

Title: Marine sedimentary uranium to barium ratios as a potential quantitative proxy for Pleistocene bottom water oxygen concentrations

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Abstract

Oxygen is essential for marine ecosystems, and it is linked by respiration to carbon storage in the deep ocean. Reconstructing oxygen concentrations in the past has been limited by the absence of quantitative, rather than qualitative, proxies, but several new (semi-) quantitative oxygen proxies have recently been developed. In this study we explore the possibility of adding bulk sedimentary uranium (U) to this list by normalizing it to barium (Ba). First, U/Ba and bottom water oxygen concentrations are compared on a global scale, using a core top database, in pelagic environments greater than 200 m water depth. Then, the relationships between U/Ba and bottom water oxygen are examined on smaller spatial scales: within each ocean basin and regionally within the Eastern Equatorial Pacific, the Arabian Sea, and Western Equatorial Atlantic. At this regional scale, where secondary influences on the behavior of both U and Ba may be more spatially uniform, empirical piecewise linear calibrations are developed and subsequently tested on downcore records. U/Ba-based oxygen reconstructions generally agree with those derived from previously published alkenone preservation and benthic foraminiferal surface porosity records. Several limitations to the utility of U/Ba as a proxy for oxygen have also been identified. The proxy should only be applied in the uppermost sedimentary intervals that contain porewater sulfate to minimize barite diagenesis, and phosphorus contents should be monitored for the potential influence of apatite on uranium content. U/Ba is more successful at recording oxygen concentrations during mean glacial and interglacial periods than during climate transitions, when the timing and amplitude may be more sensitive to burndown and smoothing. Conservative errors on the calibrations result in the greatest utility of U/Ba in regions with relatively high oxygen concentrations (e.g., $>50 \text{ } \mu\text{mol/kg}$) and large oxygen variability ($\pm 10\text{s of } \mu\text{mol/kg}$). Even with these caveats, U/Ba is only one of two quantitative oxygen proxies potentially capable of recording variability above $50 \text{ } \mu\text{mol/kg}$, and further investigation into its functionality in different environmental settings is worthwhile in the endeavor to reconstruct the full marine range of oxygen concentrations in the past.

Keywords

Bottom water oxygen; sediment geochemistry; uranium; barium; pelagic sediments; Pleistocene; glacial-interglacial cycles

1. Introduction

Oxygen concentrations are a primary chemical characteristic of the ocean, responsible not only for life in the deep but also for driving the biogeochemical cycles of C, N, P, Mn, Fe, and many other trace elements. As the oceans take up anthropogenic CO₂, oxygen concentrations are declining (Garcia et al., 1998; Stramma et al., 2008; Keeling et al., 2010) in part due to decreased solubility in warming waters (Garcia et al., 1998; Matear and Hirst, 2003), increased physical stratification (Palter and Trossman, 2018), and enhanced biological respiration (Oschlies et al., 2008). This complex, multivariate system is difficult to parameterize, and models generate disparate forecasts in terms of the sign, amplitude, and trend of oxygen concentrations in the Common Era and into the future (Stramma et al., 2012; Cabré et al., 2015; Fu et al., 2018). Constraining these parameters under past climate conditions is critical for developing the mechanistic understanding which will allow for more accurate predictions of how oxygen concentrations will change in the future.

Recently, the development of new, (semi-)quantitative oxygen paleo-proxies has refined our understanding of the temporal and spatial evolution of oxygen dynamics in the ocean over the glacial-interglacial cycles of the late Pleistocene (here defined as the last 500,000 years). These proxies include: 1) the carbon isotope gradient ($\Delta\delta^{13}\text{C}$) between epifaunal to shallow infaunal (*Cibicidoides spp.*) and deep infaunal (*Globobulimina spp.*) benthic foraminifera (McCorkle and Emerson, 1988; Hoogakker et al., 2015), 2) I/Ca in *Cibicidoides spp.* (Lu et al., 2020; Lu et al., 2021), 3) sedimentary alkenone preservation (Prahl et al., 1993; Rodrigo-Gámiz et al., 2016; Anderson et al., 2019; Jacobel et al., 2020), 4) surface porosity of *Cibicidoides spp.* (Rathburn et al., 2018; Lu et al., 2021; Lu et al., 2022), and 5) benthic foraminifera assemblages (Ohkushi et al., 2013; Tetard et al., 2017; Tetard et al., 2021; Sharon and Belanger, 2022). For example, during the last glacial maximum (LGM, 18,000-24,000 years ago, or 18-24 ka), it has been hypothesized that carbon sequestration in the deep ocean led to lower glacial oxygen concentrations in deep waters (Boyle, 1990; Sigman and Boyle, 2000; Sigman et al., 2010). Applications of the aforementioned five paleo-oxygen proxies in the deep Pacific and Atlantic not only support this hypothesis qualitatively, but the quantitative $\Delta\delta^{13}\text{C}$ and alkenone preservation proxies can also constrain the magnitude of oxygen loss to 65-100 $\mu\text{mol/kg}$. This change in oxygen can be translated to a change in deep ocean carbon storage of approximately 800 Pg carbon, using the stoichiometric relationship between the concentrations of oxygen and carbon via bacterial respiration (Anderson et al., 2019).

There are three main limitations to this new suite of quantitative proxies. First, none of the proxies explicitly distinguish between porewater oxygen concentrations and bottom water oxygen (BWO) concentrations. While oxygen concentration in porewaters are initially set by bottom waters, they may become decoupled if high organic carbon fluxes generate intense respiration in surficial sediments (<10 cm) that rapidly depletes oxygen concentrations in porewaters. As a result, when low oxygen concentrations are indicated by a proxy, that

signal may reflect lower BWO concentrations (e.g., by reduced water mass ventilation or a change in water mass), lower pore water oxygen concentrations (e.g., by higher organic carbon delivery to the sediment), or a combination of the two. While the potential effects of organic carbon fluxes are often qualitatively monitored with independent proxies, this effect is not specifically incorporated into the proxy quantifications. Second, four out of five oxygen proxies ($\Delta\delta^{13}\text{C}$, I/Ca, surface porosity, and benthic assemblages) require the presence of specific foraminifera, namely *Cibicidoides* spp. While *Cibicidoides* spp. are generally abundant in the Atlantic (Jorissen et al., 2007), they can be scarce in, for example, regions with low export productivity (e.g., subtropical gyres, which comprise much of the Pacific Ocean). Furthermore, for $\Delta\delta^{13}\text{C}$, *Cibicidoides wuellerstorfi* and *Globobulimina affinis* do not always coexist in the same sedimentary layers, which can result in individually discontinuous and mutually incoincident $\delta^{13}\text{C}$ data. Finally, in regions (e.g., the deep Pacific or Southern Ocean) and times (e.g., interglacial periods) when carbonate preservation is poor, the absence of foraminifera precludes the application of these proxies. The third major limitation is that four out of five proxies (alkenone preservation, I/Ca, surface porosity, and benthic assemblages) are sensitive to changes only at the lowest oxygen concentrations, generally less than 50 $\mu\text{mol/kg}$ (e.g., Anderson et al., 2019; Lu et al., 2021, 2022). Therefore, large changes in oxygen concentrations that do not cross this threshold (e.g., from 250 $\mu\text{mol/kg}$ to 150 $\mu\text{mol/kg}$) will not be recorded by these proxies. Currently only $\Delta\delta^{13}\text{C}$ can be applied to locations with oxygen concentrations consistently above 50 $\mu\text{mol/kg}$. However, at sites with both relatively high oxygen concentrations and low abundances of the requisite foraminifera, none of the five available quantitative oxygen proxies can be utilized.

In this study, we attempt, for the first time, to isolate the BWO signal in sedimentary uranium content by normalizing it to a proxy for organic carbon fluxes to the sediment. Uranium has previously been applied as a qualitative indicator of BWO variability in the past (Calvert and Pedersen, 1993; Sarkar et al., 1993; Frank et al., 2000; Jaccard et al., 2009; Martínez-García et al., 2009), but converting uranium content to discrete BWO concentrations has been difficult due to its complex sedimentary geochemistry (see Section 2.1). Because bulk sedimentary uranium can be measured even when benthic foraminifera are rare or absent, its quantification could greatly expand the spatial and temporal domains for reconstructing BWO concentrations in the past. Using a core top compilation (Figure 1), we examine the relationships between uranium, BWO, and organic carbon fluxes (parameterized using sedimentary barium content see Section 2.2). By normalizing uranium to barium (U/Ba), this proxy has advantages over previous approaches because 1) it accounts for dilution effects from variable sedimentation rates, 2) it is not dependent on lithogenic ratios, and 3) it identifies changes in uranium contents in excess of what is driven by organic carbon fluxes and so can be more confidently attributed to changes in (specifically) BWO concentrations. The data are evaluated at three spatial scales: global, ocean basin, and regional. Finally, we assess the proxy utility in three locations (the Eastern Equatorial Pacific, the Arabian Sea, and the Western Equatorial Atlantic) by applying the regionally-derived empirical relationships between U/Ba and BWO to downcore records and comparing the results with previously published independent oxygen reconstructions from $\Delta\delta^{13}\text{C}$ and benthic foraminifera surface porosity.

2. Background

2.1 Uranium systematics

Uranium is soluble in oxygenated seawater, and its long residence time (400,000 yrs) makes dissolved uranium concentrations quasi-conservative and scalable with salinity (Owens et al., 2011). Oxidized uranium (U[VI]) complexes with carbonate ions, predominantly in the uncharged form $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (Endrizzi and Rao, 2014). Within oxygenated porewaters, dissolved uranium maintains seawater concentrations, but as porewater oxygen concentrations are depleted by benthic respiration, soluble U(VI) reduces to insoluble U(IV) and precipitates as solid authigenic UO_2 (Anderson, 1982; Anderson et al., 1989; Morford and Emerson, 1999). Continued precipitation of uranium is supported by a diffusive flux from seawater, a practically unlimited reservoir in unrestricted marine systems, which can lead to substantial enrichments in uranium (1-10 $\mu\text{g/g}$, or ppm) relative to biogenic particles (for example, 3-4 $\mu\text{g/kg}$ (or ppb) in foraminifera (Russell et al., 2004)). Thus, high uranium content has long been interpreted as a qualitative indicator of low oxygen concentrations in the sediments.

Ideally, authigenic uranium content (i.e., uranium precipitated in situ in excess of uranium from lithogenic particles) in surficial sediments could be directly converted to BWO concentrations, but the theoretical framework of uranium is complicated by other thermodynamic, kinetic, biological, and sedimentological processes. First, the baseline oxygen concentration at which uranium reduction occurs is poorly constrained, with some studies suggesting it co-occurs with iron reduction (Langmuir, 1978; Barnes and Cochran, 1990; Crusius et al., 1996; Zheng et al., 2002) while others suggest the lower redox potential required for sulfate reduction (Klinkhammer and Palmer, 1991). Furthermore, uranium reduction may occur even when conditions are thermodynamically unfavorable. In laboratory experiments, adsorption onto mineral surfaces can facilitate abiotic uranium reduction (Kochenov et al., 1977; Nakashima et al., 1984; Liger et al., 1999), and dissimilatory iron-reducing and/or sulfate-reducing microorganisms (e.g., *Clostridium sp.*, *Desulfovibrio sp.*, *Shewanella sp.*) can catalyze uranium reduction as a byproduct of their chemolithotrophic growth (Lovley et al., 1991; Lovley and Phillips, 1992; Francis et al., 1994; Ganesh et al., 1997; Sani et al., 2004; Lee et al., 2014). However, these experiments are usually conducted under “standard” conditions (e.g., 1 atm, 25°C) that are not representative of conditions on the seafloor (e.g. 300-400 atm, 1-4°C), and so their findings may or may not be directly applicable to the marine systems of interest in this study.

The complex chemistry of uranium in porewaters and sediments can be demonstrated by comparing theoretical profiles (e.g., Froelich et al., 1979) with observed profiles in an example pelagic core, EN433-2 (36.15°N, 74.06°W, 2648 m water depth, 270 $\mu\text{mol/kg}$ bottom water oxygen) (Morford et al., 2009) (Figure 2). Theoretically, porewater oxygen decreases with increasing depth in the sediment until oxygen concentrations reach zero. Anaerobic respiration may then consume Mn, resulting in increasing porewater concentrations of the soluble reduced species Mn(II) (Figure 2A). Solid phase Mn oxides peak above the sediment horizon at which reduction commences (Figure 2B). Rather than a sharp boundary, solid phase peaks tend to be broad as a result of bioturbation, which smooths sedimentary records over a depth range of, e.g., 6-10 cm in the pelagic ocean (Berger and Johnson, 1978; Cochran, 1985; Trauth, 2013). In contrast, the reduced species U(IV) is less soluble than the oxidized species U(VI), and porewater uranium decreases (Figure 2A) and solid phase uranium increases (Figure 2B) below the uranium reduction horizon.

The observed porewater and solid phase profiles in EN433-2 (Figure 2C, 2D) demonstrate some similarities and some important differences from theoretical expectations. Where porewater oxygen concentrations reach zero (~4 cm), Mn reduction causes porewater Mn concentrations to start increasing with depth (Figure 2C). Solid phase Mn peaks at ~3 cm, just above the sediment horizon where Mn reduction commences (Figure 2D). Therefore, at this site, Mn behaves generally as expected from its theoretical predictions. However, uranium does not. Porewater uranium concentrations decrease monotonically from the sediment surface throughout the sediment profile (Figure 2C), even when oxygen is still present, and this decrease starts shallower than the increase of Mn. Porewater uranium is still relatively high (~8 μ mol/kg) when solid phase authigenic uranium content reaches its maximum (~0.9 ppm, 6-9 cm). This mismatch between theoretical and observed uranium behavior in sediments highlights the complications of using a purely thermodynamic redox model, which indeed has been described as “not appropriate for most sediments” (Burdige and Gieskes, 1983).

In addition, when considering sedimentary uranium across spatial gradients and/or over time, sedimentological properties like sedimentation rate, lithogenic flux and composition, and organic carbon fluxes can affect uranium content, complicating isolation of a purely BWO signal. For the same BWO concentration and organic carbon flux, sedimentary uranium contents may differ due to the dilution effects of variable sedimentation rates (i.e., high sedimentation rate sites would have lower uranium content than low sedimentation sites). On the other hand, at open ocean sites with low sedimentation, especially less than 2 cm/kyr, continuous exposure to relatively high oxygen bottom waters via bioturbation can cause authigenic uranium to reoxidize and diffuse out of the sediment (i.e., burndown), leaving behind no archival record of its precipitation at all (Mangini et al., 2001; Jacobel et al., 2017; Costa et al., 2018). The latter preservation bias is difficult to identify and even more challenging to account or correct for, and the primary solution is to avoid interpreting redox records from these low sedimentation sites (as demonstrated by Jacobel et al., 2020).

The dilution bias is generally amended by one of two approaches. First, linear mass accumulation rates integrate authigenic uranium content across a depth horizon to calculate the total authigenic uranium flux (aU flux) to the sediment. The main caveat to this approach is that it requires a well-constrained chronology and bulk sediment density, which may not be available. Alternatively, uranium content may be normalized to a lithogenic element (LE, such as aluminum or titanium), with the assumption that dilution will affect both elemental contents and thus cancel out. This ratio (U/LE) may be employed as such, or it can be converted to an enrichment factor (EF) by normalizing the observed U/LE (U/LE_{obs}) to the assumed U/LE of the lithogenic material (U/LE_{lith}) ($U_{EF} = U/LE_{obs} / U/LE_{lith}$). The main caveat to this approach is that it relies on constraining the lithogenic content and composition in order to isolate the fraction of uranium precipitated authigenically. The composition of the lithogenic component of marine sediments (i.e., U/LE_{lith}) varies on a regional scale as a function of the proximal crustal sources and transport pathways, but it is not always straightforward to pinpoint the specific U/LE_{lith} at any one site. For this reason, it is likely that regional calibrations using uranium enrichment may work more successfully than global ones.

Finally, sedimentary uranium content, like all of the paleo-oxygen proxies, depends not just on BWO but also on the flux of reductants to the sediment, primarily in the form of organic carbon in the open ocean. Microbial respiration of organic matter lowers porewater oxygen concentrations relative to BWO concentrations, such that uranium may precipitate even though the overlying bottom waters are oxic. For example, uranium enrichment has been observed in the Eastern Equatorial Pacific (Singh et al., 2011), the California Margin (McManus et al., 1998), and the Bering Sea (Serno et al., 2014) at sites that all have BWO concentrations $>90 \mu\text{mol/kg}$. In some settings, particularly on continental margins, high organic carbon content ($>2 \text{ wt\%}$ organic carbon, often $>5 \text{ wt\%}$) is the dominant control on porewater oxygen, and thus uranium precipitation is primarily interpreted as a productivity rather than oxygen signal (e.g., McManus et al., 2006). However, in the open ocean, sedimentary organic carbon content is much lower than on continental margins (e.g., Hayes et al., 2021; Lee et al., 2019), and so BWO can have a substantial influence on sedimentary uranium content.

In order to isolate the BWO signal, uranium content is normalized to a proxy for organic carbon fluxes to the sediment. While sedimentary organic carbon content may be the most intuitive normalization parameter, its relationship to export production from the photic zone is strongly overprinted by microbial respiration in the water column and sediments, such that in the open ocean generally less than 1% of the organic carbon exported from the photic zone is actually preserved in the sediment record (Pilson, 2012). Preservation within the water column is driven by microbial respiration, the extent of which will depend on the type of organic matter (e.g., Lee et al., 2004), sinking rate (e.g., Armstrong et al., 2001), and mineral protection (e.g., Keil et al., 1994). Subsequently, in the sediment, organic carbon preservation depends primarily on oxygen concentrations as well as processes that affect exposure to oxygen like sedimentation rates and bioturbation (Canfield et al., 1994; Arndt et al., 2013). For example, high sedimentation rates quickly bury organic carbon, and, by limiting its exposure to high BWO concentrations, high organic carbon preservation in the sediment is possible (Mueller & Suess 1979; Hartnett et al., 1998). Since organic carbon preservation is itself dependent on oxygen concentrations, it would be circular to use organic carbon content to normalize uranium. Instead, we utilize barium as an independent proxy for organic carbon fluxes because, in the open ocean, its preservation is much less sensitive to oxygen concentrations (as discussed in the next section).

2.2 Barium systematics

In the open ocean, dissolved barium concentrations have nutrient-like spatial patterns akin to those of silica (Horner et al., 2015), with the highest concentrations ($\leq 150 \mu\text{mol/kg}$) in the deep Pacific (Carter et al., 2020; GEOTRACES Intermediate Data Product Group, 2021). The solid phase of barium, barium sulfate (barite), is undersaturated in most of the ocean (Church and Wolgemuth, 1972; Monnin et al., 1999), and its precipitation in seawater should be thermodynamically unfavorable. Yet barite can be found throughout the water column throughout the global ocean (e.g., Bishop, 1988; Dehairs et al., 1980). Barite formation likely occurs in microenvironments within organic aggregates where facilitation by heterotrophic bacteria can locally overcome the impediment of undersaturation (Bishop, 1988; Bertram and Cowen, 1997; Ganeshram et al., 2003; Gonzalez-Muñoz et al., 2012; Horner et al., 2015; Martinez-Ruiz et al., 2019; Carter et al., 2020), potentially by increasing the barite saturation state as well as providing additional nucleation sites

(Martinez-Ruiz et al., 2018). As the organic-rich particulates sink and disaggregate, barite may remineralize as a result of exposure to ambient under-saturated waters. The fraction of barite that is precipitated in the water column and survives to reach the seafloor ranges from 0 to 30% as a function of both the organic matter flux and barite saturation state (Dymond et al., 1992; Paytan and Kastner, 1996).

Once barite reaches the seafloor, it may be susceptible to further remineralization as a result of redox processes within the sediment. Where oxygen concentrations are low and organic carbon fluxes are high, porewater sulfate can act as an oxidant for anaerobic respiration. Consequently, barite dissolves, the concentration of dissolved barium increases, and dissolved barium may diffuse upward in the sediment column (Von Breyman et al., 1992; Paytan and Kastner, 1996). If the depth of sulfate reduction is relatively shallow, then the dissolved barium in porewaters may diffuse upwards, potentially to the sediment-water interface, and the original deposition of barium as a function of export productivity may be distorted or lost entirely. Alternatively, if the sediment horizon where sulfate reduction occurs is relatively deep, then the dissolved barium may reprecipitate diagenetically upon reaching shallower, sulfate-replete porewaters (Torres et al., 1996), causing the barium enrichments to be shifted up-core. Redox-generated distortions in the barium sedimentary record can be diagnosed via morphological identification of diagenetic barite, evidence for anaerobic respiration, and/or the presence of sulfide species, such as pyrite (FeS_2). Constraining the depth in the sediment where preservation effects overprint the export productivity signal is important in determining the utility of barium as a normalization parameter for uranium.

The preservation of barium in the sediment is likely to vary from region to region and over time. In locations where organic carbon fluxes are high and/or BWO concentrations are low, sulfate reduction may occur at shallow depths in the sediment (e.g., less than 1 meter). For example, in the Santa Barbara Basin, sulfate reduction commences within the top 5 cm of the sediments resulting in sulfate depletion in porewaters at 100-150 cm below the sediment-water interface (Kuwabara et al., 1999; Reimers et al., 1990; Reimers et al., 1996, Raven et al., 2016), and the coincident high sedimentation rates (~ 150 cm/kyr; Thorton, 1984) limit the viability of the barium proxy to at most a few hundred years (or not at all). On the other hand, porewater oxygen is present throughout the entire sediment column in regions like the South Pacific Gyre (D'Hondt et al., 2009; D'Hondt et al., 2015), and slow sedimentation rates (e.g., < 1 cm/kyr) could potentially extend good barite preservation over timescales of millions of years (in which case the utility of U/Ba would instead be limited by the residence time of uranium). In the open ocean, BWO concentrations are typically high enough (e.g., > 100 $\mu\text{mol/kg}$) and organic carbon fluxes are typically low enough (e.g., < 1 wt%) that sulfate reduction is likely to be minimal in sediments that correspond to the late Pleistocene (Anderson et al., 2019; Singh et al., 2020). Despite this general observation, we strongly advise that, where possible, porewater sulfate concentrations be measured (or reconstructed) to ensure that barite preservation is maintained over the sediment depth range over which U/Ba is to be applied.

Assuming negligible diagenesis, sedimentary barite contents can be interpreted to reflect organic carbon fluxes. In practice, the mineral abundance of barite is often estimated by the excess barium content (exBa or Ba_{xs}), i.e. the total barium minus the barium fraction associated with lithogenic particles in the sediment. An empirical linear relationship has

been proposed between barite (or excess barium) mass accumulation rates and organic carbon fluxes (Dymond et al., 1992; Francois et al., 1995; Paytan et al., 1996). The correlation is poor when a single function is assessed on a global scale (Schoepfer et al., 2015; Hayes et al., 2021), but the relationship is greatly improved when spatial variability in, for example, organic carbon to excess barium ratios (C_{org}/Ba_{xs}) and organic carbon remineralization rates are taken under consideration (see discussion in Carter et al., 2020). Stronger quantitative relationships between excess barium and organic carbon flux on the regional scale are another potential reason why the development of U/Ba as a quantitative proxy for BWO may work better in limited spatial settings. Consequently, in this study we primarily investigate U/Ba on the smaller spatial scales of individual ocean basins (Pacific, Atlantic, Indian, and Southern) and regions (Eastern Equatorial Pacific, Arabian Sea, and Western Equatorial Atlantic).

3. Methods

3.1 Compilation of previously published data

This study leverages several previously published databases. Core tops, analyzed by Wang et al. (2022), include the full spectrum of major and trace elements including U, Ba, and P. The core top Ba database of Hayes et al. (2021) was cross-referenced with the U-Th database of Costa et al. (2020) as well as the original publications in order to compile U, Ba, and P where available (Dorta and Rona, 1971; Sarin et al., 1979; Calvert and Price, 1983; Frank et al., 1995; McManus et al., 1998; Bonn et al., 1998; Ceccaroni et al., 1998; Weber, 1998; Veeh et al., 1999; Murray et al., 2000; Sirocko et al., 2000; Veeh et al., 2000; Pfeifer et al., 2001; Nameroff et al., 2002; Prakash Babu et al., 2002; Chase et al., 2003; Eagle et al., 2003; Neimann and Geibert, 2003; Anderson and Winckler, 2005; McManus et al., 2005; Gonneea and Paytan, 2006; Shigemitsu et al., 2007; Bradtmiller et al., 2007; Anderson et al., 2009; Mills et al., 2010; Singh et al., 2011; Anderson et al., 2014; Serno et al., 2014; Calvert et al., 2015; Costa et al., 2016; Hickey, 2016; Lippold et al., 2016; Loveley et al., 2017; Wang et al., 2022). Several additional sites were included for which both U and Ba were available. Unfortunately, all three elemental contents were not available at each site, with P being the most commonly missing element. As this study focuses on open ocean sediments, sites from the continental shelf (<200 m) were explicitly omitted. Modern BWO concentrations were extracted and averaged (mean) from three data products: World Ocean Atlas 2018 (Garcia et al., 2019), GLODAPv2 (Olsen et al., 2016), and WOCE (Gouretski and Koltermann, 2004), and thus they may differ slightly from the BWO concentrations used in the original publications.

3.2 New data from Demerara Rise

Sediment cores from the Demerara Rise, in the western equatorial Atlantic (7-9°N, 53-54°W, 383-3328 m water depth), were recovered in 2010 on the KNR197-3 cruise. BWO concentrations for these sites were extracted from data products as described above. Modern BWO concentrations are lowest at the shallowest depths (~120 $\mu\text{mol/kg}$ at 400 m) and then increase monotonically to ~260 $\mu\text{mol/kg}$ by about 1750 m. Below 1750 m, BWO concentrations remain relatively constant at ~260 $\mu\text{mol/kg}$. Coretop samples from 14 sites comprise a total of 27 discrete measurements, in which two datapoints from the same site are true independent replicates sampled from different multicore barrels.

One downcore record covering the last 21 kyr was generated from KNR197-3-60GGC (8.4°N, 52.97°W, 2550 m). The chronology for this core is based on radiocarbon dating and benthic oxygen isotopes (Oppo et al., 2018).

Sediments were analyzed for uranium and barium content as well as isotopes of uranium and thorium (for ^{230}Th constant flux normalization) via complete acid digestion. Samples (100 mg) and various reference materials (BIR-1, MESS-3, DTS-2B, SGR-1, NIST2702, MAG-1, SDO-1, NIST2711, BHVO- 2) were spiked with ^{229}Th and ^{236}U for isotopic analysis. Samples and reference materials were digested in perchloric, nitric, and hydrofluoric acids, and subsequently the solution was split 1:10 for bulk elemental and isotopic analyses. The isotopic aliquot was additionally processed with column chromatography (Fleisher and Anderson, 2003). Isotopes for both uranium and thorium were measured on an Element 2 ICP-MS at Lamont-Doherty Earth Observatory of Columbia University. Because most of these sites are too shallow to utilize thorium normalization (Costa et al., 2020), we do not discuss the thorium data further. Based on replicates of the internal sediment standard VIMS (Costa and McManus, 2017) average measurement precision was 3.3% for U and 5.1% for Ba.

The elemental aliquot was further diluted and then analyzed on a Thermo Scientific iCAP 7400 DUO at Brown University. Barium content was calibrated to the in-situ digested standard reference materials.

We do not perform a lithogenic correction in this study due to poorly constrained spatial variability in lithogenic source composition (Supplementary Text, Figure S1). By including the lithogenic U and Ba, the U/Ba ratio will asymptotically approach a non-zero (implicit lithogenic) value at high oxygen concentrations where the authigenic uranium content may be negligible. At low oxygen concentrations, barium content would not go to zero even if all of the authigenic barite were remineralized. An advantage of this approach is that it limits the sensitivity of U/Ba to barite preservation at low oxygen conditions; i.e., uranium could be added infinitely, but barium removal would be finite. Therefore, total (uncorrected) U/Ba and oxygen could reasonably be made quantitative when applied to local and regional spatial scales.

Benthic foraminifera oxygen and carbon isotopes for *Globobulimina affinis* and *Cibicidoides* spp. were measured using a Finnegan MAT253 IRMS coupled to a Kiel Device at Woods Hole Oceanographic Institution. Typical analyses contained 1-5 specimens of *G. affinis* and 3-6 specimens of *Cibicidoides* spp from > 212 μm coarse fraction. Species availability of *Cibicidoides* spp. in core tops was depth dependent, with *C. pachyderma* abundant at shallow sites (less than 1500 m) and *C. wuellerstorfi* abundant at deeper sites (Oppo et al., 2018). All data from the downcore site (KNR197-3-60GGC) are from *C. wuellerstorfi*. Data were converted to Vienna Pee Dee Belemnite using NBS-19 standards analyzed in each run. Average measurement precision (1 σ), as determined by NBS-19 replicates, was $\pm 0.05\%$ for $\delta^{13}\text{C}$ and $\pm 0.08\%$ for $\delta^{18}\text{O}$.

3.3 Statistical approach

Local calibrations for the Eastern Equatorial Pacific, Arabian Sea, and Western Equatorial Atlantic were created by regressing regional core top U/Ba onto modern BWO

concentrations. An empirical relationship was defined using piecewise linear functions that allowed for up to four linear segments using a published MATLAB shape modeling script (D'Errico, 2022). The regression was run 1000 times, and for each iteration, the regression was based on a random selection of 90% of the available U/Ba datapoints, in order to minimize the sensitivity of the results to any one datapoint. When more than one linear piece was utilized, the break point(s) between pieces were free-floating and determined objectively by the shape modeling script for each iteration. The trend lines are the mean and standard deviation of the 1000 iterations. After completing this process for 1 to 4 piece linear functions, the final trend line was selected as the one that minimized the root mean squared error (RMSE). An example of this process is demonstrated in Figure S2.

In this study, the Holocene is defined as 0-6 ka, and the last glacial maximum is defined as 18-24 ka. All reported statistical significance values were determined by a two-tailed students *t*-test.

4. Results

4.1 New data from the Demerara Rise

New multicore top uranium contents range from 1.73-4.12 ppm and decrease monotonically with water depth ($p < 0.001$) (Figure 3, Supplementary Data 1). Multicore top barium contents range from 337-508 ppm and have no statistically significant trend with depth ($p = 0.81$). Thus, decreasing U/Ba from the shallowest multicore (383 m, $\ln(\text{U/Ba}) = -4.69$ to -4.58) to the deepest multicore (3328 m, $\ln(\text{U/Ba}) = -5.46$ to -5.25) is primarily driven by the uranium signal. A significant water depth trend is also present in $\Delta\delta^{13}\text{C}$, which increases from the shallowest multicore with data (556 m, $\Delta\delta^{13}\text{C} = -1.12$) to the deepest multicore (3328 m, $\Delta\delta^{13}\text{C} = 2.83$). The three $\Delta\delta^{13}\text{C}$ datapoints below 2000 m fall above the calibration range for $\Delta\delta^{13}\text{C}$ (Hoogakker et al., 2015).

New downcore uranium contents in KNR197-3-60GGC range from 2.25-5.42 ppm and decrease monotonically from the LGM to the core top (Figure 4). The difference between the LGM mean value (5.17 ± 0.24 ppm) and the Holocene mean value (2.13 ± 0.23 ppm) is statistically significant ($p = 0.006$). Downcore barium contents range from 311-564 ppm. The maximum barium content occurred at 9.3 ka, which was shortly followed by the minimum barium content at 6.6 ka. Glacial barium contents were fairly constant at 476-498 ppm, but barium content increased through the late Holocene from 322 ppm at 4.3 ka to 460-506 ppm in the multicore top. The variability in the late Holocene results in a statistically insignificant ($p = 0.30$) difference between the LGM mean value and the Holocene mean value. Downcore U/Ba values were high during the last glacial maximum ($\ln(\text{U/Ba}) = -4.54 \pm 0.03$) (Figure 4C). The values decreased through the deglaciation from 16.5 ka to ~ 10 ka. The resolution in this interval is too low to confidently affiliate deviations from a monotonic trend to particular millennial scale events. From ~ 10 ka to present, the U/Ba values were fairly constant with a late Holocene mean of $\ln(\text{U/Ba}) = -5.26 \pm 0.10$. The difference between the LGM mean value and the Holocene mean value is statistically significant ($p = 0.01$).

Downcore $\Delta\delta^{13}\text{C}$ data from KNR197-3-60GGC are at much lower resolution than U/Ba due to a paucity of coincident *G. affinis* and *C. wuellerstorfi* (Figure 4D). Minimum $\Delta\delta^{13}\text{C}$ values

of $2.12 \pm 0.18\text{‰}$ occurred during the LGM, and from 8.8-17.6 ka, $\Delta\delta^{13}\text{C}$ values were fairly constant at $2.22 \pm 0.04\text{‰}$. The absence of *G. affinis* precluded generating any late Holocene $\Delta\delta^{13}\text{C}$ values, but the corresponding multicore top $\Delta\delta^{13}\text{C}$ value is much higher (2.90 ‰) than any of the $\Delta\delta^{13}\text{C}$ values from the LGM and deglaciation. Nearly all $\Delta\delta^{13}\text{C}$ values exceed the calibration limit of the proxy.

4.2 Global data compilation

In the global coretop database, $\ln(\text{U/Ba})$ ranges from -8.60 to -0.42 (mean -5.66), and BWO concentrations range from 0 to 269 $\mu\text{mol/kg}$ (mean 147 $\mu\text{mol/kg}$) (Figure 5). The relationship between U/Ba and BWO behaves as theoretically predicted, with a general trend towards higher U/Ba as BWO concentrations decrease, but the correlation between U/Ba and BWO on a global scale is poor ($R^2 = 0.14$, $p < 0.001$). The highest U/Ba values ($\ln(\text{U/Ba}) > -3$) occur in the Arabian Sea, the Namibian Margin, and the Indo-Pacific Warm Pool (IPWP). While the Arabian Sea is consistent with the general U/Ba to BWO relationship, the Namibian margin and Indo-Pacific Warm Pool are systematically anomalous, with U/Ba increasing at relatively constant BWO concentrations.

In the Arabian Sea, high U/Ba occurs at sites (513-611 m) that have notably high phosphorus contents (1.9-10.8 wt%, Supplementary Data 2). In this region, the high U/Ba values are driven primarily by high uranium content (17.7-63.4 ppm) relative to the rest of core top database (0.11-14 ppm, median 1.6 ppm) rather than low barium content. In the Arabian Sea, the high uranium and high phosphorus content have been linked to abundant fish debris (biogenic) and authigenic apatite (see Lu et al., 2022). Apatite (calcium phosphate) can contain high uranium content (e.g., 30-110 ppm; Baturin and Kochenov, 2001; Kochenov and Baturin, 2002), and if apatite is abundant in the sediment, it may inflate the bulk sedimentary uranium content above that which can be attributed to the authigenic precipitation of uranium based on BWO concentrations. Indeed, in the Arabian Sea, the uranium in apatite was found to contribute as much as 56% of the total uranium in the sediment (Lu et al., 2022). We follow the methodology of Lu et al. (2022) to correct the Arabian Sea data for the uranium contributed by apatite, as a function of the phosphorus content in the sediment. The U/Ba of the high phosphorus samples ($\ln(\text{U/Ba}) = -2.20$ to -0.49) decreased as a result of this correction ($\ln(\text{U/Ba}) = -2.76$ to -1.31).

For samples that did not report phosphorus contents, the apatite correction could not be conducted, and instead $\ln(\text{U/Ba}) \geq -2.20$ was used as a cutoff to exclude samples with a high probability of having uranium contents that are inflated by apatite. This screening excluded an additional 4 sites from the Arabian Sea.

On the Namibian Margin, there is a strong linear positive relationship between U/Ba and phosphorus ($R^2 = 0.71$, $p < 0.001$) and no correlation with BWO ($R^2 = 0.09$, $p = 0.71$). The high U/Ba values occur at shallow sites (216-710 m) that have high phosphorus contents (0.1-9.4 wt%, Supplementary Data 2). Here, barium contents are anomalously low (52-692 ppm, median 155 ppm) relative to the rest of core top database (70-7770 ppm, median 682 ppm) in addition to the sites having high uranium (5.0-360 ppm, median 19 ppm). Unlike the Arabian Sea, sedimentary phosphorus in this region is predominantly found as organic phosphorous rather than in apatite (Küster-Heins et al., 2010), and this phosphorus phase is not associated with particularly high uranium content (Kochenov and Baturin, 2002).

The high U/Ba values may be a function of sulfate reduction leading to barite undersaturation and depressing barium content below what would be expected for this highly productive upwelling region (Brüchert et al., 2003). As a result, the U/Ba proxy is not effective as a BWO proxy, and we exclude these data and do not discuss them further.

In the IPWP, elevated U/Ba values show no correlation with BWO ($R^2 = 0.31$, $p = 0.35$) or phosphorus ($R^2 = 0.40$, $p = 0.23$). Uranium contents (3.3-8.7 ppm) are slightly elevated above the rest of the database, but it is the exceptionally low barium contents (39-66 ppm, median 42 ppm) that are primarily causing the high U/Ba values. As in the Namibian margin, the IPWP likely experiences sulfate reduction that negates the utility of barium as an export productivity proxy (Middelburg, 1991). As a result, U/Ba is not effective as a BWO proxy in this region, and we exclude these data and do not discuss them further.

Adjusting for apatite-bound uranium and excluding the sites as described above, the global correlation (log-linear) slightly improves for sedimentary U/Ba and BWO concentrations ($R^2 = 0.25$, $p < 0.001$). The relationship between U/Ba and BWO improves substantially when the data are separated into different ocean basins (Figure 5B-E). U/Ba and BWO are strongly correlated (log-linear) in the Indian Ocean ($n=80$, $R^2 = 0.73$, $p < 0.001$), the Pacific Ocean ($n=119$, $R^2 = 0.56$, $p < 0.001$), and the Atlantic Ocean ($n=46$, $R^2 = 0.63$, $p < 0.001$). For the Southern Ocean, the sites included in this study only cover a narrow range of BWO concentrations, and thus the correlation between U/Ba and BWO is predictably negligible ($n=32$, $R^2 = 0.01$, $p = 0.63$).

5. Discussion

Qualitatively, U/Ba increases as a function of BWO concentrations, but the spread of the data (particularly below $\ln(\text{U/Ba}) = -5$) precludes the quantitative use of the proxy on a global scale. This limitation is not unexpected given the numerous regionally specific effects on both uranium and barium, as discussed in Section 2. Zooming in on smaller spatial scales should provide more robust and reasonably quantifiable relationships between U/Ba and BWO concentrations as the regional factors become more uniform and/or better constrained. In the next section, we explore the potential efficacy of U/Ba calibrations in three regions (Eastern Equatorial Pacific, Arabian Sea, and Western Equatorial Atlantic) where independent BWO reconstructions from other proxies are available for intercomparison.

5.1 Test cases for regional U/Ba quantification of oxygen concentrations

5.1.1 Eastern Equatorial Pacific

First, we investigate U/Ba in the Eastern Equatorial Pacific (EEP) using data from ODP Leg 202 Site 1240 (0.02 °N, -86.5°E, 2921 m; Figure 6A, yellow star), where Jacobel et al. (2020) quantitatively reconstructed BWO concentrations over the past 150,000 years using $\Delta\delta^{13}\text{C}$ (Figure 6C). This timespan corresponds to the upper ~17 meters of the sediment column at this site, over which porewater sulfate concentrations are relatively stable (Shipboard Scientific Party, 2003) and suggest minimal impact of sulfate reduction on barium preservation.

Past BWO concentrations were found to be significantly lower ($p < 0.01$) in glacial periods than in interglacial periods (Figure 6E, F). For example, the LGM ($115 \pm 2.9 \text{ } \mu\text{mol/kg}$) had about 100 $\mu\text{mol/kg}$ lower BWO concentrations than in the Holocene ($215 \pm 9.8 \text{ } \mu\text{mol/kg}$). Low glacial BWO concentrations were qualitatively corroborated with high alkenone contents (Calvo et al., 2011) and high authigenic uranium contents (Jacobel et al., 2020) that were independent from variability in export productivity. However, quantitative discrepancies between Holocene ($215 \pm 9.8 \text{ } \mu\text{mol/kg}$) and modern ($121 \pm 4.7 \text{ } \mu\text{mol/kg}$) BWO concentrations and between glacial $\Delta\delta^{13}\text{C}$ ($115 \pm 2.9 \text{ } \mu\text{mol/kg}$) and glacial alkenone-based ($<50 \text{ } \mu\text{mol/kg}$) BWO concentrations suggest that the $\Delta\delta^{13}\text{C}$ proxy may be susceptible to a positive bias (i.e., BWO concentrations that are too high). This effect may arise as a result of anaerobic processes that contribute additional negative $\delta^{13}\text{C}$ to *G. affinis* (McCorkle and Emerson, 1988; Piña-Ochoa et al., 2010; Nomaki et al., 2015; Jacobel et al., 2020), such as functional or facultative denitrification conducted by *G. affinis* itself. Holding *C. wuellerstorfi* $\delta^{13}\text{C}$ constant, a more negative *G. affinis* $\delta^{13}\text{C}$ generates a more positive $\Delta\delta^{13}\text{C}$ that in turn yields BWO concentrations that are too high. Empirically, better alignment with modern BWO concentrations and with glacial alkenone-based BWO reconstructions at ODP Site 1240 could be obtained by shifting the $\Delta\delta^{13}\text{C}$ -based oxygen concentrations lower by 65-100 $\mu\text{mol/kg}$ (greater offset in interglacial periods). This inter-proxy inconsistency motivates developing another quantitative proxy capable of recording variability in BWO concentrations above 50 $\mu\text{mol/kg}$.

To test the viability of U/Ba as a quantitative BWO proxy in this region, we subsampled the Pacific dataset (Figure 5C) for only those core tops within the EEP (Figure 6A). The regional calibration was generated as described in the methods (also see Figure S2) and is comprised of three linear functions (Table 1) covering a BWO range from 16-142 $\mu\text{mol/kg}$ ($\ln(\text{U/Ba}) = -4.17$ to -8.60) (Figure 6B). The greatest sensitivity (highest slope) occurs between 52-136 $\mu\text{mol/kg}$, although this range is constrained by only a few datapoints. We then applied this calibration to the previously published uranium and barium data of Jacobel et al. (2020) (Figure 6D). The variability in downcore $\ln(\text{U/Ba})$ record at this site spans a wide range (-5.24 to -7.17 , Figure 6D), but all the data fall within the range of the calibration. BWO concentrations comparable to modern values ($121 \pm 4.7 \text{ } \mu\text{mol/kg}$) occurred in interglacial periods like the Holocene ($126 \pm 11 \text{ } \mu\text{mol/kg}$) and MIS 5 (110-120 ka, $100 \pm 6 \text{ } \mu\text{mol/kg}$) (Figure 6E, F). BWO concentrations were significantly lower ($p < 0.01$) in glacial periods like the LGM ($52 \pm 7 \text{ } \mu\text{mol/kg}$) and MIS 6 (135-145 ka, $49 \pm 9 \text{ } \mu\text{mol/kg}$).

The overall patterns of BWO variability reconstructed from U/Ba and $\Delta\delta^{13}\text{C}$ are remarkably similar over the past two glacial-interglacial cycles. Both proxies indicate that BWO concentrations were lower in glacial periods than in interglacial periods, by $100 \pm 10 \text{ } \mu\text{mol/kg}$ from $\Delta\delta^{13}\text{C}$ and $64 \pm 8 \text{ } \mu\text{mol/kg}$ from U/Ba. Absolute BWO concentrations derived from U/Ba are almost always lower than those from $\Delta\delta^{13}\text{C}$, but they align better with both modern BWO concentrations and with the glacial alkenone-based BWO concentrations ($<50 \text{ } \mu\text{mol/kg}$). Considering the aforementioned hypothesis of Jacobel et al. (2020) that the $\Delta\delta^{13}\text{C}$ -based BWO concentrations may be biased too high, it is possible that, in this region, U/Ba provides more accurate quantification of BWO concentrations in the past.

On the other hand, $\Delta\delta^{13}\text{C}$ likely has the advantage over uranium-based proxies for accurately recording the timing of transitions between different BWO mean states. At ODP1240, $\Delta\delta^{13}\text{C}$ indicates that relatively high BWO concentrations persisted from 125 to 60

ka, then decreased to a minimum at ~22 ka, and subsequently increased into the Holocene. U/Ba suggests that interglacial BWO concentrations started to decline at 94 ka, then maintained low glacial concentrations from 60 to 12 ka, and subsequently rose abruptly into the Holocene. This discrepancy in timing is likely driven by diagenetic remobilization of uranium (i.e. burndown, see Section 2.1). At this site, the premature decline of U/Ba out of the last interglacial period may be attributed to dissolution and downcore reprecipitation of high glacial uranium contents, as demonstrated by Jacobel et al. (2020) in the Equatorial Pacific. Consequently, the application of U/Ba may only be appropriate for capturing the amplitude of BWO variability between mean states (e.g., the LGM vs. the Holocene) rather than constraining the timing or amplitude of transitions.

We propose that the most robust reconstructions of BWO in the EEP can be obtained by the combination of $\Delta\delta^{13}\text{C}$ and U/Ba. The BWO concentrations derived from $\Delta\delta^{13}\text{C}$ capture the timing of transitions, while U/Ba may provide better constraints on the absolute BWO concentrations. Furthermore, substantial discrepancies between the two proxies can identify regions and time periods where $\Delta\delta^{13}\text{C}$ may be affected by anaerobic processes like sulfate reduction or denitrification (by *G. affinis* or other denitrifiers). For example, at ODP1240, the inter-proxy offset appears larger in interglacial periods ($\Delta\delta^{13}\text{C}$ -based BWO concentrations are higher than U/Ba-based BWO by ~100 $\mu\text{mol/kg}$) than in glacial periods (higher by ~60 $\mu\text{mol/kg}$). While it may be expected that anaerobic respiration would be greater in glacial periods when absolute BWO concentrations were lower, this effect may instead be more sensitive to organic carbon fluxes, which were higher in interglacial periods than in glacial periods (Jacobel et al., 2020). There is certainly more work to be done to better understand the intra-proxy mechanics and inter-proxy differences; both proxies would benefit from larger and more robust calibration datasets. Yet, empirically, the utility of U/Ba as a quantitative proxy for BWO appears promising in the EEP.

5.1.2 Arabian Sea

A multiproxy (benthic foraminiferal surface porosity, $\Delta\delta^{13}\text{C}$, benthic I/Ca, aU) reconstruction of BWO was generated by Lu et al. (2022) for the last 30,000 years at site TN41-8PG/JPC (17.8°N, 57.5°E, 761 m) (Figure 7). This timespan corresponds to the upper ~130 cm of the sediment column at this site. At nearby ODP Leg 117 Site 727 (17.8°N, 57.6°E, 915 m), porewater sulfate concentrations decrease from 25 mmol/L (at 600 cm sediment depth) to 1.6 mmol/L (at 3590 cm sediment depth) (Shipboard Scientific Party, 1979), but no data are provided shallower than 600 cm. Another nearby site, boxcore NIOP484 (19.5°N, 58.43°W, 527 m), shows relatively constant porewater sulfate concentrations over the ~30 cm length of the core (Schenau et al., 2001), and subsequent studies on the barium content of the accompanying piston core found no evidence for porewater sulfate depletion or barium diagenesis in sediments covering the past 30,000 years (~500 cm) (Reichart et al., 2002). Therefore, it seems reasonable to assume that barite preservation at TN41-8PG/JPC is not affected either.

Lu et al. (2022) determined that benthic foraminiferal surface porosity was the most robust paleo-BWO proxy in this region, and porosity-based BWO concentrations were found to be significantly higher ($p = 0.03$) in the LGM ($20 \pm 7.7 \mu\text{mol/kg}$) than in the Holocene ($7 \pm 4.7 \mu\text{mol/kg}$). $\Delta\delta^{13}\text{C}$ also captured a decline in BWO from the LGM to the Holocene, but it suggested unrealistically high BWO concentrations (LGM $91 \pm 14 \mu\text{mol/kg}$; Holocene 51 ± 23

$\mu\text{mol/kg}$) that could be attributed to the positive bias on $\Delta\delta^{13}\text{C}$, as observed in the EEP (Section 5.1.1). The semi-quantitative benthic I/Ca and sedimentary aU corroborated that BWO concentrations at this site have remained under the proposed threshold of 50 $\mu\text{mol/kg}$ over the past 30,000 years, but neither proxy was able to detect BWO variability below those limits (Lu et al., 2022). Overall, low BWO concentrations ($<30 \mu\text{mol/kg}$) that may have decreased since the LGM would be consistent with (generally qualitative) evidence for more ventilated oxygen minimum zones in the LGM relative to the Holocene in the Arabian Sea (Altabet et al., 2002; Gaye et al., 2018) and globally (e.g., Erdem et al., 2020; Jaccard & Galbraith, 2012; Tetard et al., 2017).

To test the viability of U/Ba as a quantitative BWO proxy in this region, we subsampled the Indian Ocean dataset (Figure 5A) for only those core tops within the Arabian Sea (Figure 7A). The regional calibration was generated as described in the methods, with a three-piece linear function (Table 1) providing the minimum RMSE. The calibration covers a BWO range from 2.9-149 $\mu\text{mol/kg}$ ($\ln(\text{U/Ba}) = -1.31$ to -7.67) and has the greatest sensitivity between 32-122 $\mu\text{mol/kg}$ (Figure 7B). The variability in the downcore $\ln(\text{U/Ba})$ record at this site is small (-3.87 to -2.77 , Figure 7D) and, unfortunately, within the lowest sensitivity part of the calibration. The result is constant BWO concentrations of around 19 $\mu\text{mol/kg}$ over the past 30,000 years (Figure 7E). Due to the relatively large error ($\sim 13 \mu\text{mol/kg}$), there is no significant difference at any time between U/Ba-based and modern BWO concentrations (Holocene $p = 0.19$; LGM $p = 0.16$) or between U/Ba-based and porosity-based BWO concentrations (Holocene $p = 0.08$; LGM $p = 0.95$). Unsurprisingly, the U/Ba proxy could not register a significant ($p = 0.58$) difference between the LGM ($21 \pm 7.6 \mu\text{mol/kg}$) and the Holocene ($18 \pm 6.4 \mu\text{mol/kg}$).

Like in the EEP, U/Ba seems to more reliably capture absolute BWO concentrations than relative temporal trends. BWO concentrations persistently below 30 $\mu\text{mol/kg}$ at this site match the conclusions of Lu et al. (2022) based on aU. They interpreted aU as a semiquantitative BWO proxy such that at their core site aU content greater than 3 ppm reflected BWO concentrations below 30 $\mu\text{mol/kg}$. This threshold behavior is consistent with the slope change to lower sensitivity at 30 $\mu\text{mol/kg}$ in the regional Arabian Sea U/Ba calibration, and it strongly suggests that U/Ba is not an effective quantitative proxy in regions where BWO concentrations have likely remained below 30 $\mu\text{mol/kg}$ in the past, such as in oxygen minimum zones. Considering that there are existing quantitative (e.g., porosity, benthic foraminifera assemblages) and semi-quantitative (e.g., benthic I/Ca) proxies that are more suitable for these low BWO concentrations, we propose that future proxy development of U/Ba focuses primarily on regions, like the EEP, with high BWO concentrations (e.g., $>50 \mu\text{mol/kg}$) and large BWO variability ($\pm 10\text{s of } \mu\text{mol/kg}$).

5.1.3 Western Equatorial Atlantic

Finally, we test new $\Delta\delta^{13}\text{C}$ and U/Ba from the deep Western Equatorial Atlantic (WEA) at site KNR197-3-60GGC (8.4°N , 52.97°W , 2550 m) over the last 20,000 years. This timespan corresponds to the upper ~ 50 cm of the sediment column at this site. Nearby core GeoB4418-3 (9.26°N , 54.06°W , 2495m) has nearly constant sulfate concentrations over the upper ~ 7 meters at $27.2 \pm 0.8 \text{ mmol/kg}$ (Kasten, 2004), and so we expect that the barite content at our site is well-preserved in the sediment.

Modern BWO concentrations are 260 $\mu\text{mol/kg}$, which is above the calibration limit of $\Delta\delta^{13}\text{C}$ (235 $\mu\text{mol/kg}$, $\Delta\delta^{13}\text{C} = 2.02\text{‰}$; Hoogakker et al., 2015). Indeed, seven out of nine $\Delta\delta^{13}\text{C}$ datapoints fall outside the calibration range (Figure 4D and 8). The two datapoints within the calibration range may indicate that BWO concentrations were lower ($200 \pm 12 \mu\text{mol/kg}$) than modern during the last glacial maximum (18.8-19.6 ka), but just 1 kyr earlier (19.6-20.5 ka) BWO concentrations were still higher than 235 $\mu\text{mol/kg}$. Because the majority of the $\Delta\delta^{13}\text{C}$ values are outside of the calibration, this proxy is ineffective for reconstructing BWO concentrations. Without $\Delta\delta^{13}\text{C}$, there are no previously established proxies that are capable of operating at the high BWO concentrations in this region.

U/Ba could potentially address this issue. To test the viability of U/Ba as a quantitative BWO proxy in this region, we subsampled the Atlantic Ocean dataset (Figure 5D) for only those core tops within the WEA (Figure 8A). The regional calibration was generated as described in the methods, and it is comprised of two linear functions (Table 1, Figure 8B) covering a BWO range from 0-273 $\mu\text{mol/kg}$ ($\ln(\text{U/Ba}) = -2.47$ to -5.50). The segment covering the lowest BWO concentrations is defined by sites at sulfidic depths (i.e., BWO = 0) in the Cariaco Basin, and so they should be evaluated with caution. The greatest sensitivity occurs in the most constrained segment from 137-273 $\mu\text{mol/kg}$ ($\ln(\text{U/Ba}) = -4.85$ to -5.5), which is where most of the downcore $\ln(\text{U/Ba})$ values lie (-4.42 to -5.49 , Figure 8D). While the mean late Holocene value ($224 \pm 6 \mu\text{mol/kg}$) is significantly lower ($p < 0.01$) than the modern BWO concentrations, the multicore top reconstructed BWO concentration ($253 \pm 13 \mu\text{mol/kg}$) is statistically indistinguishable from the modern ($p = 0.29$). Regardless, BWO concentrations in the LGM ($84 \pm 5 \mu\text{mol/kg}$) were significantly lower ($p < 0.01$) than both the modern and the mean late Holocene (Figure 8E).

The offset in U/Ba and $\Delta\delta^{13}\text{C}$ in the WEA is consistent with the positive bias in $\Delta\delta^{13}\text{C}$ observed in both the EEP and the Arabian Sea. In the EEP, $\Delta\delta^{13}\text{C}$ -based BWO concentrations are 60-100 $\mu\text{mol/kg}$ higher than those reconstructed by U/Ba, and in the Arabian Sea, $\Delta\delta^{13}\text{C}$ -based BWO concentrations are greater by $\sim 70 \mu\text{mol/kg}$ than those reconstructed by U/Ba and surface porosity. Shifting the WEA $\Delta\delta^{13}\text{C}$ -based BWO concentrations down by similar offsets (60, 90, and 120 $\mu\text{mol/kg}$) better aligns the absolute values of U/Ba and $\Delta\delta^{13}\text{C}$ BWO concentrations (as noted in previous sections, the absolute values of mean U/Ba are more reliable than their relative trends). Interestingly, optimizing the agreement between U/Ba and $\Delta\delta^{13}\text{C}$ in the LGM requires a large offset ($\sim 120 \mu\text{mol/kg}$), while no discrepancy is apparent in the Holocene. Temporally variable $\Delta\delta^{13}\text{C}$ offsets from U/Ba were also observed at site ODP1240 in the EEP, and this concurrence may imply that $\Delta\delta^{13}\text{C}$ is more sensitive than U/Ba to additional climate-related processes besides changes in BWO concentrations. At the Demerara Rise, the greater offset between U/Ba and $\Delta\delta^{13}\text{C}$ in the LGM relative to the Holocene corresponds with higher glacial organic carbon fluxes (e.g., Figure 4B). More abundant organic matter would fuel respiration in the sediment and potentially intensify the anaerobic processes like denitrification that lower the $\delta^{13}\text{C}$ of *G. affinis*. As yet, the above exercise is only an empirical demonstration of the possibility, and future work is required to investigate whether or not this offset is a real signal and whether its magnitude may vary spatially or temporally.

6. Conclusions

U/Ba has potential to operate regionally as a quantitative proxy for BWO concentrations in the late Pleistocene (last 500,000 years). This new parameterization of uranium normalized to barium has advantages over previous parameterizations, such as authigenic uranium or uranium enrichment factors, by explicitly accounting for changes in organic carbon flux and minimizing the effects of variable sedimentation rates. Although there is no singular global relationship between U/Ba and BWO (Figure 5A), more robust relationships emerge when the data are restricted to smaller spatial scales like ocean basins (Figure 5B-E) and even smaller regional scales like the Eastern Equatorial Pacific (Figure 6B), the Arabian Sea (Figure 7B), and the Western Equatorial Atlantic (Figure 8B). The test calibrations for each of these regions are distinct and non-transferrable, and they should not be applied to sites outside of the domain of the calibration. Future work in other areas will depend on the development of well-constrained, regionally specific core top calibrations.

In the three test regions, the U/Ba proxy performed well at capturing absolute BWO concentrations during mean climate states, like the Holocene and the Last Glacial Maximum. In the Eastern Equatorial Pacific, it was demonstrated that U/Ba is less well suited to capturing the timing of transient BWO variability due to potential remobilization effects from uranium burndown. U/Ba aligned better than $\Delta\delta^{13}\text{C}$ with 1) modern BWO concentrations and reconstructions from alkenone preservation (EEP) and 2) reconstructions from benthic foraminifera surface porosity (Arabian Sea). In all three regions the $\Delta\delta^{13}\text{C}$ -based BWO concentrations appear to be skewed high on the order of 60-150 $\mu\text{mol/kg}$. This offset may indicate that denitrification by *Globobulimina spp.* and its effects on $\Delta\delta^{13}\text{C}$ are not taken into consideration as often as they perhaps should. Future proxy development of both U/Ba and $\Delta\delta^{13}\text{C}$, as well as other paleo-oxygen proxies, will continue to improve our ability to robustly reconstruct oxygen concentrations in the past.

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Appendix A. Supplementary Material.

Online supplementary material include one supplemental discussion section on lithogenic corrections, two figures that support the methodology used in this study, and two datasets for the new Demerara Rise and coretop data.

References

- Altabet, M. A., Higginson, M. J., Murray, D. W., 2002. The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric CO₂. *Nature* **415**, 159–162.
- Anderson, R. F., 1982. Concentration, vertical flux, and remineralization of particulate uranium in seawater. *Geochim. Cosmochim. Acta* **46**, 1293–1299.
- Anderson, R. F., Ali, S., Bradtmiller, L. I., Nielson, S. H. H., Fleisher, M. Q., Anderson, B. E., Burckle, L. H., 2009. Wind-driven upwelling in the Southern Ocean and the deglacial rise in atmospheric CO₂. *Science* **323**, 1443–1448.
- Anderson, R. F., Barker, S., Fleisher, M., Gersonde, R., Goldstein, S. L., Kuhn, G., Mortyn, P. G., Pahnke, K., Sachs, J. P., 2014. Biological response to millennial variability of dust and nutrient supply in the Subantarctic South Atlantic Ocean. *Philos. Trans. R. Soc. London* **372**, 20130054.
- Anderson, R. F., Fleisher, M. Q., LeHuray, A. P., 1989. Concentration, oxidation state, and particulate flux of uranium in the Black Sea. *Geochim. Cosmochim. Acta* **53**, 2215–2224.
- Anderson, R. F., Sachs, J. P., Fleisher, M. Q., Allen, K. A., Yu, J., Koutavas, A., Jaccard, S. L., 2019. Deep-Sea Oxygen Depletion and Ocean Carbon Sequestration During the Last Ice Age. *Global Biogeochem. Cycles* **33**.
- Anderson, R. F., Winckler, G., 2005. Problems with paleoproductivity proxies. *Paleoceanography* **20**, 1–7.
- Armstrong, R. A., Lee, C., Hedges, J. I., Honjo, S., Wakeham, S. G., 2001. A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. *Deep Sea Research Part II: Topical Studies in Oceanography*, **49**, 219–236.
- Arndt, S., Jørgensen, B. B., LaRowe, D. E., Middelburg, J. J., Pancost, R. D., Regnier, P., 2013. Quantifying the degradation of organic matter in marine sediments: A review and synthesis. *Earth-Science Reviews*, **123**, 53–86.
- Barnes, C. E., Cochran, J. K., 1990. Uranium removal in oceanic sediments and the oceanic U balance. *Earth Planet. Sci. Lett.* **97**, 94–101.
- Baturin, G. N., Kochenov, A. V., 2001. Uranium in phosphorites. *Lithology and mineral resources*, **36**, 303–321.
- Berger, W. H., Johnson, R. F., 1978. On the thickness and the ¹⁴C age of the mixed layer in deep-sea carbonates. *Earth Planet. Sci. Lett.* **41**, 223–227.
- Bertram, M. A., Cowen, J. P., 1997. Morphological and compositional evidence for biotic precipitation of marine barite. *J. Mar. Res.* **55**, 577–593.
- Bishop, J. K. B., 1988. The barite-opal-organic carbon association in oceanic particulate matter. *Nature* **332**, 341–343.
- Bonn, W. J., Gingele, F. X., Grobe, H., Mackensen, A., Fütterer, D. K., 1998. Palaeoproductivity at the Antarctic continental margin: opal and barium records for the last 400 ka. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **139**, 195–211.
- Boyle, E. A., 1990. Quaternary Deepwater Paleoceanography. *Science* **249**, 863–870.
- Bradtmiller, L. I., Anderson, R. F., Fleisher, M. Q., Burckle, L. H., 2007. Opal burial in the equatorial Atlantic Ocean over the last 30 ka: Implications for glacial-interglacial changes in the ocean silicon cycle. *Paleoceanography* **22**.
- Brüchert, V., Jørgensen, B. B., Neumann, K., Riechmann, D., Schlösser, M., Schulz, H., 2003. Regulation of bacterial sulfate reduction and hydrogen sulfide fluxes in the central Namibian coastal upwelling zone. *Geochim. Cosmochim. Acta* **67**, 4505–4518.
- Burdige, D. J., Gieskes, J. M., 1983. A pore water/solid phase diagenetic model for manganese in marine sediments. *Am. J. Sci.* **283**, 29–47.
- Cabré, A., Marinov, I., Bernardello, R., Bianchi, D., 2015. Oxygen minimum zones in the tropical Pacific across CMIP5 models: mean state differences and climate change trends. *Biogeosciences* **12**, 5429–5454.
- Calvert, S. E., Pedersen, T. F., 1993. Geochemistry of recent oxic and anoxic sediments: Implications for the geological record. *Mar. Geol.* **113**, 67–88.
- Calvert, S. E., Piper, D. Z., Thunell, R. C., Astor, Y., 2015. Elemental settling and burial fluxes in the

- Cariaco Basin. *Mar. Chem.* **177**, 607–629..
- Calvert, S. E., Price, N. B., 1983. Geochemistry of Namibian Shelf Sediments. In *Coastal Upwelling and Its Sediment Record* (ed. E. Suess). Plenum Press, New York, NY. pp. 337–375.
- Calvo, E., Pelejero, C., Pena, L. D., Cacho, I., Logan, G. A., 2011. Eastern equatorial pacific productivity and related-CO₂ changes since the last glacial period. *Proc. Natl. Acad. Sci. U. S. A.* **108**, 5537–5541.
- Carter, S. C., Paytan, A., Griffith, E. M., 2020. Toward an improved understanding of the marine barium cycle and the application of marine barite as a paleoproductivity proxy. *Minerals* **10**, 1–24.
- Ceccaroni, L., Frank, M., Frignani, M., Langone, L., Ravaioli, M., Mangini, A., 1998. Late Quaternary fluctuations of biogenic component fluxes on the continental slope of the Ross Sea, Antarctica. *J. Mar. Syst.* **17**, 515–525.
- Chase, Z., Anderson, R. F., Fleisher, M. Q., Kubik, P. W., 2003. Scavenging of ²³⁰Th, ²³¹Pa and ¹⁰Be in the Southern Ocean (SW Pacific sector): The importance of particle flux and advection. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **50**, 739–768.
- Church, T. M., Wolgemuth, K., 1972. Marine barite saturation. *Earth Planet. Sci. Lett.* **15**, 35–44.
- Cochran, J. K., 1985. Particle mixing rates in sediments of the eastern equatorial Pacific: Evidence from ²¹⁰Pb, ^{239,240}Pu and ¹³⁷Cs distributions at MANOP sites. *Geochim. Cosmochim. Acta* **49**, 1195–1210.
- Costa, K. M., Anderson, R. F., McManus, J. F., Winckler, G., Middleton, J. L., Langmuir, C. H., 2018. Trace element (Mn, Zn, Ni, V) and authigenic uranium (aU) geochemistry reveal sedimentary redox history on the Juan de Fuca Ridge, North Pacific Ocean. *Geochim. Cosmochim. Acta* **236**, 79–98.
- Costa, K. M., Hayes, C. M., Anderson, R. F., Pavia, F. J., Bausch, A., Deng, F., Dutay, J., Geibert, W., Heinze, C., Henderson, G., Hillaire-Marcel, C., Hoffmann, S., Jaccard, S. L., Jacobel, A. W., Kienast, S. S., Kipp, L., Lerner, P., Lippold, J., Lund, D., Marcantonio, F., McGee, D., McManus, J. F., Mekik, F., Middleton, J. L., Missiaen, L., Not, C., Pichat, S., Robinson, L. F., Rowland, G. H., Roy-Barman, M., Tagliabue, A., Torfstein, A., Winckler, G., Zhou, Y., 2020. ²³⁰Th normalization: New insights on an essential tool for quantifying sedimentary fluxes in the modern and Quaternary ocean. *Paleoceanogr. Paleoclimatology* **35**.
- Costa, K. M., McManus, J. F., 2017. Efficacy of ²³⁰Th normalization in sediments from the Juan de Fuca Ridge, northeast Pacific Ocean. *Geochim. Cosmochim. Acta* **197**, 215–225.
- Costa, K. M., McManus, J. F., Anderson, R. F., Ren, H., Sigman, D. M., Winckler, G., Fleisher, M. Q., Marcantonio, F., Ravelo, A. C., 2016. No iron fertilization in the equatorial Pacific Ocean during the last ice age. *Nature* **529**, 519–522.
- Crusius, J., Calve, S., Pedersen, T., Sage, D., 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. *Earth Planet. Sci. Lett.* **145**, 65–78.
- D'Errico J. (2022) SLM - Shape Language Modeling.
<https://www.mathworks.com/matlabcentral/fileexchange/24443-slm-shape-language-modeling>.
- D'Hondt, S., Spivack, A. J., Pockalny, R., Ferdelman, T. G., Fischer, J. P., Kallmeyer, J., Abrams, L. J., Smith, D. C., Graham, D., Hasiuk, F., Schrum, H., 2009. Subseafloor sedimentary life in the South Pacific Gyre. *Proceedings of the National Academy of Sciences*, **106**, 11651–11656.
- D'Hondt, S., Inagaki, F., Zarikian, C. A., Abrams, L. J., Dubois, N., Engelhardt, T., Evans, H., Ferdelman, T., Gribsholt, B., Harris, R. N., Hoppie, B. W., 2015. Presence of oxygen and aerobic communities from sea floor to basement in deep-sea sediments. *Nature Geoscience*, **8**, 299–304.
- Dehairs, F., Chesselet, R., Jedwab, J., 1980. Discrete suspended particles of barite and the barium cycle in the open ocean. *Earth Planet. Sci. Lett.* **49**, 528–550.
- Dorta, C. C., Rona, E., 1971. Geochemistry of Uranium in the Cariaco Trench. *Bull. Mar. Sci.*, 754–765.
- Dymond, J., Suess, E., Lyle, M. W., 1992. Barium in deep-sea sediment: A geochemical proxy for paleoproductivity. *Paleoceanography* **7**, 163–181.
- Eagle, M., Paytan, A., Murray, R. W., 2003. A comparison between excess barium and barite as

- indicators of carbon export. *Paleoceanography* **18**, 1–13.
- Endrizzi, F., Rao, L., 2014. Chemical speciation of uranium(VI) in marine environments: Complexation of calcium and magnesium ions with [(UO₂)(CO₃)₃]⁴⁻ and the effect on the extraction of uranium from seawater. *Chem. - A Eur. J.* **20**, 14499–14506.
- Erdem, Z., Schönfeld, J., Rathburn, A. E., Pérez, M. E., Cardich, J., Glock, N., 2020. Bottom-water deoxygenation at the Peruvian margin during the last deglaciation recorded by benthic foraminifera. *Biogeosciences* **17**, 3165–3182.
- Fleisher, M. Q., Anderson R. F., 2003. Assessing the collection efficiency of Ross Sea sediment traps using ²³⁰Th and ²³¹Pa. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **50**, 693–712.
- Francis, A. J., Dodge, C. J., Lu, F., Halada, G. P., Clayton, C. R., 1994. XPS and XANES studies of uranium reduction by *Clostridium* sp. *Environ. Sci. Technol.* **28**, 636–639.
- Frank, M., Eisenhauer, A., Bonn, W. J., Walter, P., Grobe, H., Kubik, P. W., Dittrich-Hannen, B., Mangini, A., 1995. Sediment redistribution versus paleoproductivity change: Weddell Sea margin sediment stratigraphy and biogenic particle flux of the barium profiles. *Earth Planet. Sci. Lett.* **136**, 559–573.
- Frank, M., Gersonde, R., Rutgers van der Loeff, M. M., Bohrmann, G., Nurnberg, C. C., Kubik, P. W., Suter, M., Mangini, A., 2000. Similar glacial and interglacial export bioproductivity in the Atlantic sector of the Southern Ocean: Multiproxy evidence and implications for glacial atmospheric CO₂. *Paleoceanography* **15**, 642–658.
- Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta* **43**, 1075–1090.
- Fu, W., Primeau, F., Moore, K. J., Lindsay, K., Randerson J. T., 2018. Reversal of Increasing Tropical Ocean Hypoxia Trends With Sustained Climate Warming. *Global Biogeochem. Cycles* **32**, 551–564.
- Ganesh, R., Robinson, K. G., Reed, G. D., 1997. Reduction of Hexavalent Uranium from Organic Complexes by Sulfate- and Iron-Reducing Bacteria. *Appl. Environ. Microbiol.* **63**, 4385–4391.
- Ganeshram, R. S., François, R., Commeau, J., Brown-Leger, S. L., 2003. An experimental investigation of barite formation in seawater. *Geochim. Cosmochim. Acta* **67**, 2599–2605.
- Garcia, H. E., Cruzado, A., Gordon, L., Escanez, J., 1998. Decadal-scale chemical variability in the subtropical North Atlantic deduced from nutrient and oxygen data. *J. Geophys. Res.* **103**, 2817–2830.
- Garcia, H. E., Weathers, K., Paver, C. R., Smolyar, I., Boyer T. P., Locarnini, M. M., Zweng, M. M., Mishonov, A. V., Baranova, O. K., Seidov, D., Reagan J. R., 2019. *World Ocean Atlas 2018, Volume 3: Dissolved Oxygen, Apparent Oxygen Utilization, and Dissolved Oxygen Saturation*. <https://archimer.ifremer.fr/doc/00651/76337/>.
- Gaye, B., Böll, A., Segschneider, J., Burdanowitz, N., Emeis, K.-C., Ramaswamy, V., Lahajnar, N., Lückge, A., Rixen, T., 2018. Glacial–interglacial changes and Holocene variations in Arabian Sea denitrification. *Biogeosciences* **15**, 507–527.
- GEOTRACES Intermediate Data Product Group G., 2021. The GEOTRACES Intermediate Data Product 2021 (IDP2021).
- Gonneea, M. E., Paytan, A., 2006. Phase associations of barium in marine sediments. *Mar. Chem.* **100**, 124–135.
- Gonzalez-Muñoz, M. T., Martinez-Ruiz, F., Morcillo, F., Martin-Ramos, J. D., Paytan, A., 2012. Precipitation of barite by marine bacteria: A possible mechanism for marine barite formation. *Geology* **40**, 675–678.
- Gouretski, V., Koltermann, K. P., 2004. *WOCE global hydrographic climatology*.
- Hartnett, H. E., Keil, R. G., Hedges, J. I., Devol, A. H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature*, 391(February), 572–575.
- Hayes, C. T., Costa, K. M., Anderson, R. F., Calvo, E., Chase, Z., Demina, L. L., Dutay, J. C., German, C. R., Heimbürger-Boavida, L. E., Jaccard, S. L., Jacobel, A., Kohfeld, K. E., Kravchishina, M. D., Lippold, J., Mekik, F., Missiaen, L., Pavia, F. J., Paytan, A., Pedrosa-

Pamies, R., Petrova, M. V., Rahman, S., Robinson, L. F., Roy-Barman, M., Sanchez-Vidal, A.,
 Shiller, A., Tagliabue, A., Tessin, A. C., van Hulten, M., Zhang, J., 2021. Global Ocean
 Sediment Composition and Burial Flux in the Deep Sea. *Global Biogeochem. Cycles* **35**, 1–25.
 Hickey, B., 2016. Reconstructing past flow rates of southern component water masses using
 sedimentary $^{231}\text{Pa}/^{230}\text{Th}$. Ph.D dissertation, University of Oxford.
 Hoogakker, B. A. A., Elderfield, H., Schmiedl, G., McCave, I. N., Rickaby, R. E. M., 2015. Glacial-
 interglacial changes in bottom-water oxygen content on the Portuguese margin. *Nat. Geosci.* **8**,
 2–5.
 Horner, T. J., Kinsley, C. W., Nielsen S. G., 2015. Barium-isotopic fractionation in seawater
 mediated by barite cycling and oceanic circulation. *Earth Planet. Sci. Lett.* **430**, 511–522.
 Jaccard, S. L., Galbraith, E. D., 2012. Large climate-driven changes of oceanic oxygen concentrations
 during the last deglaciation. *Nat. Geosci.* **5**, 151–156.
 Jaccard, S. L., Galbraith, E. D., Sigman, D. M., Haug, G. H., Francois, R., Pedersen, T. F., Dulski, P.,
 Thierstein, H. R., 2009. Subarctic Pacific evidence for a glacial deepening of the oceanic
 respired carbon pool. *Earth Planet. Sci. Lett.* **277**, 156–165.
 Jacobel, A. W., Anderson, R. F., Jaccard, S. L., McManus, J. F., Pavia, F. J., Winckler, G., 2020. Deep
 Pacific storage of respired carbon during the last ice age: Perspectives from bottom water
 oxygen reconstructions. *Quat. Sci. Rev.* **230**, 106065.
 Jacobel, A. W., McManus, J. F., Anderson, R. F., Winckler, G., 2017. Repeated storage of respired
 carbon in the equatorial Pacific Ocean over the last three glacial cycles. *Nat. Commun.* **8**.
 Jorissen, F. J., Fontanier, C., Thomas, E., 2007. Paleooceanographical Proxies Based on Deep-Sea
 Benthic Foraminiferal Assemblage Characteristics. *Dev. Mar. Geol.* **1**, 263–325.
 Kasten, Sabine, 2004. Porewater geochemistry of sediment core GeoB4418-3. PANGAEA,
<https://doi.org/10.1594/PANGAEA.222556>
 Keeling, R. F., Kortzinger, A., Gruber, N., 2010. Ocean Deoxygenation in a Warming World. *Ann.*
Rev. Mar. Sci. **2**, 199–229.
 Klinkhammer, G. P., Palmer, M. R., 1991. Uranium in the oceans: Where it goes and why. *Geochim.*
Cosmochim. Acta **55**, 1799–1806.
 Kochenov, A. V., Baturin, G. N., 2002. The Paragenesis of Organic Matter, Phosphorus, and
 Uranium in Marine Sediments. *Lithol. Miner. Resour.* **37**, 107–120.
 Kochenov A. V., Korloev, K. G., Dubinchuk, V. T., Medvedev Y. L., 1977. Experimental data on the
 conditions of precipitation of uranium from aqueous solutions. *Geochemistry Int.* **14**, 82–87.
 Küster-Heins, K., Steinmetz, E., De Lange, G. J., Zabel, M., 2010. Phosphorus cycling in marine
 sediments from the continental margin off Namibia. *Mar. Geol.* **274**, 95–106.
 Kuwabara, J. S., Geen, A. V., McCorkle, D. C., Bernhard, J. M., 1999. Dissolved sulfide distributions
 in the water column and sediment pore waters of the Santa Barbara Basin. *Geochim.*
Cosmochim. Acta **63**, 2199–2209.
 Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to
 sedimentary ore deposits. *Geochim. Cosmochim. Acta* **42**, 547–569.
 Lee, C., Wakeham, S., Arnosti, C., 2004. Particulate organic matter in the sea: the composition
 conundrum. *AMBIO: A Journal of the Human Environment*, **33**, 565–575.
 Lee, S. Y., Cha, W. S., Kim, J. G., Baik, M. H., Jung, E. C., Jeong, J. T., Kim, K., Chung, S. Y., Lee,
 Y. J., 2014. Uranium (IV) remobilization under sulfate reducing conditions. *Chemical*
Geology, **370**, 40–48.
 Lee, T. R., Wood, W. T., Phrampus, B. J., 2019. A Machine Learning (kNN) Approach to Predicting
 Global Seafloor Total Organic Carbon. *Global Biogeochem. Cycles* **33**, 37–46.
 Liger, E., Charlet, L., Van Cappellen, P., 1999. Surface catalysis of uranium (VI) reduction by iron
 (II). *Geochim. Cosmochim. Acta* **63**, 2939–2955.
 Lippold, J., Gutjahr, M., Blaser, P., Christner, E., de Carvalho Ferreira, M. L., Mulitza, S., Christl,
 M., Wombacher, F., Böhm, E., Antz, B., Cartapanis, O., Vogel, H., Jaccard, S. L., 2016. Deep
 water provenance and dynamics of the (de)glacial Atlantic meridional overturning circulation.
Earth Planet. Sci. Lett. **445**, 68–78.
 Loveley, M. R., Marcantonio, F., Wisler, M. M., Hertzberg, J. E., Schmidt, M. W., Lyle, M. W., 2017.

1019 Millennial-scale iron fertilization of the eastern equatorial Pacific over the past 100,000 years.
 1020 *Nat. Geosci.* **10**, 1–4.
 1021 Lovley, D. R., Phillips, E. J. P., Gorby, Y. A., Landa, E. R., 1991. Microbial reduction of Uranium.
 1022 *Nature* **350**, 413–416.
 1023 Lovley, D. R., Phillips, E. J., 1992. Reduction of uranium by *Desulfovibrio desulfuricans*. *Applied and*
 1024 *environmental microbiology*, **58**, 850–856.
 1025 Lu, W., Barbosa, C. F., Rathburn, A. E., Xavier, P. da M., Cruz, A. P. S., Thomas, E., Rickaby, R. E.
 1026 M., Zhang, Y. G., Lu, Z., 2021. Proxies for paleo-oxygenation: A downcore comparison between
 1027 benthic foraminiferal surface porosity and I/Ca. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **579**,
 1028 110588.
 1029 Lu, W., Rickaby, R. E. M., Hoogakker, B. A. A., Rathburn, A. E., Burkett, A. M., Dickson, A. J.,
 1030 Martínez-Méndez, G., Hillenbrand, C. D., Zhou, X., Thomas, E., Lu, Z., 2020. I/Ca in epifaunal
 1031 benthic foraminifera: A semi-quantitative proxy for bottom water oxygen in a multi-proxy
 1032 compilation for glacial ocean deoxygenation. *Earth Planet. Sci. Lett.* **533**, 116055.
 1033 Lu, W., Wang, Y., Oppo, D. W., Nielsen, S. G., Costa, K. M., 2022. Comparing paleo-oxygenation
 1034 proxies (benthic foraminiferal surface porosity, I/Ca, authigenic uranium) on modern sediments
 1035 and the glacial Arabian Sea. *Geochim. Cosmochim. Acta* **331**, 69–85.
 1036 Mangini, A., Jung, M., Laukenmann, S., 2001. What do we learn from peaks of uranium and of
 1037 manganese in deep sea sediments? *Mar. Geol.* **177**, 63–78.
 1038 Martínez-García, A., Rosell-Melé, A., Geibert, W., Gersonde, R., Masqué, P., Gaspari, V., Barbante,
 1039 C., 2009. Links between iron supply, marine productivity, sea surface temperature, and CO₂
 1040 over the last 1.1 Ma. *Paleoceanography* **24**.
 1041 Martínez-Ruiz, F., Jroundi, F., Paytan, A., Guerra-Tschuschke, I., Abad, M. D. M., González-Muñoz,
 1042 M. T., 2018. Barium bioaccumulation by bacterial biofilms and implications for Ba cycling and
 1043 use of Ba proxies. *Nat. Commun.* **9**, 1–9.
 1044 Martínez-Ruiz, F., Paytan, A., González-Muñoz, M. T., Jroundi, F., Abad, M. M., Lam, P. J., Bishop,
 1045 J. K. B., Horner, T. J., Morton, P. L., Kastner, M., 2019. Barite formation in the ocean: Origin of
 1046 amorphous and crystalline precipitates. *Chem. Geol.* **511**, 441–451.
 1047 Matear, R. J., Hirst, A. C., 2003. Long-term changes in dissolved oxygen concentrations in the ocean
 1048 caused by protracted global warming. *Global Biogeochem. Cycles* **17**, 1125.
 1049 McCorkle, D. C., Emerson, S. R., 1988. The relationship between pore water carbon isotopic
 1050 composition and bottom water oxygen concentration. *Geochim. Cosmochim. Acta* **52**, 1169–1178.
 1051 McManus, J., Berelson, W. M., Klinkhammer, G. P., Hammond, D. E. and Holm C. (2005) Authigenic
 1052 uranium: relationship to oxygen penetration depth and organic carbon rain. *Geochim.*
 1053 *Cosmochim. Acta* **69**, 95–108.
 1054 McManus, J., Berelson, W. M., Klinkhammer, G. P., Johnson, K. S., Coale, K. H., Anderson, R. F.,
 1055 Kumar, N., Burdige, D. J., Hammond, D. E., Brumsack, H. J., McCorkle, D. C., Rushdi, A.,
 1056 1998. Geochemistry of barium in marine sediments: implications for its use as a paleoproxy.
 1057 *Geochim. Cosmochim. Acta* **62**, 3453–3473.
 1058 McManus, J., Berelson, W. M., Klinkhammer, G. P., Kilgore, T. E., Hammond, D. E., 1994.
 1059 Remobilization of barium in continental margin sediments. *Geochim. Cosmochim. Acta* **58**,
 1060 4899–4907.
 1061 McManus, J., Berelson, W. M., Severmann, S., Poulson, R. L., Hammond, D. E., Klinkhammer, G. P.,
 1062 Holm C., 2006. Molybdenum and uranium geochemistry in continental margin sediments: 1063
 Paleoproxy potential. *Geochim. Cosmochim. Acta* **70**, 4643–4662.
 1064 Middelburg, J. J., 1991. Organic carbon, sulphur, and iron in recent semi-euxinic sediments of Kau
 1065 Bay, Indonesia. *Geochim. Cosmochim. Acta* **55**, 815–828.
 1066 Mills, R. A., Taylor, S. L., Pälike, H., Thomson, J., 2010. Hydrothermal sediments record changes in
 1067 deep water oxygen content in the SE Pacific. *Paleoceanography* **25**, PA4226.
 1068 Monnin, C., Jeandel, C., Cattaldo, T., Dehairs, F., 1999. The marine barite saturation state of the
 1069 world's oceans. *Mar. Chem.* **65**, 253–261.
 1070 Morford, J. L., Emerson, S., 1999. The geochemistry of redox sensitive trace metals in sediments.
 1071 *Geochim. Cosmochim. Acta* **63**, 1735–1750.

- Morford, J. L., Martin, W. R., Carney, C. M., 2009. Uranium diagenesis in sediments underlying bottom waters with high oxygen content. *Geochim. Cosmochim. Acta* **73**, 2920–2937.
- Müller, P. J., Suess, E., 1979. Productivity, sedimentation rate, and sedimentary organic matter in the oceans-I. Organic carbon preservation. *Deep Sea Research Part A. Oceanographic Research Papers*, 26(12), 1347–1362.
- Murray, R. W., Knowlton, C., Leinen, M., Mix, A. C., Polsky, C. H., 2000. Export production and carbonate dissolution in the central equatorial Pacific Ocean over the past 1 Myr. *Paleoceanography* **15**, 570–592.
- Nakashima, S., Disnar, J.-R., Perruchot, A., Trichet, J., 1984. Experimental study of mechanisms of fixation and reduction of uranium by sedimentary organic matter under diagenetic or hydrothermal conditions. *Geochim. Cosmochim. Acta* **48**, 2321–2329.
- Nameroff, T. J., Balistrieri, L. S., Murray, J. W., 2002. Suboxic trace metal geochemistry in the eastern tropical North Pacific. *Geochim. Cosmochim. Acta* **66**, 1139–1158.
- Neimann, S., Geibert, W., 2003. 231Pa ex and 230Th ex at the southeast South American continental margin - Is the 231Pa ex / 230Th ex ratio a proxy for particle flux or ocean circulation? Ph.D. dissertation, Freie Universität Berlin.
- Nomaki, H., Chikaraishi, Y., Tsuchiya, M., Toyofuku, T., Suga, H., Sasaki, Y., Uematsu, K., Tame, A., Ohkouchi, N., 2015. Variation in the nitrogen isotopic composition of amino acids in benthic foraminifera: Implications for their adaptation to oxygen-depleted environments. *Limnol. Oceanogr.* **60**, 1906–1916.
- Ohkushi, K., Kennett, J. P., Zeleski, C. M., Moffitt, S. E., Hill, T. M., Robert, C., Beaufort, L., Behl, R. J., 2013. Quantified intermediate water oxygenation history of the NE Pacific: A new benthic foraminiferal record from Santa Barbara basin. *Paleoceanography* **28**, 453–467.
- Olsen, A., Key, R. M., Van Heuven, S., Lauvset, S. K., Velo, A., Lin, X., Schirnick, C., Kozyr, A., Tanhua, T., Hoppema, M., Jutterström, S., Steinfeldt, R., Jeansson, E., Ishii, M., Pérez, F. F., Suzuki, T., 2016. The global ocean data analysis project version 2 (GLODAPv2) - An internally consistent data product for the world ocean. *Earth Syst. Sci. Data* **8**, 297–323.
- Oppo, D. W., Gebbie, G., Huang, K., 2018. Data Constraints on Glacial Atlantic Water Mass Geometry and Properties. *Paleoceanogr. Paleoclimatology* **33**, 1013–1034.
- Orsi, A. H., Whitworth, T., Nowlin, W. D., 1995. On the meridional extent and fronts of the Antarctic Circumpolar Current. *Deep-Sea Research Part I*, **42**, 641–673.
- Oschlies, A., Schulz, K. G., Riebesell, U., Schmittner, A., 2008. Simulated 21st century's increase in oceanic suboxia by CO₂-enhanced biotic carbon export. *Global Biogeochem. Cycles* **22**, GB4008.
- Owens, S. A., Buesseler, K. O., Sims, K. W. W., 2011. Re-evaluating the 238U-salinity relationship in seawater: Implications for the 238U–234Th disequilibrium method. *Mar. Chem.* **127**, 31–39.
- Palter, J. B., Trossman, D. S., 2018. The Sensitivity of Future Ocean Oxygen to Changes in Ocean Circulation. *Global Biogeochem. Cycles* **32**, 738–751.
- Paytan, A., Kastner, M., 1996. Benthic Ba fluxes in the central Equatorial Pacific, implications for the oceanic Ba cycle. *Earth Planet. Sci. Lett.* **142**, 439–450.
- Pfeifer, K., Kasten, S., Hensen, C., Schulz, H. D., 2001. Reconstruction of primary productivity from the barium contents in surface sediments of the South Atlantic Ocean. *Mar. Geol.* **177**, 13–24.
- Pilson, M.E., 2012. *An Introduction to the Chemistry of the Sea*. Cambridge University Press.
- Piña-Ochoa, E., Koho, K., Geslin, E., Risgaard-Petersen, N., 2010. Survival and life strategy of the foraminiferan *Globobulimina turgida* through nitrate storage and denitrification. *Mar. Ecol. Prog. Ser.* **417**, 39–49.
- Prahl, F. G., Collier, R. B., Dymond, J., Lyle, M., Sparrow, M. A., 1993. A biomarker perspective on prymnesiophyte productivity in the northeast pacific ocean. *Deep. Res. Part I* **40**, 2061–2076.
- Prakash Babu, C., Brumsack, H. J., Schnetger, B., Böttcher, M. E., 2002. Barium as a productivity proxy in continental margin sediments: A study from the eastern Arabian Sea. *Mar. Geol.* **184**, 189–206.
- Rathburn, A. E., Willingham, J., Ziebis, W., Burkett, A. M., Corliss, B. H., 2018. A New biological proxy for deep-sea paleo-oxygen: Pores of epifaunal benthic foraminifera. *Sci. Rep.* **8**, 1–8.
- Reichart, G. J., Schenau, S. J., De Lange, G. J., Zachariasse, W. J., 2002. Synchronicity of oxygen

- minimum zone intensity on the Oman and Pakistan Margins at sub-Milankovitch time scales. *Mar. Geol.* **185**, 403-415.
- Reimers, C. E., Lange, C., Tabak, M., Bernhard, J. M., 1990. Seasonal spillover and varve formation in the Santa Barbara Basin, California. *Limn. Ocean* **35**, 1577-1585.
- Reimers, C. E., Ruttenberg, K. C., Canfield, D. E., Christiansen, M. B., Martin, J. B., 1996. Porewater pH and authigenic phases formed in the uppermost sediments of Santa Barbara Basin. *Geochim. Cosmochim. Acta* **60**, 4037-4057.
- Raven, M. R., Sessions, A. L., Fischer, W. W., Adkins, J. F., 2016. Sedimentary pyrite $\delta^{34}\text{S}$ differs from porewater sulfide in Santa Barbara Basin: Proposed role of organic sulfur. *Geochim. Cosmo. Acta* **186**, 120-134.
- Rodrigo-Gámiz, M., Rampen, S. W., Schouten, S., Sinninghe Damsté, J. S., 2016. The impact of oxic degradation on long chain alkyl diol distributions in Arabian Sea surface sediments. *Org. Geochem.* **100**, 1-9.
- Rudnick, R. L., Gao, S., 2003. Composition of the Continental Crust. In *The crust* pp. 1-64.
- Russell, A. D., Hönisch, B., Spero, H. J., Lea, D. W., 2004. Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera. *Geochim. Cosmochim. Acta* **68**, 4347-4361.
- Sani, R. K., Peyton, B. M., Amonette, J. E., Geesey, G. G., 2004. Reduction of uranium (VI) under sulfate-reducing conditions in the presence of Fe (III)-(hydr)oxides. *Geochim. Cosmochim. Acta* **68**, 2639-2648.
- Sarin, M. M., Borole, D. V., Krishnaswami, S., 1979. Geochemistry and geochronology of sediments from the Bay of Bengal and the equatorial Indian Ocean. *Proc. Indian Acad. Sci. - Earth Planet. Sci.* **88A**, 131-154.
- Sarkar, A., Bhattacharya, S. K., Sarin, M. M., 1993. Geochemical evidence for anoxic deep water in the Arabian Sea during the last glaciation. *Geochim. Cosmochim. Acta* **57**, 1009-1016.
- Schenau, S. J., Prins, M. A., De Lange, G. J., Monnin, C., 2015. Barium accumulation in the Arabian Sea: controls on barite preservation in marine sediments. *Geochim. Cosmochim. Acta* **65**, 1545-1556.
- Schoepfer, S. D., Shen, J., Wei, H., Tyson, R. V., Ingall, E., Algeo, T. J., 2015. Total organic carbon, organic phosphorus, and biogenic barium fluxes as proxies for paleomarine productivity. *Earth-Science Rev.* **149**, 23-52.
- Serno, S., Winckler, G., Anderson, R. F., Hayes, C. T., McGee, D., Machalett, B., Ren, H., Straub, S. M., Gersonde, R., Haug, G. H., 2014. Eolian dust input to the Subarctic North Pacific. *Earth Planet. Sci. Lett.* **387**, 252-263.
- Sharon, Belanger, C. L., 2022. Placing North Pacific paleo-oxygenation records on a common scale using multivariate analysis of benthic foraminiferal assemblages. *Quat. Sci. Rev.* **280**, 107412.
- Shigemitsu, M., Narita, H., Watanabe, Y. W., Harada, N., Tsunogai, S., 2007. Ba, Si, U, Al, Sc, La, Th, C and $\delta^{13}\text{C}/\delta^{12}\text{C}$ in a sediment core in the western subarctic Pacific as proxies of past biological production. *Mar. Chem.* **106**, 442-455.
- Shipboard Scientific Party, 1989. Site 727. In Prell, W.L., Niitsuma, N., et al., Proc. ODP, Init. Repts., 117: College Station, TX (Ocean Drilling Program), 467-493. doi:10.2973/odp.proc.ir.117.114.1989
- Shipboard Scientific Party, 2003. Site 1240. In Mix, A.C., Tiedemann, R., Blum, P., et al., Proc. ODP, Init. Repts., 202: College Station, TX (Ocean Drilling Program), 1-82. doi:10.2973/odp.proc.ir.202.111.2003
- Sigman, D. M., Boyle, E. A., 2000. Glacial/interglacial variations in atmospheric carbon dioxide. *Nature* **407**, 859-869.
- Sigman, D. M., Hain, M. P., Haug, G. H., 2010. The polar ocean and glacial cycles in atmospheric CO_2 concentration. *Nature* **466**, 47-55.
- Singh, A. K., Marcantonio, F., Lyle, M., 2020. An Assessment of xsBa Flux as a Paleoproductivity Indicator and Its Water-Depth Dependence in the Easternmost Equatorial Pacific Ocean. *Paleoceanogr. Paleoclimatology* **35**, 1-17.
- Singh, A. K., Marcantonio, F., Lyle, M. W., 2011. Sediment focusing in the panama basin, eastern

1178 equatorial pacific ocean. *Earth Planet. Sci. Lett.* **309**, 33–44.

1179 Sirocko, F., Garbe-Schonberg, D., Devey C., 2000. Processes controlling trace element geochemistry
1180 of Arabian Sea sediments during the last 25,000 years. *Glob. Planet. Change* **26**, 217–303.

1181 Stramma, L., Johnson, G. C., Sprintall, J., Mohrholz, V., 2008. Expanding Oxygen-Minimum Zones
1182 in the Tropical Oceans. *Science* **320**, 655–659.

1183 Stramma, L., Oschlies, A., Schmidtke, S., 2012. Mismatch between observed and modeled trends in
1184 dissolved upper-ocean oxygen over the last 50 yr. *Biogeosciences* **9**, 4045–4057.

1185 Taylor, S. R., McLennan, S. M., 1995. The geochemical evolution of the continental crust. *Rev.*
1186 *Geophys.* **33**, 241–265.

1187 Tetard, M., Licari, L., Beaufort, L., 2017. Oxygen history off Baja California over the last 80 kyr: A
1188 new foraminiferal-based record. *Paleoceanography*, 246–264.

1189 Tetard, M., Ovsepyan, E., Licari, L., 2021. Eubuliminella tenuata as a new proxy for quantifying
1190 past bottom water oxygenation. *Mar. Micropaleontol.* **166**, 102016.

1191 Thorton, S.E., 1984. Basin model for hemipelagic sedimentation in a tectonically active continental
1192 margin: Santa Barbara Basin, California Continental Borderland. In *Geological Society,*
1193 *London, Special Publications*, London, United Kingdom. **15**, pp. 377-394.

1194 Torres, M. E., Brumsack, H. J., Bohrmann, G., Emeis K.-C., 1996. Barite fronts in continental
1195 margin sediments: a new look at barium remobilization in the zone of sulfate reduction and
1196 formation of heavy barites in diagenetic fronts. *Chem. Geol.* **127**, 125–139.

1197 Trauth, M. H., 2013. TURBO2: A MATLAB simulation to study the effects of bioturbation on
1198 paleoceanographic time series. *Comput. Geosci.* **61**, 1–10.

1199 Veeh, H. H., Heggie, D. T., Crispe, A. J., 1999. Biogeochemistry of southern Australian continental
1200 slope sediments. *Aust. J. Earth Sci.* **46**, 563–575.

1201 Veeh H. H., McCorkle, D. C., Heggie, D., 2000. Glacial/interglacial variations of sedimentation on the
1202 West Australian continental margin: constraints from excess ²³⁰Th. *Mar. Geol.* **166**, 11–30.

1203 Von Breymann, M. T., Brumsack, H. J., Emeis, K.-C., Camerlenghi, A., 1992. Depositional and
1204 Diagenetic Behavior of Barium in the Japan Sea. In *Proceedings of the Ocean Drilling Program,*
1205 *127/128 Scientific Results* College Station, TX, USA. pp. 651–665.

1206 Wang, Y., Lu, W., Costa, K. M., Nielsen, S. G., 2022. Beyond anoxia: exploring sedimentary thallium
1207 isotopes in paleo-redox reconstructions from a new core top collection. *Geochim. Cosmochim.*
1208 *Acta* **333**, 347–361.

1209 Weber, M. E., 1998. Estimation of biogenic carbonate and opal by continuous non-destructive
1210 measurements in deep-sea sediments: application to the eastern Equatorial Pacific. *Deep Sea*
1211 *Res. Part I Oceanogr. Res. Pap.* **45**, 1955–1975.

1212 Zheng, Y., Anderson, R. F., Geen, A. Van, Fleisher, M. Q., 2002. Preservation of particulate non-
1213 lithogenic uranium in marine sediments. *Geochim. Cosmochim. Acta* **66**, 3085–3092.

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1216 **Table 1.** Regional calibration functions of the form $BWO=m\pm\Delta m * \ln(U/Ba) + b\pm\Delta b$.
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Eastern Equatorial Pacific					
Piece #	Applicable $\ln(U/Ba)$ range	m	Δm	b	Δb
1	-8.60 to -7.06	-3.59	1.29	111.4	10.0
2	-7.06 to -5.46	-59.5	1.94	-276.4	12.2
3	-5.46 to -4.17	-24.9	2.72	-90.5	13.1
Arabian Sea					
Piece #	Applicable $\ln(U/Ba)$ range	m	Δm	b	Δb
1	-7.67 to -6.26	-11.6	0.99	-58.0	6.93
2	-6.26 to -4.87	-76.1	1.04	-343.3	5.87
3	-4.87 to -1.31	-8.50	2.26	-9.27	10.4
Western Equatorial Atlantic					
Piece #	Applicable $\ln(U/Ba)$ range	m	Δm	b	Δb
1	-5.50 to -4.12	-194.6	1.25	-800.5	6.06
2	-4.12 to -2.47	-1.63	1.04	4.02	3.53

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Figure Captions

Figure 1. Map of coretop sediment locations. Data are colorcoded by ocean basin: Indian (gray), Pacific (blue), Atlantic (red), and Southern (green). The northern boundary of the Southern Ocean (dashed line) is defined by the subtropical front (Orsi et al., 1995). New data from the Demerara Rise in the Western Equatorial Atlantic are shown as yellow stars.

Figure 2. Theoretical vs. observed profiles of trace metal concentrations in porewaters and authigenic phases. Theoretical predictions for the relationship between oxygen, manganese, and uranium in porewaters (panel A) and authigenic solid phases (panel B), after (Froelich et al., 1979). Observed profiles (C, D) are shown for example pelagic core EN433-2 (36.15°N, 74.06°W, 2648 m water depth, 270 μ mol/kg bottom water oxygen) (Morford et al., 2009). Authigenic uranium and manganese contents were calculated by subtracting from the total content a lithogenic component constrained with aluminum and average upper continental crust composition. (Taylor & McClennan, 1995). While observed Mn concentrations in both the porewaters and the authigenic phases (primarily Mn oxides) correspond fairly well with theoretical expectations, the uranium profiles diverge as a result of non-thermodynamic effects as discussed in Section 2.1.

Figure 3. New multicore top U, Ba, and $\Delta\delta^{13}\text{C}$ data from the Demerara Rise in the Western Equatorial Atlantic. A) Modern bottom water oxygen concentrations, extracted from global data products as described in Section 3. Dashed gray line indicates the depth of the downcore records shown in Figure 4. B) Total uranium content of core top samples. C) Total barium content of core top samples. D) The ratio of U/Ba shown in natural log space. E) $\Delta\delta^{13}\text{C}$ in core top samples. Availability of the requisite foraminifera for this proxy limited the number of core tops for which data could be generated. Datapoints that fall within the gray hatched region exceed the upper limit of the $\Delta\delta^{13}\text{C}$ calibration (Hoogakker et al., 2015).

Figure 4. New downcore U, Ba, and $\Delta\delta^{13}\text{C}$ data from the Demerara Rise in the Western Equatorial Atlantic. All data are from KNR197-3-60GGC (8.4°N, 52.97°W, 2550 m) except for the zero age datapoints, which are from the corresponding multicore KNR197-3-37MC. A) Total uranium content. B) Total barium content. C) The ratio of U/Ba shown in natural log space. D) $\Delta\delta^{13}\text{C}$ in the few downcore samples for which the requisite foraminifera for this proxy were available. The majority of the data exceed the upper limit of the $\Delta\delta^{13}\text{C}$ calibration (Hoogakker et al., 2015) (grey hatched region).

Figure 5. Relationship between U/Ba and oxygen on global and ocean basin scale. Symbols are as in Figure 1. New data from the Demerara Rise are shown as yellow stars. Note that x-axes are natural log while y-axes are linear. U/Ba generally increases as oxygen concentrations decrease. Two regions systematically fall off this trend: the Namibian Margin (maroon circles) and the Indo-Pacific Warm Pool (blue circles), where relatively high $\ln(\text{U/Ba})$ values correspond to oxygen concentrations between 100 and 200 μ mol/kg. Panels B-E show ocean basin scale relationships between U/Ba and oxygen (see text for details). The Namibian Margin and Indo-Pacific Warm Pool have been excluded from the Atlantic and Pacific, respectively.

Figure 6. Eastern Equatorial Pacific calibration test data. (A) Map showing the coretop sites used in the regional calibration (Loveley et al., 2017; Wang et al., 2022; Weber,

1998). Yellow star is the location of the downcore record from ODP Site 1240 (0.02 °N, -86.5°E, 2921 m). (B) The calibration is comprised of three linear functions (Table 1). (C) Raw $\Delta\delta^{13}\text{C}$ data from ODP Site 1240. Datapoints that fall within the gray hatched region exceed the limits of the $\Delta\delta^{13}\text{C}$ calibration (Hoogakker et al., 2015). (D) Raw U/Ba data from ODP Site 1240. All datapoints fall within the range of the calibration shown in panel B. (E) Calibrated $\Delta\delta^{13}\text{C}$ (yellow diamonds) and U/Ba (pink circles). Shaded regions show 1 σ error. Data that fell outside the calibration for $\Delta\delta^{13}\text{C}$ were set to the maximum calibration limit (open diamonds). Gray line shows the modern bottom water oxygen concentration at ODP Site 1240. Blue box indicates the alkenone-based glacial oxygen concentrations of < 50 $\mu\text{mol/kg}$ proposed by Anderson et. al. (2019). (F) Same as panel E, except that the two proxies are shown on independent y-axes to highlight the similar trends despite different absolute values. All downcore records have been previously published by Jacobel et al. (2020).

Figure 7. Arabian Sea calibration test data. (A) Map showing the coretop sites used in the regional calibration (Lu et al., 2022; McManus et al., 1998; Prakash Babu et al., 2002; Sirocko et al., 2000). Yellow star is the location of the downcore record from TN41-8PG/JPC (17.8°N, 57.5°E, 761 m). (B) The calibration is comprised of three linear functions (Table 1). (C) Raw surface porosity record from TN41-8PG/JPC. Datapoints that fall within the gray hatched region exceed the limits of the surface porosity calibration (Lu et al., 2022). (D) Raw U/Ba data from TN41-8PG/JPC. (E) Calibrated surface porosity (blue squares) and U/Ba (pink circles). Yellow diamonds show $\Delta\delta^{13}\text{C}$ for comparison, in which the right yellow y-axis provides the raw (uncalibrated) values and the left black y-axis provides the calibrated oxygen concentrations. Shaded regions show 1 σ error. Data that fell outside the calibration for $\Delta\delta^{13}\text{C}$ were set to the maximum calibration limit (open symbols). Gray line shows the modern bottom water oxygen concentration at TN41-8PG/JPC. All downcore records are from Lu et al. (2022)

Figure 8. Western Equatorial Atlantic calibration test data. (A) Map showing the coretop sites used in the regional calibration. Small yellow stars are new multicore data from this study, and the large yellow star is the location of the downcore record from KNR197-3-60GGC (8.4°N, 52.97°W, 2550 m). Pink circle is GeoB1515 (Pfeifer et al., 2001). Pink diamonds are from the Cariaco Basin (Calvert et al., 2015; Dorta & Rona, 1971). (B) The calibration is comprised of two linear functions (Table 1). (C) Raw $\Delta\delta^{13}\text{C}$ data from KNR197-3-60GGC. Datapoints that fall within the gray hatched region exceed the limits of the $\Delta\delta^{13}\text{C}$ calibration (Hoogakker et al., 2015). The zero age datapoint is from the corresponding multicore KNR197-3-37MC. (D) Raw U/Ba data from KNR197-3-60GGC. (E) Calibrated $\Delta\delta^{13}\text{C}$ (yellow diamonds) and U/Ba (pink circles). Shaded regions show 1 σ error. Data that fell outside the calibration for $\Delta\delta^{13}\text{C}$ were set to the maximum calibration limit (open diamonds). Gray line shows the modern bottom water oxygen concentration at KNR197-3-60GGC. (F) Hypothetical $\Delta\delta^{13}\text{C}$ -based oxygen reconstructions if the record were adjusted downwards by 60, 90, or 120 $\mu\text{mol/kg}$. U/Ba-based oxygen reconstructions (as in panel E) are only shown for the LGM (18-21 ka) and late Holocene (0-6 ka).