosmochimica Acta, 60, 3631-3642, 1996.

Hofmann, A. F., Peltzer, E. T., Walz, P. M., and Brewer, P. G.: Hypoxia by degrees: Establishing definitions for a changing ocean, Deep Sea Research Part I: Oceanographic Research Papers, 58, 1212-1226, 2011.

Horikawa, K., Asahara, Y., Yamamoto, K., and Okazaki, Y.: Intermediate water formation in the Bering Sea during glacial periods: Evidence from neodymium isotope ratios, Geology, 38, 435-438, 2010.

Ichikawa, H. and Beardsley, R. C.: The Current System in the Yellow and East China Seas, Journal of Oceanography, 58, 77-92, 2002.

Itaki, T., Khim, B. K., and Ikehara, K.: Last glacial-Holocene water structure in the southwestern Okhotsk Sea inferred from radiolarian assemblages, Marine Micropaleontology, 67, 191-215, 2008.

Itaki, T., Kim, S., Rella, S. F., Uchida, M., Tada, R., and Khim, B. K.: Millennial-scale variations of late Pleistocene radiolarian assemblages in the Bering Sea related to environments in shallow and deep waters, Deep-Sea Research Part Ii-Topical Studies in Oceanography, 61-64, 127-144, 2012.

Ivanochko, T. S. and Pedersen, T. F.: Determining the influences of Late Quaternary ventilation and productivity variations on Santa Barbara Basin sedimentary oxygenation: a multi-proxy approach, Quaternary Science Reviews, 23, 467-480, 2004.

Jaccard, S. L. and Galbraith, E. D.: Direct ventilation of the North Pacific did not reach the deep ocean during the last deglaciation, Geophysical Research Letters, 40, 199-203, 2013.

Jaccard, S. L. and Galbraith, E. D.: Large climate-driven changes of oceanic oxygen concentrations during the last deglaciation, Nature Geoscience, 5, 151-156, 2012.

Jaccard, S. L. and Galbraith, E. D.: Push from the Pacific, Nature Geoscience, 11, 299-300, 2018.

Jaccard, S. L., Galbraith, E. D., Martínez-García, A., and Anderson, R. F.: Covariation of deep Southern Ocean oxygenation and atmospheric CO2 through the last ice age, Nature, 530, 207-210, 2016.

Jaccard, S. L., Galbraith, E. D., Sigman, D. M., Haug, G. H., Francois, R., Pedersen, T. F., Dulski, P., and Thierstein, H. R.: Subarctic Pacific evidence for a glacial deepening of the oceanic respired carbon pool, Earth and Planetary Science Letters, 277, 156-165, 2009.

https://doi.org/10.5194/cp-2019-70
Preprint. Discussion started: 20 June 2019

Jian, Z. M., Chen, R. H., and Li, B. H.: Deep-sea benthic foraminiferal record of the paleoceanography in the southern Okinawa trough over the last 20000 years, Science in China Series D-Earth Sciences, 39, 551-560, 1996.

Kao, S. J., Horng, C. S., Hsu, S. C., Wei, K. Y., Chen, J., and Lin, Y. S.: Enhanced deepwater circulation and shift of sedimentary organic matter oxidation pathway in the Okinawa Trough since the Holocene, Geophysical Research Letters, 32, L15609, doi:15610.11029/12005GL023139, 2005.

Kao, S. J., Liu, K. K., Hsu, S. C., Chang, Y. P., and Dai, M. H.: North Pacific-wide spreading of isotopically heavy nitrogen during the last deglaciation: Evidence from the western Pacific, Biogeosciences, 5, 1641-1650, 2008.

Kao, S. J., Wu, C.-R., Hsin, Y.-C., and Dai, M.: Effects of sea level change on the upstream Kuroshio Current through the Okinawa Trough, Geophysical Research Letters, 33, L16604, doi:16610.11029/12006gl026822, 2006.

Keigwin, L. D.: Glacial-age hydrography of the far northwest Pacific Ocean, Paleoceanography, 13, 323-339, 1998.

Kim, S., Khim, B. K., Uchida, M., Itaki, T., and Tada, R.: Millennial-scale paleoceanographic events and implication for the intermediate-water ventilation in the northern slope area of the Bering Sea duriing the last 71 kyrs, Global and Planetary Change, 79, 89-98, 2011.

Klinkhammer, G. P. and Palmer, M. R.: Uranium in the oceans: Where it goes and why, Geochimica et Cosmochimica Acta, 55, 1799-1806, 1991.

Kohfeld, K. E. and Chase, Z.: Controls on deglacial changes in biogenic fluxes in the North Pacific Ocean, Quaternary Science Reviews, 30, 3350-3363, 2011.

Kubota, Y., Kimoto, K., Tada, R., Oda, H., Yokoyama, Y., and Matsuzaki, H.: Variations of East Asian summer monsoon since the last deglaciation based on Mg/Ca and oxygen isotope of planktic foraminifera in the northern East China Sea, Paleoceanography, 25, PA4205, doi:4210.1029/2009pa001891, 2010.

Lam, P. J., Robinson, L. F., Blusztajn, J., Li, C., Cook, M. S., McManus, J. F., and Keigwin, L. D.: Transient stratification as the cause of the North Pacific productivity spike during deglaciation, Nature Geosci, 6, 622-626, 2013.

Lee, K. E., Lee, H. J., Park, J.-H., Chang, Y.-P., Ikehara, K., Itaki, T., and Kwon, H. K.: Stability of the Kuroshio path with respect to glacial sea level lowering, Geophysical Research Letters, 40, 392–396, doi:310.1002/grl.50102, 2013.

Li, D., Zheng, L.-W., Jaccard, S. L., Fang, T.-H., Paytan, A., Zheng, X., Chang, Y.-P., and Kao, S.-J.: Millennial-scale ocean dynamics controlled export productivity in the subtropical North Pacific, Geology, 45, 651-654, 2017.

Li, T. G., Xiang, R., Sun, R. T., and Cao, Q. Y.: Benthic foraminifera and bottom water evolution in the middle-southern Okinawa Trough during the last 18 ka, Science in China Series D-Earth Sciences, 48, 805-814, 2005.

Li, Y. H. and Schoonmaker, J. E.: Chemical Composition and Mineralogy of Marine Sediments. In: Treatise on Geochemistry (Second Edition), Turekian, K. K. (Ed.), Elsevier, Oxford, 2014.

Liu, Y. H., Henderson, G. M., Hu, C. Y., Mason, A. J., Charnley, N., Johnson, K. R., and Xie, S. C.: Links between the East Asian monsoon and North Atlantic climate during the 8,200 year event, Nature Geosci, 6, 117-120, 2013.

Liu, Z., Otto-Bliesner, B. L., He, F., Brady, E. C., Tomas, R., Clark, P. U., Carlson, A. E., Lynch-Stieglitz, J., Curry, W., Brook, E., Erickson, D., Jacob, R., Kutzbach, J., and Cheng, J.: Transient

https://doi.org/10.5194/cp-2019-70
Preprint. Discussion started: 20 June 2019

Simulation of Last Deglaciation with a New Mechanism for Bølling-Allerød Warming, Science, 325, 310-314, 2009.

Lu, Z., Hoogakker, B. A. A., Hillenbrand, C.-D., Zhou, X., Thomas, E., Gutchess, K. M., Lu, W., Jones, L., and Rickaby, R. E. M.: Oxygen depletion recorded in upper waters of the glacial Southern Ocean, Nature Communication, 7, doi: 10.1038/ncomms11146, 2016.

Lyons, T. W., Anbar, A. D., Severmann, S., Scott, C., and Gill, B. C.: Tracking Euxinia in the Ancient Ocean: A Multiproxy Perspective and Proterozoic Case Study, Annual Review of Earth and Planetary Sciences, 37, 507-534, 2009.

Machida, H.: The stratigraphy, chronology and distribution of distal marker-tephras in and around Japan, Global and Planetary Change, 21, 71-94, 1999.

Maithani, P. B. and Srinivasan, S.: Felsic Volcanic Rocks, a Potential Source of Uranium - An Indian Overview, Energy Procedia, 7, 163-168, 2011.

Marchitto, T. M., Lehman, S. J., Ortiz, J. D., Flückiger, J., and van Geen, A.: Marine Radiocarbon Evidence for the Mechanism of Deglacial Atmospheric CO2 Rise, Science, 316, 1456-1459, 2007.

Marcott, S. A., Bauska, T. K., Buizert, C., Steig, E. J., Rosen, J. L., Cuffey, K. M., Fudge, T. J., Severinghaus, J. P., Ahn, J., Kalk, M. L., McConnell, J. R., Sowers, T., Taylor, K. C., White, J. W. C., and Brook, E. J.: Centennial-scale changes in the global carbon cycle during the last deglaciation, Nature, 514, 616-619, 2014.

Matsumoto, K., Oba, T., Lynch-Stieglitz, J., and Yamamoto, H.: Interior hydrography and circulation of the glacial Pacific Ocean, Quaternary Science Reviews, 21, 1693-1704, 2002.

Max, L., Lembke-Jene, L., Riethdorf, J. R., Tiedemann, R., Nurnberg, D., Kuhn, H., and Mackensen, A.: Pulses of enhanced North Pacific Intermediate Water ventilation from the Okhotsk Sea and Bering Sea during the last deglaciation, Climate of the Past, 10, 591-605, 2014.

McManus, J., Berelson, W. M., Klinkhammer, G. P., Hammond, D. E., and Holm, C.: Authigenic uranium: Relationship to oxygen penetration depth and organic carbon rain, Geochimica et Cosmochimica Acta, 69, 95-108, 2005.

McManus, J. F., Francois, R., Gherardi, J. M., Keigwin, L. D., and Brown-Leger, S.: Collapse and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes, Nature, 428, 834-837, 2004.

Menviel, L., England, M. H., Meissner, K. J., Mouchet, A., and Yu, J.: Atlantic-Pacific seesaw and its role in outgassing CO2 during Heinrich events, Paleoceanography, 29, 58-70, 2014.

Morford, J. L. and Emerson, S.: The geochemistry of redox sensitive trace metals in sediments, Geochimica et Cosmochimica Acta, 63, 1735-1750, 1999.

Nakamura, H., Nishina, A., Liu, Z. J., Tanaka, F., Wimbush, M., and Park, J. H.: Intermediate and deep water formation in the Okinawa Trough, Journal of Geophysical Research-Oceans, 118, 6881-6893, 2013.

Nameroff, T. J., Balistrieri, L. S., and Murray, J. W.: Suboxic trace metal geochemistry in the Eastern Tropical North Pacific, Geochimica et Cosmochimica Acta, 66, 1139-1158, 2002.

Nameroff, T. J., Calvert, S. E., and Murray, J. W.: Glacial-interglacial variability in the eastern tropical North Pacific oxygen minimum zone recorded by redox-sensitive trace metals, Paleoceanography, 19, PA1010, doi:1010.1029/2003PA000912, 2004.

Nishina, A., Nakamura, H., Park, J.-H., Hasegawa, D., Tanaka, Y., Seo, S., and Hibiya, T.: Deep ventilation in the Okinawa Trough induced by Kerama Gap overflow, Journal of Geophysical Research: Oceans, 121, 6092-6102, 2016.

https://doi.org/10.5194/cp-2019-70
Preprint. Discussion started: 20 June 2019

Ohkushi, K., Hara, N., Ikehara, M., Uchida, M., and Ahagon, N.: Intensification of North Pacific intermediate water ventilation during the Younger Dryas, Geo-Mar Lett, 36, 353-360, 2016.

Ohkushi, K., Itaki, T., and Nemoto, N.: Last Glacial-Holocene change in intermediate-water ventilation in the Northwestern Pacific, Quaternary Science Reviews, 22, 1477-1484, 2003.

Ohkushi, K., Kennett, J. P., Zeleski, C. M., Moffitt, S. E., Hill, T. M., Robert, C., Beaufort, L., and Behl, R. J.: Quantified intermediate water oxygenation history of the NE Pacific: A new benthic foraminiferal record from Santa Barbara basin, Paleoceanography, 28, 453-467, 2013.

Okazaki, Y., Kimoto, K., Asahi, H., Sato, M., Nakamura, Y., and Harada, N.: Glacial to deglacial ventilation and productivity changes in the southern Okhotsk Sea, Palaeogeography Palaeoclimatology Palaeoecology, 395, 53-66, 2014.

Okazaki, Y., Sagawa, T., Asahi, H., Horikawa, K., and Onodera, J.: Ventilation changes in the western North Pacific since the last glacial period, Climate of the Past, 8, 17-24, 2012.

Okazaki, Y., Seki, O., Nakatsuka, T., Sakamoto, T., Ikehara, M., and Takahashi, K.: Cycladophora davisiana (Radiolaria) in the Okhotsk Sea: A key for reconstructing glacial ocean conditions, Journal of Oceanography, 62, 639-648, 2006.

Okazaki, Y., Timmermann, A., Menviel, L., Harada, N., Abe-Ouchi, A., Chikamoto, M. O., Mouchet, A., and Asahi, H.: Deepwater Formation in the North Pacific During the Last Glacial Termination, Science, 329, 200-204, 2010.

Okumura, Y. M., Deser, C., Hu, A., Timmermann, A., and Xie, S.-P.: North Pacific Climate Response to Freshwater Forcing in the Subarctic North Atlantic: Oceanic and Atmospheric Pathways, Journal of Climate, 22, 1424-1445, 2009.

Porter, S. C. and Zhisheng, A.: Correlation between climate events in the North Atlantic and China during the last glaciation, Nature, 375, 305-308, 1995.

Praetorius, S. K., Mix, A. C., Walczak, M. H., Wolhowe, M. D., Addison, J. A., and Prahl, F. G.: North Pacific deglacial hypoxic events linked to abrupt ocean warming, Nature, 527, 362-366, 2015.

Qu, T. and Lukas, R.: The Bifurcation of the North Equatorial Current in the Pacific, Journal of Physical Oceanography, 33, 5-18, 2003.

Rühlemann, C., Müller, P. J., and Schneider, R. R.: Organic Carbon and Carbonate as Paleoproductivity Proxies: Examples from High and Low Productivity Areas of the Tropical Atlantic. In: Use of Proxies in Paleoceanography: Examples from the South Atlantic, Fischer, G. and Wefer, G. (Eds.), Springer Berlin Heidelberg, Berlin, Heidelberg, 1999.

Rae, J. W. B., Sarnthein, M., Foster, G. L., Ridgwell, A., Grootes, P. M., and Elliott, T.: Deep water formation in the North Pacific and deglacial CO2 rise, Paleoceanography, 29, 645-667, 2014.

Reimer, P. J., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Bronk Ramsey, C., Buck, C. E., Cheng, H., Edwards, R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Haflidason, H., Hajdas, I., Hatté, C., Heaton, T. J., Hoffmann, D. L., Hogg, A. G., Hughen, K. A., Kaiser, K. F., Kromer, B., Manning, S. W., Niu, M., Reimer, R. W., Richards, D. A., Scott, E. M., Southon, J. R., Staff, R. A., Turney, C. S. M., and van der Plicht, J.: IntCal13 and Marine13 Radiocarbon Age Calibration Curves 0–50,000 Years cal BP, Radiocarbon, 55, 1869-1887, 2013.

Rella, S. F., Tada, R., Nagashima, K., Ikehara, M., Itaki, T., Ohkushi, K., Sakamoto, T., Harada, N., and Uchida, M.: Abrupt changes of intermediate water properties on the northeastern slope of the Bering Sea during the last glacial and deglacial period, Paleoceanography, 27, PA3203, doi:3210.1029/2011pa002205, 2012.

Riethdorf, J.-R., Max, L., Nuernberg, D., Lembke-Jene, L., and Tiedemann, R.: Deglacial development

https://doi.org/10.5194/cp-2019-70
Preprint. Discussion started: 20 June 2019

of (sub) sea surface temperature and salinity in the subarctic northwest Pacific: Implications for upper-ocean stratification, Paleoceanography, 28, doi:10.1002/palo.20014, 2013.

Riethdorf, J.-R., Thibodeau, B., Ikehara, M., Nürnberg, D., Max, L., Tiedemann, R., and Yokoyama, Y.: Surface nitrate utilization in the Bering sea since 180kA BP: Insight from sedimentary nitrogen isotopes, Deep Sea Research Part II: Topical Studies in Oceanography, 125-126, 163-176, 2016.

Rodríguez-Sanz, L., Mortyn, P. G., Herguera, J. C., and Zahn, R.: Hydrographic changes in the tropical and extratropical Pacific during the last deglaciation, Paleoceanography, 28, 529-538, 2013.

Saenko, O. A., Schmittner, A., and Weaver, A. J.: The Atlantic-Pacific seesaw, Journal of Climate, 17, 2033-2038, 2004.

Sagawa, T. and Ikehara, K.: Intermediate water ventilation change in the subarctic northwest Pacific during the last deglaciation, Geophysical Research Letters, 35, 5, doi: 10.1029/2008gl035133, 2008.

Savrda, C. E. and Bottjer, D. J.: Oxygen-related biofacies in marine strata: an overview and update, Geological Society, London, Special Publications, 58, 201-219, 1991.

Scott, C. and Lyons, T. W.: Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies, Chemical Geology, 324–325, 19-27, 2012.

Scott, C., Lyons, T. W., Bekker, A., Shen, Y., Poulton, S. W., Chu, X., and Anbar, A. D.: Tracing the stepwise oxygenation of the Proterozoic ocean, Nature, 452, 456-459, 2008.

Shao, H., Yang, S., Cai, F., Li, C., Liang, J., Li, Q., Hyun, S., Kao, S.-J., Dou, Y., Hu, B., Dong, G., and Wang, F.: Sources and burial of organic carbon in the middle Okinawa Trough during late Quaternary paleoenvironmental change, Deep Sea Research Part I: Oceanographic Research Papers, 118, 46-56, 2016.

Shcherbina, A. Y., Talley, L. D., and Rudnick, D. L.: Direct observations of North Pacific ventilation: Brine rejection in the Okhotsk Sea, Science, 302, 1952-1955, 2003.

Shi, X., Wu, Y., Zou, J., Liu, Y., Ge, S., Zhao, M., Liu, J., Zhu, A., Meng, X., Yao, Z., and Han, Y.: Multiproxy reconstruction for Kuroshio responses to northern hemispheric oceanic climate and the Asian Monsoon since Marine Isotope Stage 5.1 (~88 ka), Climate of the Past, 10, 1735-1750, 2014.

Shibahara, A., Ohkushi, K., Kennett, J. P., and Ikehara, K.: Late Quaternary changes in intermediate water oxygenation and oxygen minimum zone, northern Japan: A benthic foraminiferal perspective, Paleoceanography, 22, PA3213, doi:3210.1029/2005pa001234, 2007.

Shimmield, G. B. and Price, N. B.: The behaviour of molybdenum and manganese during early sediment diagenesis — offshore Baja California, Mexico, Marine Chemistry, 19, 261-280, 1986.

Sibuet, J. C., Letouzey, J., Barbier, F., Charvet, J., Foucher, J. P., Hilde, T. W. C., Kimura, M., Chiao, L.-Y., Marsset, B., Muller, C., and Stéphan, J. F.: Back Arc Extension in the Okinawa Trough, Journal of Geophysical Research: Solid Earth, 92, 14041-14063, 1987.

Sigman, D. M. and Boyle, E. A.: Glacial/interglacial variations in atmospheric carbon dioxide, Nature, 407, 859-869, 2000.

Spratt, R. M. and Lisiecki, L. E.: A Late Pleistocene sea level stack, Clim. Past, 12, 1079-1092, 2016.

Sun, Y., Clemens, S. C., Morrill, C., Lin, X., Wang, X., and An, Z.: Influence of Atlantic meridional overturning circulation on the East Asian winter monsoon, Nature Geosci, 5, 46-49, 2012.

Sun, Y. B., Oppo, D. W., Xiang, R., Liu, W. G., and Gao, S.: Last deglaciation in the Okinawa Trough: Subtropical northwest Pacific link to Northern Hemisphere and tropical climate, Paleoceanography, 20, PA4005, doi:4010.1029/2004pa001061, 2005.

Sundby, B., Martinez, P., and Gobeil, C.: Comparative geochemistry of cadmium, rhenium, uranium,

https://doi.org/10.5194/cp-2019-70
Preprint. Discussion started: 20 June 2019

and molybdenum in continental margin sediments, Geochimica et Cosmochimica Acta, 68, 2485-2493, 2004.

Talley, L. D.: Distribution foramtion of North Pacific Intermediate water, Journal of Physical Oceanography, 23, 517-537, 1993.

Talley, L. D.: Hydrographic Atlas of the World Ocean Circulation Experiment (WOCE). In: Volume 2: Pacific Ocean, Sparrow, M., Chapman, P., and Gould, J. (Eds.), International WOCE Project Office, Southampton, UK, 2007.

Tribovillard, N., Algeo, T. J., Lyons, T., and Riboulleau, A.: Trace metals as paleoredox and paleoproductivity proxies: An update, Chemical Geology, 232, 12-32, 2006.

Ujiié, H. and Ujiié, Y.: Late Quaternary course changes of the Kuroshio Current in the Ryukyu Arc region, northwestern Pacific Ocean, Marine Micropaleontology, 37, 23-40, 1999.

Ujiié, Y., Asahi, H., Sagawa, T., and Bassinot, F.: Evolution of the North Pacific Subtropical Gyre during the past 190 kyr through the interaction of the Kuroshio Current with the surface and intermediate waters, Paleoceanography, 31, 1498-1513, 2016.

Ujiié, Y., Ujiié, H., Taira, A., Nakamura, T., and Oguri, K.: Spatial and temporal variability of surface water in the Kuroshio source region, Pacific Ocean, over the past 21,000 years: evidence from planktonic foraminifera, Marine Micropaleontology, 49, 335-364, 2003.

Vorlicek, T. P. and Helz, G. R.: Catalysis by mineral surfaces: Implications for Mo geochemistry in anoxic environments, Geochimica et Cosmochimica Acta, 66, 3679-3692, 2002.

Wahyudi and Minagawa, M.: Response of benthic foraminifera to organic carbon accumulation rates in the Okinawa Trough, Journal of Oceanography, 53, 411-420, 1997.

Wan, S. and Jian, Z.: Deep water exchanges between the South China Sea and the Pacific since the last glacial period, Paleoceanography, 29, 1162-1178, 2014.

Wang, W. L. and Wang, L. C.: Reconstruction of oceanographic changes based on the diatom records of the central Okhotsk Sea over the last 500000 years, Terrestrial Atmospheric and Oceanic Sciences, 19, 403-411, 2008.

Wang, Y., Cheng, H., Edwards, R. L., He, Y., Kong, X., An, Z., Wu, J., Kelly, M. J., Dykoski, C. A., and Li, X.: The Holocene Asian Monsoon: Links to Solar Changes and North Atlantic Climate, Science, 308, 854-857, 2005.

Wu, Y., Cheng, Z., and Shi, X.: Stratigraphic and carbonate sediment characteristics of Core CSH1 from the northern Okinawa Trough, Advances in Marine Science, 22, 163-169, 2004 (in Chinese with English Abstract).

Wu, Y., Shi, X., Zou, J., Cheng, Z., Wang, K., Ge, S., and Shi, F.: Benthic foraminiferal δ 13C minimum events in the southeastern Okhotsk Sea over the last 180ka, Chinese Science Bulletin, 59, 3066-3074, 2014.

You, Y. Z.: The pathway and circulation of North Pacific Intermediate Water, Geophysical Research Letters, 30, doi:10.1029/2003gl018561, 2003.

You, Y. Z., Suginohara, N., Fukasawa, M., Yasuda, I., Kaneko, I., Yoritaka, H., and Kawamiya, M.: Roles of the Okhotsk Sea and Gulf of Alaska in forming the North Pacific Intermediate Water, Journal of Geophysical Research-Oceans, 105, 3253-3280, 2000.

You, Y. Z., Suginohara, N., Fukasawa, M., Yoritaka, H., Mizuno, K., Kashino, Y., and Hartoyo, D.: Transport of North Pacific Intermediate Water across Japanese WOCE sections, Journal of Geophysical Research-Oceans, 108, doi: 10.1029/2002jc001662, 2003.

Yu, H., Liu, Z. X., Berne, S., Jia, G. D., Xiong, Y. Q., Dickens, G. R., Wei, G. J., Shi, X. F., Liu, J. P.,

Climate of the Past
Discussions

and Chen, F. J.: Variations in temperature and salinity of the surface water above the middle Okinawa Trough during the past 37 kyr, Palaeogeography Palaeoclimatology Palaeoecology, 281, 154-164, 2009.

Zheng, X., Kao, S., Chen, Z., Menviel, L., Chen, H., Du, Y., Wan, S., Yan, H., Liu, Z., Zheng, L., Wang, S., Li, D., and Zhang, X.: Deepwater circulation variation in the South China Sea since the Last Glacial Maximum, Geophysical Research Letters, 43, 8590-8599, 2016.

Zheng, Y., Anderson, R., van Geen, A., and Fleisher, M.: Remobilization of authigenic uranium in marine sediments by bioturbation, Geochimica et Cosmochimica Acta, 66, 1759-1772, 2002.

Zheng, Y., Anderson, R., van Geen, A., and Kuwabara, J.: Authigenic molybdenum formation in marine sediments: a link to pore water sulfide in the Santa Barbara Basin, Geochimica et Cosmochimica Acta, 64, 4165-4178, 2000.

Zou, J., Shi, X., Liu, Y., Liu, J., Selvaraj, K., and Kao, S.-J.: Reconstruction of environmental changes using a multi-proxy approach in the Ulleung Basin (Sea of Japan) over the last 48 ka, Journal of Quaternary Science, 27, 891-900, 2012.

https://doi.org/10.5194/cp-2019-70
Preprint. Discussion started: 20 June 2019

Captions

Table 1. Locations of different records and their source references discussed in the text.

Table 2. Age control points adopted between planktic $\delta^{18}O$ of Core CSH1 and Chinese stalagmite $\delta^{18}O$ (Cheng et al., 2016) for tuning the age model between 10 ka and 60 ka in this study. A linear interpolation was assumed between age control points.

Figure 1. (a) Spatial distribution of dissolved oxygen content at 700 m water depth in the North Pacific. Black arrows denote simplified Kuroshio and Oyashio circulations and North Pacific Intermediate Water (NPIW) in the North Pacific. The red thick dashed line indicates transformation of Okhotsk Sea Intermediate Water (OSIW) by cabbeling the subtropical NPIW along the subarctic-tropical frontal zone (You, 2003). The light brown solid line with arrow indicates the spreading path of subtropical NPIW from northeast North Pacific southward toward the low-latitude northwest North Pacific (You, 2003). Yellow solid lines with arrow represent two passages through which NPIW enter into the Okinawa Trough. This figure was created with Ocean Data View (odv.awi.de). (b) Location of sediment core CSH1 investigated in this study (red diamond). Also shown are locations of sediment cores investigated previously from the Okinawa Trough (PN-3，E017，255 and MD012404; white cross line), the northern and southern Japan (GH08-2004 and GH02-1030), the Bering Sea (PC-23A) and the northeastern Pacific (ODP167-1017). The detailed information for these cores can be seen in Table 1.

Figure 2. Spatial distribution of sea surface salinity in the East China Sea. (a) summer (July to September); (b) winter (January to March). Lower sea surface salinity in summer relative to that of winter indicates strong effects of summer East Asian Monsoon.

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Figure 3. (a) Lithology and oxygen isotope ($\delta^{18}O$) profile of planktic foraminiferal species *Globigerinoides ruber* (*G.ruber*) in core CSH1. (b) Plot of ages versus depth for core CSH1. Three known ash layers are indicated by solid red rectangles. (c) Time series of linear sedimentation rate (LSR) from core CSH1. (d) Comparison of age model of core CSH1 with Chinese Stalagmite composite $\delta^{18}O$ curve of (Cheng et al., 2016).Tie points for CSH1 core chronology (Table 2) in Figures2b and 2c are designated by blue and red solid dots.

Figure 4. Age versus (a) linear sedimentation rate (LSR), (b) C/N molar ratio, (c) Total organic carbon (TOC) concentration, (d) Total nitrogen (TN) concentration, (e) $CaCO_3$ concentration, (f) Al concentration, (g) Mn concentration, (h) Mo/Mn ratio, (i) Mo concentration, (j) excess Mo concentration, (k) U concentration and (l) excess U concentration in core CSH1. Gray and black vertical bars indicate different sediment intervals in core CSH1. MIS indicates Marine Isotope Stage. 8.2 ka, PB, YD, B/A, HS1, LGM and HS2 refer to 8,200 year cold event, Preboreal, Younger Dryas, Bölling - Alleröd, Heinrich Stadial 1, Last Glacial Maximum and Heinrich Stadial 2, respectively, which were identified in core CSH1. Blue solid diamonds in Figure 3l indicate the age control points.

Figure 5. Scatter plots of Mo_{excess} vs Mn concentrations and U_{excess} concentration vs Mo/Mn ratio at different time intervals in core CSH1. A various correlation is present in core CSH1 at different time intervals, which shows their complicated geochemical behaviors. Strong positive correlation between U_{excess} concentration and Mo/Mn ratio suggest that they are suitable to track redox conditions in the past.

Figure 6. Proxy-related reconstructions of intermediate water oxygenation at site CSH1 (this study) compared with oxygenation records from other locations of the North Pacific and published climatic and environmental records from the Okinawa Trough. From top to bottom: (a) $CaCO_3$ concentration, (b) U_{excess} concentration, (c) Mo/Mn ratio, (d) Mn concentration and (e) abundance of *P.obliquiloculata* in core

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CSH1 (Shi et al., 2014) and (f) $\delta^{15}N$ of TOC in core MD01-2404 (Kao et al., 2008), (g) $\delta^{13}C$ of *C.wuellerstorfi* in core PN-3(Wahyudi and Minagawa, 1997), (h) Dysoxic taxa (%) in core ODP 167-1017 in the northeastern Pacific (Cannariato and Kennett, 1999) and (i) $\delta^{13}C$ of *Uvigerina akitaensisthe* in core PC23A in the Bering Sea (Rella et al., 2012). Gray and black vertical bars are the same as those in Figure 4.

Figure 7. Proxy records favoring the existence of oceanic ventilation seesaw between the subtropical North Pacific and North Atlantic during the last deglaciation and enhanced carbon storage at mid-depth waters. (a) Atmospheric CO_2 concentration (Marcott et al., 2014) (b) Indicator of strength of Atlantic Meridional Ocean Circulation ($^{231}Pa/^{230}Th$) (Bohm et al., 2015; McManus et al., 2004); (c) benthic $\delta^{13}C$ record in core PC-23A in the Bering Sea (Rella et al., 2012); (d) Mo/Mn ratio in core CSH1; (e) U_{excess} concentration in core CH1. Blue diamonds are the same as those in Figure 3.

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Table 1

Label in Figure 1b	Station	Latitude(°N)	Longitude(°E)	Water depth (m)	Area	Reference
	CSH1	31.23	128.72	703	Okinawa Trough	this study
A	PN-3	28.10	127.34	1058	Okinawa Trough	Wahyudi and Minagawa, (1997)
B	MD012404	26.65	125.81	1397	Okinawa Trough	Kao et al., (2008)
C	E017	26.57	126.02	1826	Okinawa Trough	Li et al., (2005)
D	255	25.20	123.12	1575	Okinawa Trough	Jian et al., (1996)
E	GH08-2004	26.21	127.09	1166	East of Ryukyu Island	Kubota et al. (2010)
	GH02-1030	42.23	144.21	1212	Off Japan	Sagawa and Ikehara, (2008)
	PC-23A	60.16	179.46	1002	Bering Sea	Rella et al.,(2012)
	ODP167-1017	34.54	239.11	955	NE Pacific	Cannariato and Kennett, (1999)

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Table 2

Depth(cm)	AMS ^{14}C (yr)	Error (yr)	Calibrated Age (yr)	Tie Point Type	LSR (cm/ka)	Source
10	3420	±35	3296	^{14}C		Shi et al., (2014)
106	7060	± 40	7545	^{14}C	22.59	Shi et al., (2014)
218			12352	Stalagmite, YD	23.30	This study
322			16029	Stalagmite, H1	28.28	This study
362			19838	Stalagmite	10.50	This study
466			23476	Stalagmite, DO2	28.59	This study
506			24163	Stalagmite, H2	58.22	This study
698			28963	Stalagmite, DO4	40.00	This study
746			29995	Stalagmite, H3	46.51	This study
834			32442	Stalagmite, DO5	35.96	This study
938			37526	Stalagmite, DO8	20.46	This study
978			39468	Stalagmite, H4	20.60	This study
1058			46151	Stalagmite, DO12	11.97	This study
1122			49432	Stalagmite, DO13	19.51	This study
1242			52831	Stalagmite, DO14	35.30	This study
1282			57241	Stalagmite, DO16	9.07	This study
1346			61007	Stalagmite, H6	16.99	This study
1530		±2590	73910	MIS4/5	14.26	Shi et al., (2014)
1610		±3580	79250	MIS 5.1	14.98	Shi et al., (2014)

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Fig.1

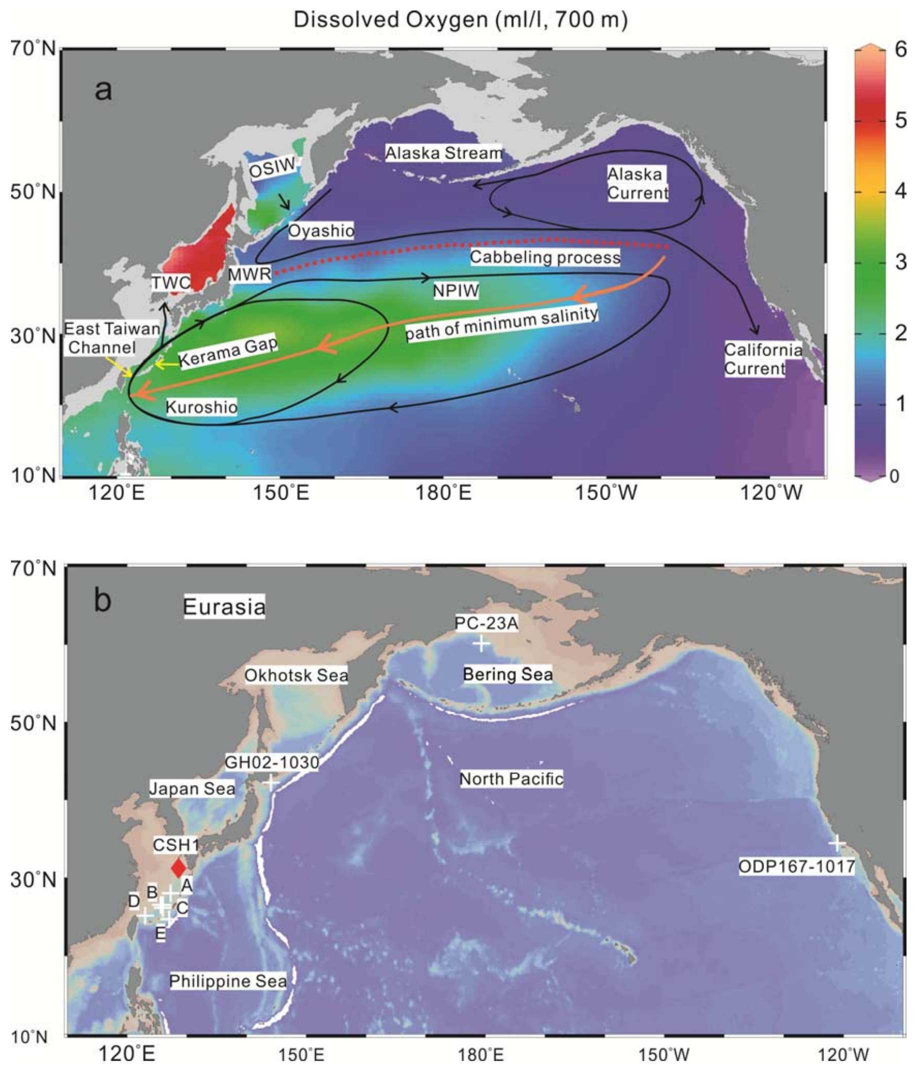

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Fig.2

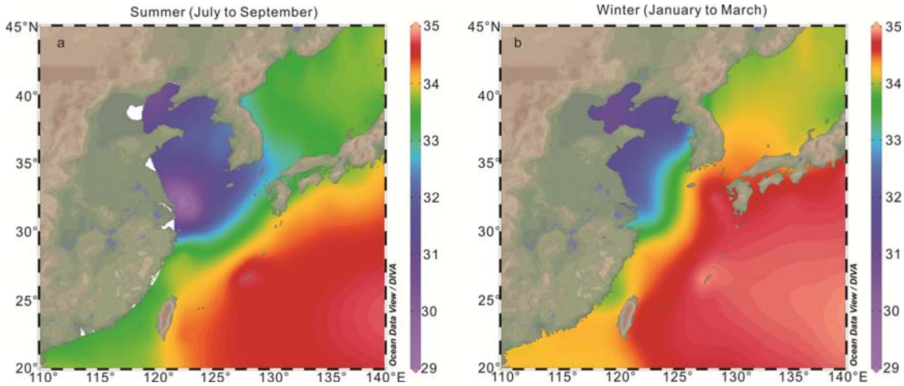

Fig.3

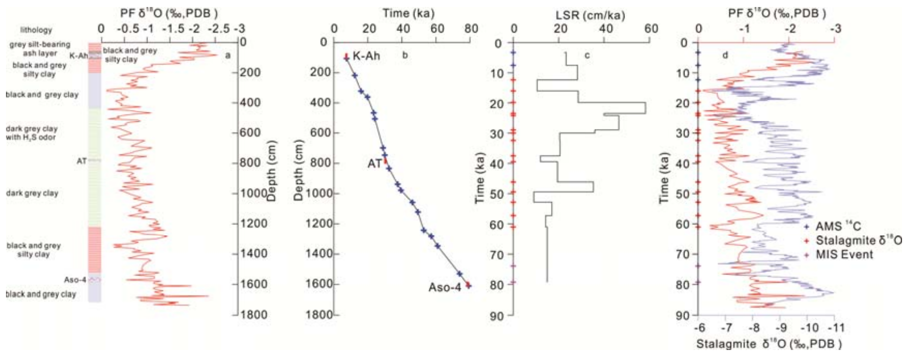

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Fig.4

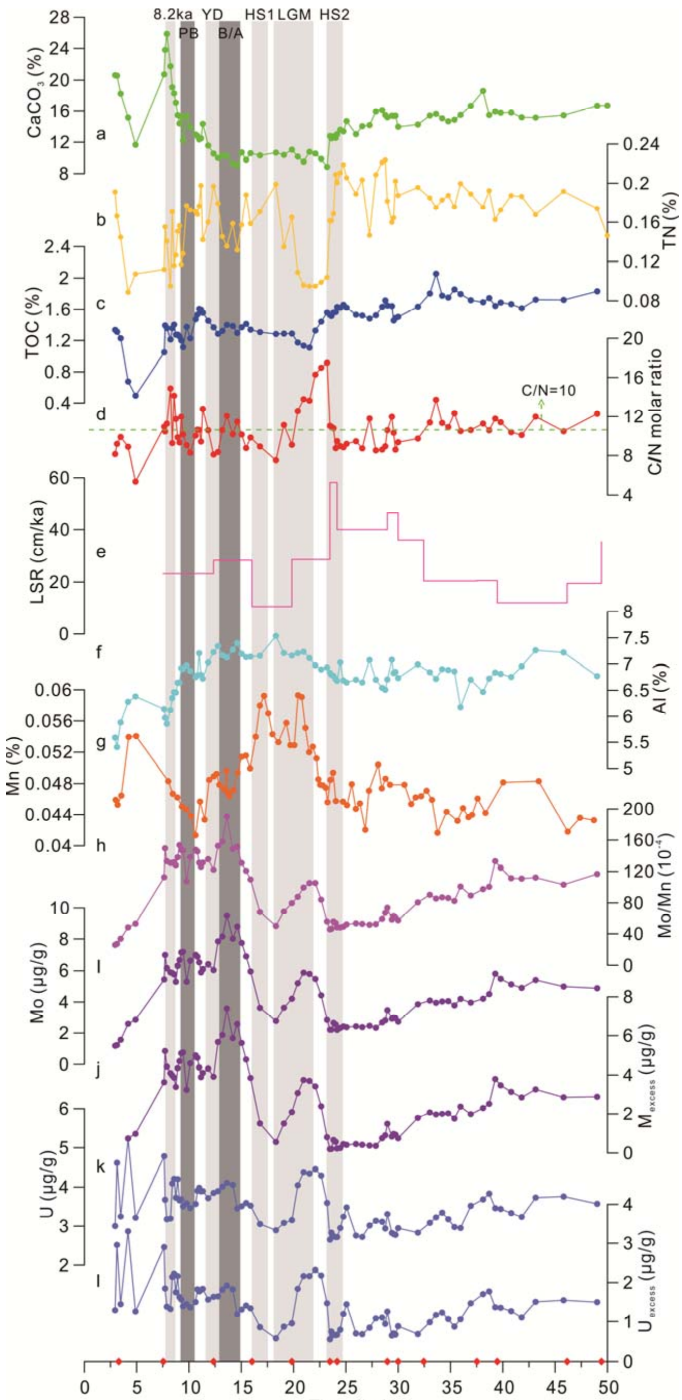

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Fig.5

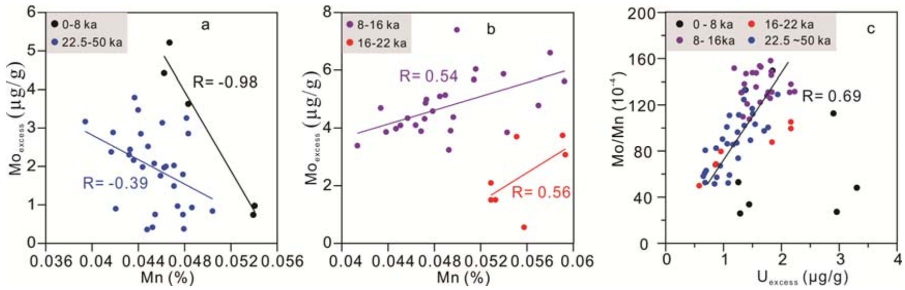

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Fig.6

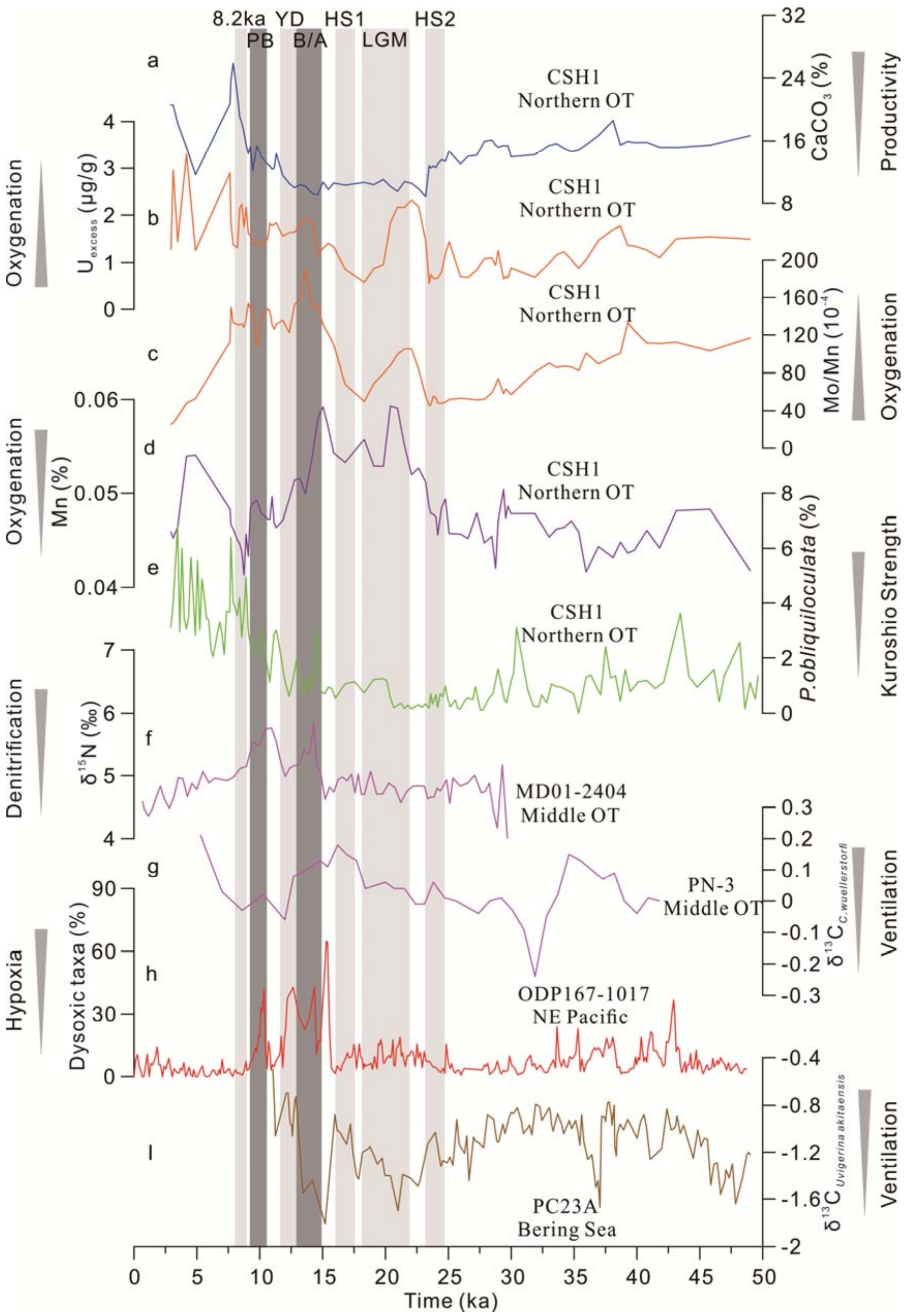

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Fig.7