



Records of trace metals in sediments from the Oregon shelf and slope: Investigating the occurrence of hypoxia over the past several thousand years

Andrea M. Erhardt^{a,b,*}, Clare E. Reimers^c, David Kadko^d, Adina Paytan^b

^a Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, United States

^b Institute of Marine Sciences, University of California Santa Cruz, Santa Cruz, CA 95064, United States

^c College of Earth, Ocean and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, United States

^d Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, United States

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ABSTRACT

Hypoxic (<62 $\mu\text{mol/kg}$ or 1.43 mL/L O_2) to anoxic conditions have been repeatedly observed over the last 10 years on the Oregon shelf, while similar conditions are absent in historical records from 1950 to 1999. This study seeks to identify whether similar instances of decadal length hypoxia/anoxia have occurred in the Oregon coastal zone prior to recorded history and to shed light on potential causes for these events. We have measured redox-sensitive metals, uranium, vanadium, and molybdenum concentration profiles in 7 cores across the coastal affected region and in 3 cores from deeper water sites. Results indicate regional variability in redox conditions through time. The northern sites show no metal enrichment throughout the cores, while the southern sites show strong metal enrichment at the base of the cores, indicative of previous hypoxic/anoxic conditions. The southern sites indicate progression in time toward less hypoxic/anoxic burial, in conflict with recent hydrographic trends. Analysis of offshore sediments representing sites beneath the California Undercurrent shows an opposite trend to that observed in the coastal sites. Excess Mo concentrations generally increase toward the present in cores collected within the upwelling source waters at ~300 m water depth, suggesting a trend toward oxygen depletion. The Mo enrichment corresponds to increases in $\delta^{13}\text{C}$, total organic carbon (TOC), and declines in carbon:nitrogen (C:N) ratios which may indicate that a localized rise in marine productivity has contributed to oxygen drawdown. However, these metal and associated geochemical enrichments are not clearly seen in other cores collected in deeper water in the same region, suggesting that widespread changes in productivity or hypoxia may not have occurred. When the Mo enrichment records for two dated mid-depth sites are compared to climatic indicators such as the Pacific Decadal Oscillation no clear relationships are found on decadal time scales. These results are consistent with the hypothesis that modern hypoxic conditions observed on the continental shelf throughout the region are driven by modern climate changes, not observed in this region for the past hundreds to thousands of years.

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1. Introduction

1.1. Oregon shelf hypoxia

Repeated occurrences of oxygen deficient (hypoxic) water along the continental shelf off the coast of central Oregon have been reported over the last 10 years, resulting in die-offs of bottom dwelling organisms, including the commercially important Dungeness crab (Grantham et al., 2004). These hypoxic conditions and related die-offs are unprecedented in historical records and hydrographic data from the last half century (Chan et al., 2008; Pierce et al., 2012). While local processes that may

contribute to the hypoxic events are being investigated (Grantham et al., 2004; Hales et al., 2006; Reimers et al., 2012) it is still unclear if centennial or millennial scale climate oscillations have caused similar conditions in the past, prior to available records.

The present-day Oregon coast hypoxic zone consists of a region where shelf water oxygen concentrations decline to <62 $\mu\text{mol kg}^{-1}$ recurrently during summer months (Pierce et al., 2012). The occurrence of seasonal hypoxia was first reported in July 2002, and lasted through September 2002. During that time, bottom dissolved oxygen concentrations of 10–70 $\mu\text{mol kg}^{-1}$ were found from nearshore stations to ~70 m of water depth (Grantham et al., 2004). The total area impacted by this event covered at least 820 km^2 .

Since 2002, Oregon shelf hypoxic events have expanded in size and severity. During 2006, hypoxic conditions off Oregon covered 3000 km^2 and extended to a water depth of ~100 m (Chan et al., 2008) (Fig. 1).

* Corresponding author at: Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, United Kingdom. Tel.: +44 7453 858 665.
E-mail address: ame48@cam.ac.uk (A.M. Erhardt).

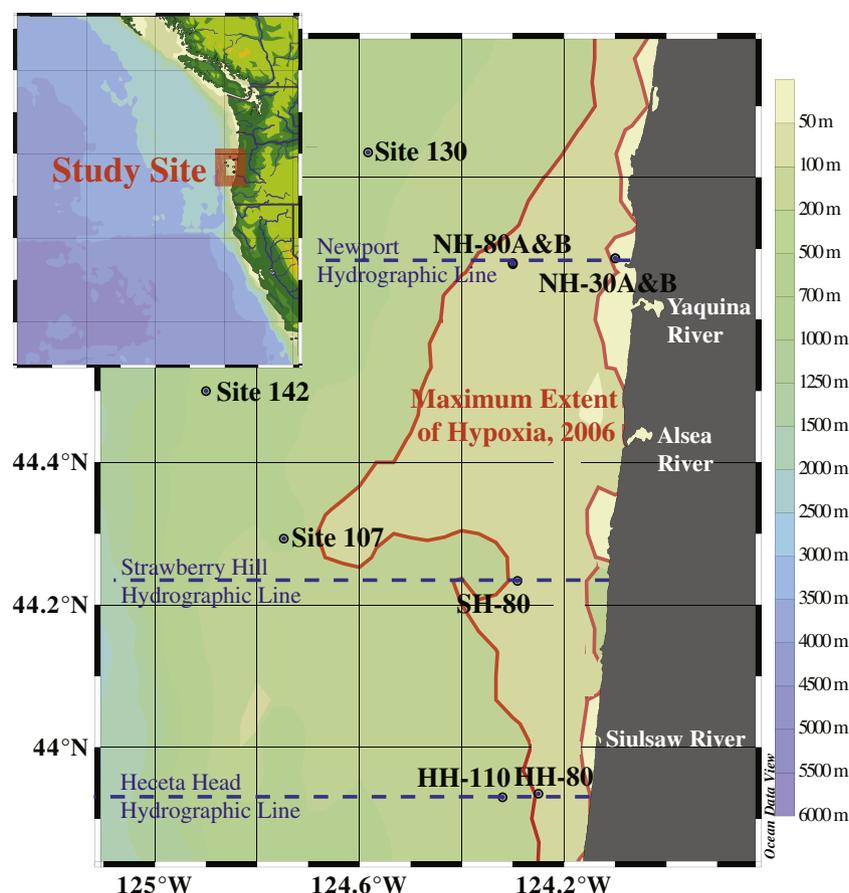


Fig. 1. Study region and sampling locations along the central Oregon coast described in this study. The maximum extent of hypoxia from 2006 is delineated in solid red. The three hydrographic lines are notated in dashed blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Massive blooms of the diatom *Thalassiosira* have been observed to coincide with these events, with bloom degradation contributing to oxygen depletion. During the 2006 event, oxygen levels approaching zero were reported in some locations (Gewin, 2010). The re-occurring hypoxia in this region has effects on biodiversity and biomass at higher trophic levels (Keller et al., 2010). The hypoxic events do not appear to be related to El Niño–Southern Oscillation (ENSO) cycles (Service, 2004), but available data is insufficient to determine if they correspond with longer-frequency climatic cycles (i.e. Pacific Decadal Oscillation (PDO)). Based on predictive circulation models the global oxygen content of the ocean in general, and of the North Pacific in particular, is expected to decline by 1–7% over the next century potentially exacerbating the situation along the Oregon coast (Keeling et al., 2010).

It has been suggested that generation of these “dead zones” off Oregon results from change in ocean circulation and wind conditions during the coastal upwelling season, with some speculation that the underlying driver is global warming (Barth et al., 2007; McGregor et al., 2007; Pierce et al., 2012). Specifically, the degree of anoxia is determined by the length and frequency of upwelling events (Hales et al., 2006), the oxygen content of the source water, and the circulation and ventilation of shelf water masses (Pierce et al., 2012).

A record of past hypoxia occurrence frequency would help distinguish human-induced causes from those related to natural climate changes (Helz et al., 2004). Determining trends in trace metal abundances can serve as an indicator for changes in oxygenation conditions over time. By analyzing redox sensitive trace metal content in sediments from cores distributed regionally and representing multiple water depths, we have endeavored in this study to identify past temporal or spatial changes in oxygen levels in this region. In addition, carbon isotopic analysis and C:N ratios of the bulk sediment organic matter in

cores from the slope and outer shelf are used to determine if significant changes in the balance of terrestrial and marine organic matter sources can be observed. An increase in marine organic matter may be indicative of higher productivity, which could contribute to lower oxygen in the water.

1.2. Trace metals as redox proxies

Redox sensitive trace metal concentrations and ratios in sediments are established proxies for the characterization of redox conditions (e.g. Morford and Emerson, 1999; McKay et al., 2005; Swarzenski et al., 2006). For this investigation, molybdenum (Mo), uranium (U), and vanadium (V) were considered. Mo and U are conservative in oxic seawater while V is nearly conservative (Collier, 1985); all three metals undergo chemical transformations and are incorporated into authigenic mineral phases when oxygen is depleted. Usually these metal accumulations occur within a few to 10s of centimeters of the sediment–water interface, where pore waters are affected by chemical conditions of the overlying water (Scholz et al., 2011). Particularly, if the water column is low in oxygen pore waters will be suboxic to anoxic. A highly oxic water column can lead to more oxic pore waters transitioning to suboxic, especially when sediments are bioturbated or subject to wave pumping as in the Oregon shelf. As such, trace metal accumulations in sediments can be used to shed light on water column conditions on multiple time scales (Scholz et al., 2011).

In oxic seawater Mo is present primarily as the soluble oxianion MoO_4^{2-} . As oxygen is depleted MoO_4^{2-} is converted to particle reactive thiomolybdates ($\text{MoO}_x\text{S}_{4-x}^{2-x-}$) under anoxic conditions or to molybdenum sulfide (MoS_2) under euxinic conditions and is removed to the sediment resulting in authigenic enrichment of Mo (Crusius et al., 1996;

Poulson-Brucker et al., 2009). As a result, increases in Mo concentrations can be indicative of oxygen-depleted environments. Similarly, authigenic U deposition dominantly occurs in anoxic basins and organic-rich sediments (Klinkhammer and Palmer, 1991; Barnes and Cochran, 1993). U is removed through diffusion of $[\text{UO}_2(\text{CO}_3)_3]^{2-}$ from the water column to the sediments, followed by microbially-driven enzymatic reduction (Lovley et al., 1991, 1993) and subsequent adsorption or precipitation, possibly as uraninite, $(\text{U(IV)}\text{O}_2(\text{s}))$ (Barnes and Cochran, 1991; Klinkhammer and Palmer, 1991; Crusius et al., 1996). V is also soluble in oxic conditions but under anoxic conditions is reduced to V(IV) forming the particle-reactive oxocation VO(II) (vanadyl) which forms complexes with humic acids and retained in the sediment (Szalay and Szilágyi, 1967; Shiller and Boyle, 1991; Shiller and Mao, 1999, 2000). However, riverine particulate fluxes of V are significantly higher than those of U and Mo (2 and $3 \mu\text{g g}^{-1}$ for U and Mo respectively vs. $170 \mu\text{g g}^{-1}$ for V) (Emerson and Husted, 1991) potentially obscuring records of authigenic V accumulation in nearshore environments.

Besides the changes in redox conditions, two other mechanisms can contribute to trace metal enrichments in sediments. Particulate shuttles due to ferromanganese redox cycling in the water column can transport trace metals to the sediment. In this process, particulate manganese oxides absorb molybdate oxyanions in the water column, transporting Mo to the sediment (Algeo and Tribovillard, 2009; Tribovillard et al., 2012). This results in highly enhanced authigenic Mo accumulation in comparison to U (Algeo and Tribovillard, 2009). Such Mo enrichment compared to U typically occurs in water columns with suboxic to sulfidic conditions, particularly those with high degrees of variation on short time scales (Murray, 1975; Crusius et al., 1996; Algeo and Tribovillard, 2009). Changes in water chemistry resulting from restricted circulation can also affect trace metal abundance in sediments. Such conditions are typically identified in sediments through enhanced Mo accumulation followed by a secondary increase in U (Algeo and Tribovillard, 2009). Based on the Oregon coast seafloor topography, however, it is unlikely that restricted circulation has impacted the area over the past few thousand years.

It has been repeatedly shown that aluminosilicate minerals are the dominant metal-bearing phases for a large number of trace elements in organic poor sediments, therefore changes in the abundance of these minerals may contribute to variability in Mo, U and V independent of redox changes (Windom et al., 1989; Poulton and Raiswell, 2000). Aluminum (Al) typically has only a small authigenic component, and Al normalized trace element ratios are relatively constant in the Earth's crust (Windom et al., 1989; Schropp et al., 1990; Tribovillard et al., 2006). Accordingly, to account for any changes in accumulation of lithogenic minerals we derive the excess metal concentrations by normalization of metal content to Al using crustal metal/Al ratios. This allows for the determination of excess (authigenic) metal precipitation and for comparison between samples from different locations. This normalization works best in sediments with greater than 3–5% detrital fractions (Tribovillard et al., 2006), which includes most continental shelf and slope environments including samples used in this study.

1.3. Study area and core description

The study region (Fig. 1) is located along the central Oregon continental margin, with sample sites ranging from 30 m to 817 m water depth. The shelf break is located generally between 100 and 200 m water depth. This region contains the area impacted by the current hypoxia events and is located within the northern segment of the California Current (Checkley and Barth, 2009), an eastern boundary current that brings cool water from the north toward the equator.

In winter, the water column on the shelf is well mixed due to large waves associated with North Pacific storm patterns (Allan and Komar, 2006) with mixing reaching as deep as 200 m (Kulm et al., 1975). These poleward winds result in offshore displacement of the California Current and the development of the poleward Inshore Countercurrent

(i.e. Davidson Current) (Hickey, 1998; Strub and James, 2000). In contrast, spring and summer months are dominated by wind driven upwelling of deeper nutrient-rich and oxygen depleted water through Ekman transport. During a typical upwelling event, water from 100 to 400 m is brought up onto shallower regions of the shelf (Pierce et al., 2012). The upwelling water originates from the California Undercurrent, a poleward moving water mass characterized by a relatively high contribution of Pacific Equatorial Water along the Newport Hydrographic Line, a well-documented oceanographic transect (40% equatorial water at 100 m water depth, Thomson and Krassovski, 2010). The core of this water mass has been shown to have low oxygen concentrations throughout the time for which direct instrumental observations are available (Pierce et al., 2012). Upwelling of this water lowers the oxygen in the shelf environment during spring and summer. This upwelled nutrient-rich water spurs enhanced primary productivity during the upwelling season further lowering oxygen below the euphotic zone as organic matter is remineralized. ENSO variability also affects productivity leading to annual to decadal changes in productivity and seawater chemistry (Chen et al., 2004). Specifically, the strength of upwelling is reduced during El Niño years lowering nutrient supply and productivity (Chen et al., 2004).

Further offshore, this region is underlain by an extensive oxygen minimum zone (OMZ) between 600 and 1200 m water depth (Kamykowski and Zentara, 1990). Given that this water is dominantly sourced by equatorial water via the California Undercurrent it has been proposed that changes to the equatorial OMZ may affect oxygen supply to the entire eastern boundary system (Stramma et al., 2008; Pierce et al., 2012). Indeed Pierce et al. (2012) suggested that the recent expansion and shoaling of the OMZ off the Oregon coast might be linked to climate change impacts on the equatorial OMZ.

The sediments in this region vary in composition with distance from shore. Within the 100 m isobath fine sand dominates, allowing bioturbation and physical transport to mix surface sediments (Komar et al., 1972; Kulm, 1978). This mixing may also allow silt and clay size materials to bypass the shelf and be deposited on the lower slope (Kulm et al., 1975). Three small rivers, the Yaquina, Alsea, and Siulsaw Rivers, are included in the study area, while one larger river, the Umpqua River, is located 28 km south of the Heceta Head (HH) hydrographic line (Fig. 1). The average sediment load for these rivers is relatively small. Using the values for sediment yield and basin areas in Karlin (1980), we find that the Yaquina, Alsea, and Siulsaw Rivers have average annual sediment loads of 8.5×10^7 , 1.6×10^8 , and $1.9 \times 10^8 \text{ kg yr}^{-1}$ respectively. The Umpqua River sediment load is much higher at $3.2 \times 10^9 \text{ kg yr}^{-1}$. Sediment from the Umpqua River, however, has a well-defined depocenter and does not significantly impact the locations studied here (Hastings et al., 2012).

2. Methods and materials

Sediment cores from 5 shelf sites ranging in depth from 30 to 110 m within the area impacted by the recent hypoxia were collected during a series of three cruises on the R/V *Wecoma* in March, June, and August 2009. These samples fall along three hydrographic lines, the Newport hydrographic line (NH), the Strawberry Hill hydrographic line (SH), and the Heceta Head hydrographic line (HH) (Fig. 1). Summaries of the sample locations are found in Table 1. Samples were collected using a 10.5 cm diameter slow gravity corer described in Reimers et al. (2012). This corer was designed to optimally collect sandy matrix samples and to preserve the sediment–water interface. Cores varied in length between 10 and 60 cm. Cores were subsampled every cm for the first 5 cm and at 1–2 cm increments for the remainder of the core length. Samples from three additional cores located on the outer continental shelf and slope were provided by the Oregon State University Core Repository. These cores were collected in May of 1979 from the R/V *Wecoma*. The cores were collected at water depths of 298–817 m. Two of the sites are overlain by the California Undercurrent water

Table 1
Sample names, locations, and core lengths.

Core name	Core number	Collection date	Lat. N	Long. W	Water depth (m)	Core length (cm)
<i>Cores collected in 2009</i>						
NH-30A	W0903B-36	3/26/2008	44.687	124.100	30	23
NH-30B	W0903B-40	3/26/2008	44.686	124.100	30	57
NH-80A	W0903B-5	3/24/2008	44.678	124.300	82	23
NH-80B	W0903B-18	3/25/2008	44.680	124.300	80	25
SH-80	W0906A-85	6/14/2008	44.234	124.314	80	51
HH-80	W0906A-60	6/12/2008	43.935	124.250	81.5	56
HH-110	W0906A-70	6/13/2008	43.930	124.320	110	44
<i>Cores ordered from repository</i>						
107	W7905A-107	5/20/1979	44.293	124.748	817	213
130	W7905A-130	5/22/1979	44.835	124.583	298	156
142	W7905A-142	5/23/1979	44.5	124.9	456	139

mass and the deepest site coincides with the core of the present-day OMZ. Cores from the repository were 139–213 cm in length and collected using a conventional gravity corer. These cores were sampled at 5 cm intervals.

Samples for trace metal and isotopic analysis were processed using plastic sampling tools, placed in plastic sample bags, and kept chilled or frozen until analysis. Samples were freeze-dried and an aliquot was powdered and homogenized by hand using an agate mortar and pestle. For trace metal analysis, ~50 mg of sample was weighed into an acid cleaned 30 mL Teflon screw-top beaker. Two mL each of concentrated trace metal grade nitric and hydrofluoric acids were added to each sample. The vessels were tightly closed and placed in an ultrasonic bath for 1 h. After sonication, they were heated on a 90 °C hotplate overnight. On the next day, each beaker was opened, and 2 mL of hydrogen peroxide was added to each sample to remove organics. In a handful of samples significant reactions were observed and additional hydrogen peroxide was added to ensure complete oxidation of organic material. The vessels were again closed and allowed to react overnight on the hotplate. The samples were gently dried down and were reconstituted in 4 mL of 6 N trace metal grade hydrochloric acid. The vessels were again closed and placed on a hotplate overnight. This procedure was repeated with 4 mL of 7 N trace metal grade nitric acid. Finally, samples were dried down and reconstituted with 1 mL of 7 N trace metal grade nitric acid and diluted to 50 mL in acid cleaned centrifuge tubes for analysis. Blanks were similarly processed and contributions from the blanks to the measured trace metals were negligible.

Samples were analyzed on an ICP-MS (Element-XR) at the University of California, Santa Cruz. A 2% trace metal grade nitric acid solution with Rh and Bi added at 1 ppb was used as an internal standard. Standards spanning the range of concentrations in the samples were run every 12 samples to monitor for instrument drift and linearity. Samples of NIST SRM 2702 were analyzed according to the same procedure to determine the reproducibility and efficiency of the digestion procedures. Measured Mo contents were within the range of published values, while recovery for other elements varied between 78% and 95% and was internally consistent. 10% of the samples were processed in duplicate or triplicate to evaluate reproducibility. To account for variations in lithology, all metal concentrations were normalized to Al content (i.e. Calvert and Pedersen, 1993). These normalized ratios were then compared to a reference value of average shale (Wedepohl, 1971; Taylor and McLennan, 1985; McLennan, 2001), as well as to average sandstone due to the sandy matrix of these samples. This normalization allows for estimation of the degree of enrichment or depletion of a particular trace element relative to lithogenic material and comparison to previously published data. Enrichment factors were calculated by dividing the metal/aluminum ratio of the sample to that of the average shale.

Percent total nitrogen and organic carbon and carbon isotopes in organic matter were analyzed on ~5 mg of powdered sediment. Samples were weighed into silver capsules, carbonate was removed through

the successive addition of chilled sulfurous acid until no reaction was evident, and samples were analyzed on an Elemental Analyzer coupled to an isotope ratio mass spectrometer at the University of California, Santa Cruz. Isotopic ratios were normalized to Acetanilide and Pugel isotopic standards.

Concentrations of $^{210}\text{Pb}_{\text{excess}}$ ($T_{1/2} = 22.3$ y) were measured in samples from cores HH-110 and NH-30B by counting the short lived daughter isotope ^{210}Po ($T_{1/2} = 138.4$ days (Supplemental Table 1)). Two-gram aliquots of sample powders from different depths were taken into solution by repeated digestion in concentrated HF, HNO₃, and HCl acid sequentially. A known amount of ^{209}Po spike was added at the beginning to assess the ^{210}Po recovery. The solution was dried and taken up in 1.5 N HCl and Po was then plated onto Ag planchets (Flynn, 1968; Fleer and Bacon, 1984). The Po was counted with a surface barrier alpha detector/spectrometer system. Excess ^{210}Pb was calculated as (total ^{210}Pb – ^{226}Ra). The ^{226}Ra was measured by the radon emanation method (e.g. Kadko et al., 1987). Reimers et al. (2012) made additional $^{210}\text{Pb}_{\text{excess}}$ measurements in samples representing the upper 5 cm of the 80 m water depth cores (NH-80, SH-80, and HH-80).

3. Results

3.1. Age determination

Five samples from core HH-110, spanning between 0 and 18 cm from the sediment water interface, had detectable concentrations of $^{210}\text{Pb}_{\text{excess}}$. Samples from below this depth and samples from core NH-30B did not contain measurable $^{210}\text{Pb}_{\text{excess}}$. Apparent sedimentation rates decreased with depth due to higher rates of bioturbation within the upper 10 cm of sediment, consistent with published observations from nearby cores of similar composition (Wheatcroft and Sommerfield, 2005; Wheatcroft et al., 2013). The sedimentation rate determined for the deepest dated section of the core was applied to the whole core (0.12 cm yr⁻¹) and the age/depth relationship was used to estimate the age of each sample assuming constant sedimentation rates. Using this approach an age of 370 years for the base of the 44 cm core was obtained.

Significant work has been recently conducted to quantify sedimentation rates just south of our study site (Wheatcroft et al., 2013). An extensive survey of ^{210}Pb measurements from an array of 73 cores extending from 43.5°N to 44.1°N at water depths from 60 to 200 m was performed. This survey overlaps the most southern cores from our study, allowing for comparison with the sedimentation rate we obtained and rates for other cores analyzed by Reimers et al. (2012). The published sedimentation rate in Wheatcroft et al. (2013) for a core taken at the same location as HH-110 shows a similar, though slightly higher sedimentation rate (1.6 versus 1.2 mm yr⁻¹ from this study). Sedimentation rates for a core measured at the same location as core HH-80 were 1.2 mm yr⁻¹, and data for 7 additional cores in the area with water depths ranging from 80 to 116 m show an average sedimentation rate of 1.2 mm yr⁻¹ ± 0.06 (2SD). We therefore use a

sedimentation rate of 1.2 mm yr^{-1} for core HH-80. Additional existing ^{210}Pb records from cores in the study region suggest regional homogeneity in sedimentation. Reimers et al. (2012) published ^{210}Pb records for three of the cores from this study, NH-80, SH-80, and HH-80. Although ^{210}Pb was low, profiles were similar in all of these cores.

Wheatcroft et al. (2013) report that sedimentation rates for samples at ~200 m water depth fall within the same general range as the shallower sites, with sedimentation rates between 0.5 and 1.2 mm yr^{-1} . While it would be difficult to extrapolate these results to the much deeper cores from the continental slope used in our study, these values are in line with the results from ODP Site 1251, located at $44^{\circ}34'N$ $125^{\circ}4'W$ at 1210 m water depth (sedimentation rate of between 0.6 and 1.6 mm yr^{-1} for the upper sections of the core) (Tréhu et al., 2003). These similarities suggest that the sedimentation rates we obtained are realistic for the continental slope.

Wheatcroft et al. (2013) focused focuses on documenting centennial changes in sediment accumulation and the influence of human activity in Umpqua river discharge on sedimentation. It is interesting to note that these changes were dominantly constrained to the region near the outflow of the river with sedimentation rates up to 5 mm yr^{-1} similar to the findings of Hastings et al. (2012). Relevant for this study, we see that the samples outside the vicinity of the river outflow do not show enhanced sedimentation ($\sim 1 \text{ mm yr}^{-1}$) in the upper sections of the cores. These findings confirm the limited influence of river discharge on sites utilized in our study.

No substantial unconformities were observed at ODP Site 1251 until 130 m downcore. Additionally, the linear fit of the ^{210}Pb results for the majority of the cores in Wheatcroft et al. (2013), particularly those from the deeper environments, suggests minimal breaks in the sediment record. While disconformities cannot be completely ruled out in such a tumultuous environment, cores from the outer continental shelf and slope appear to contain representative records of recent sediment accumulation.

Wheatcroft et al. (2013) also concluded that the sedimentation in this region for cores from 70 m and deeper was generally continuous. This includes the 80 m and 110 m depth cores collected for this study. It is likely that locations at shallower water depths, specifically those at 30 m water depth, will be more subject to winnowing, bioturbation, and other disturbances that disrupt the continuity of the record. The two shallowest cores, NH30A&B, which have high sand content and low organic matter, did not have detectable ^{210}Pb excess. This could result from a variety of factors, including age hiatus due to winnowing, sediment bypass, or enhanced mixing and bioturbation. These characteristics preclude the use of ^{210}Pb to determine sedimentation rates in these cores.

Despite the potential complications of deriving accurate sedimentation rates for sandy coastal sediments overall, the cores used in this study provide us with a longer time series of conditions in the Oregon shelf than can be ascertained from historical or instrumental records (i.e. Chan et al., 2008). While seasonal or annual changes, including ENSO cycles, cannot be resolved due to bioturbation and low sedimentation rates, lower frequency changes and relative differences and shifts in mean average condition over the time interval represented by the length of each core can be assessed.

3.2. Trace metal content

To better characterize changes in oxygen levels over time at each site, elements of particular utility for determining oxygenation conditions, including Mo, U, and V, all normalized to Al, are reported. These ratios are compared to global mean sandstone and shale values. Samples with ratios higher than the global average values (e.g. metal enrichment) are indicative of oxygen-deficient environments (Morford and Emerson, 1999). Although the Re/Al ratio has also been used as an anoxia proxy, Re concentrations in these samples were at or near detection

limits as we did not employ any preconcentration techniques and thus are not used in this investigation.

3.2.1. Molybdenum to aluminum ratios

The most southern cores on the mid-shelf, sites HH-80 and HH-110 at 80 and 110 m water depths respectively (Fig. 2) were ≤ 50 cm in length. Both cores show higher Mo/Al in the deepest core sections (25–50 cm) compared to upper sections. From the base of the cores upward the Mo/Al ratios decrease progressively over nearly the full length of the core, with ratios lower than the global mean shale values at depths above 28 cm and 25 cm, respectively. In contrast, at the northern mid-shelf sites, cores NH-80A and NH-80B at 80 m water depth, Mo/Al ratios are relatively constant throughout the length of the cores, remaining well below global mean shale ratios but not showing significant trends over time (Fig. 2).

The mid-latitude mid-shelf site, Core SH-80 at 80 m water depth, shows a combination of the trends observed to the north and south of this location (Fig. 2). An overall decrease in the Mo/Al ratio from the base to the top of the core is consistent with the southern sites (HH-110 & 80), but the absolute ratios are similar to those from the northern sites (NH-80A & B). The percent fines are similar in cores SH-80 and NH-80 (Reimers et al., 2012), consistent with deposition in an environment with similar sediment transport characteristics.

At the shallow water (30 m water depth) sites, Cores NH-30A&B, the Mo/Al ratios are slightly higher than in the cores from 80 m along the same hydrographic line (NH-80A&B) but remain relatively constant with depth in the core (Fig. 2). The Mo/Al ratios at those sites are dominantly above the global sandstone ratio but below the global shale ratio.

In contrast to the aforementioned shelf locations, the sites located along the slope (Sites 130, 142, and 107) show higher concentrations of Mo, with Al normalized ratios generally above the global sandstone or shale values (Fig. 2). The most southern location, Site 107 at 817 m water depth, shows little change in Mo/Al ratios over the upper 100 cm of the core but slightly higher enrichments in older sections. In contrast, the northern location, Site 130, at 298 m water depth, has a broad Mo/Al ratio maximum within the upper 80 cm of the core with ratios sharply declining at the core top. At the mid-latitude Site 142, at 456 m water depth, no temporal trends are discernable and there is high variability in the ratios.

3.2.2. Other metals: U/Al and V/Al

Trends for U/Al ratios are similar to those of Mo/Al, consistent with a common response to oxygen levels. The southern mid-shelf sites (Cores HH-80 and HH-110; Fig. 2) also show an overall decrease in the U/Al ratio from the base to the top of the core. The deeper core, HH-110, has ratios greater than the global shale average from the base of the core until the upper 7 cm where it decreases. Site HH-80, at a slightly shallower 80 m water depth, has ratios lower than the global shale average for much of the core with only the bottom 5 cm having higher values. The mid-latitude site (SH-80) also shows a slight overall decreasing trend from the base to the top of the core, with ratios below the global shale value at the bottom of the core (>40 cm depth), though values remain below the global sandstone average throughout. A slight decline upcore is also observed at the northern 80 m water depth sites (NH-80A&B). Finally, the shallow sites at 30 m water depth (NH-30A&B; Fig. 2) are slightly more enriched than the 80 m sites along the same hydrographic line. The upper 10 cm of each core shows some variation, with a small peak at approximately 5 cm and a decline for the upper 2–4 cm. These trends are less pronounced in the Mo records. The three slope locations (Sites 130, 142, and 107) show more enriched values compared to global shale. The trends observed in the U/Al record are generally similar to those of the Mo/Al ratios. The southern site (107) shows slightly decreasing values upcore (Fig. 2), the mid-latitude Site 142 U/Al ratios show similar variability as Mo/Al, and at the

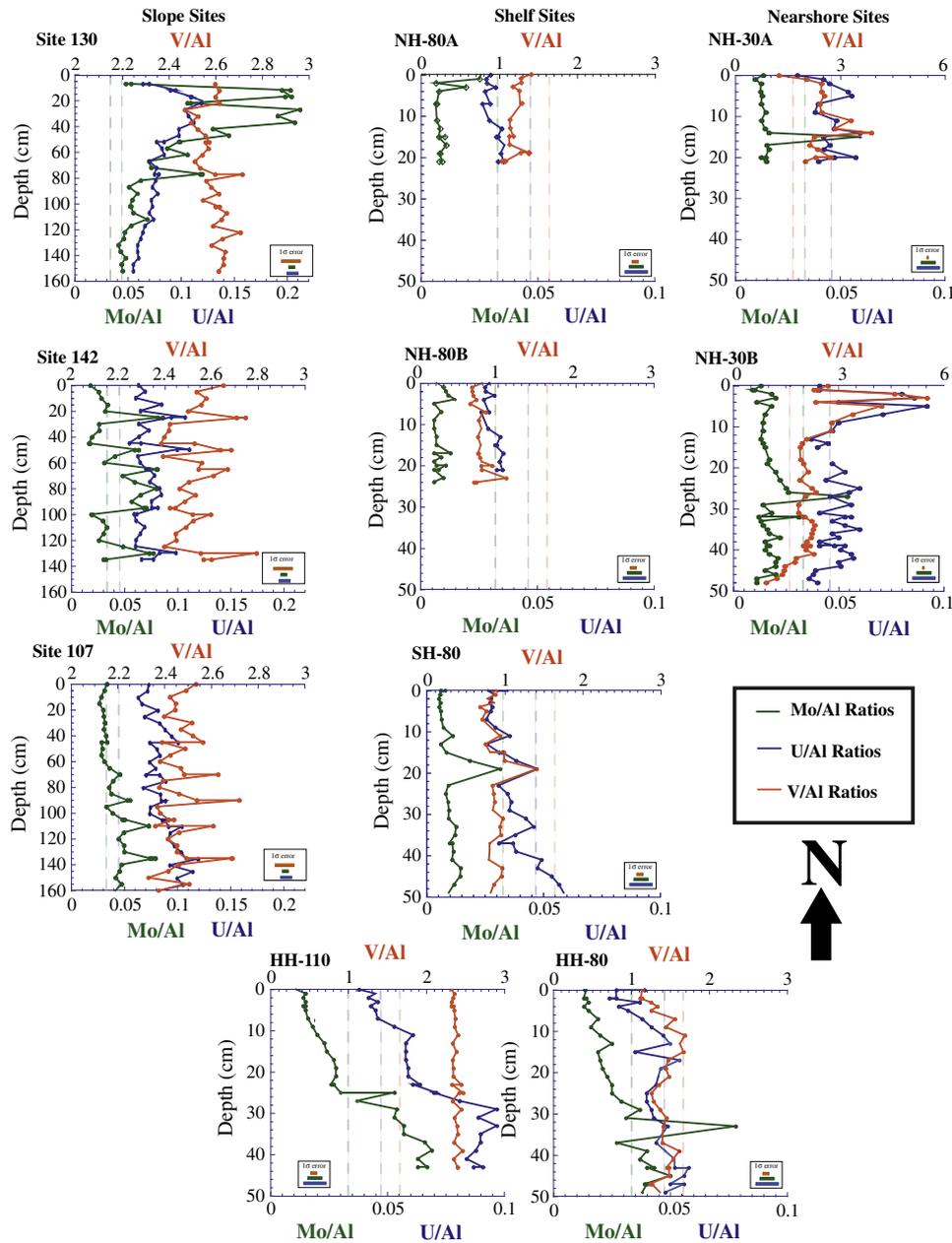


Fig. 2. Concentrations of Mo, U, and V normalized to Al for the ten cores from this study. The graphs are arranged based on their relative position along the coast with the deeper water locations to the left and the shallower water site to the right, with north orientated to the top of the page. Mo/Al ratios are notated in green, U/Al ratios in blue, and V/Al in orange. The dashed vertical lines represent the global shale average. Enrichment above these lines indicates potential reduced oxygen conditions. V/Al ratios from Sites 107, 130, and 142 are all significantly above the global shale averages and as a result are not shown in this figure. The scales for Sites 107, 130, and 142 have an expanded range for Mo/Al and U/Al and a compressed range for V/Al to better show downcore trends. The range for V/Al in cores NH40-A&B has also been expanded. Standard deviation on a known matrix matched solution over the course of the analytical runs for Mo/Al, U/Al, and V/Al were 0.006, 0.016, and 0.080 respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

northern Site 130 U/Al ratios show a rise in ratios in the upper sections of the core similar to the Mo/Al ratios.

The V/Al ratios show less pronounced trends than the Mo/Al and U/Al ratios, though generally support the previous observations. One exception is Site HH-110, at 110 m water depth, which has a greater overall V enrichment than other sites of similar depth, but does not show the temporal changes observed in Mo and U. In the shallowest (30 m water depth) sites (Fig. 2) V show more enriched ratios and more variability than at other locations. Site NH-30B, at 30 m water depth, displays the strongest temporal trends, increasing from V/Al ratios of 1 at 48 cm core depth to 5.5 at 6 cm core depth, similar to trends observed in the U/Al ratios in the upper 10 cm of the core at this site. Slope Sites 107

and 142 do not show strong temporal trends, and display significant variability in measured ratios.

3.3. Carbon and nitrogen measurements

To further evaluate environmental changes in this system, carbon isotopes ($\delta^{13}\text{C}$), carbon to nitrogen (C:N) ratios, and total organic carbon (TOC) were analyzed from the three slope cores (Fig. 3). Due to the shallow water depth and low organic matter content of the shelf sites, measurement of these samples did not provide reliable results for $\delta^{13}\text{C}$ and C:N, and are not reported in this study. Overall, $\delta^{13}\text{C}$ values from each of the three slope cores range between -23.5% and -22% , with the

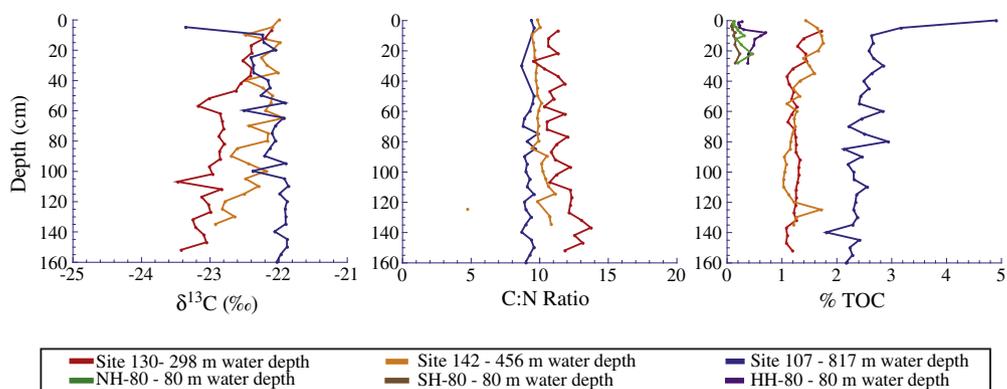


Fig. 3. Carbon isotopic values, C:N ratios and TOC for the three outer shelf/slope cores from this study. Site 130 is shown in red, Site 142 is shown in orange, and Site 107 is shown in blue. TOC results from Reimers et al. (2012) are also reported. Core NH-80 is shown in green, Core SH-80 is shown in brown, and Core HH-80 is shown in purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

most southern and deepest water core (Site 107) having the least negative values and the most northern and shallowest water core (Site 130) having the most negative. Within each core, temporal changes are observed. $\delta^{13}\text{C}$ values at both Sites 142 and 130 appear to gradually become less negative through time, with this trend most clearly observed at Site 130. Site 107, however, becomes slightly more negative from the base to the top of the core. Additionally, the uppermost point at Site 107 is significantly more negative than the remainder of the core.

C:N ratios at these sites range between 8 and 14. The deepest most southern core (Site 107) has an average value of 9, for the core at mid-depth (Site 142) the average ratio is 10, and the shallowest most northern core (Site 130) has ratios between 10 and 12. Site 130 shows a gradual decline from the base to the top of the core while the remaining two sites show little temporal trends.

TOC concentrations for the three cores range from 1% to 5%. Site 130 at 298 m water depth averages 1.2%, Site 142 at 346 m water depth averages 1.3%, while at Site 107 at 817 m water depth TOC gradually increases from 2.2% to 2.6% from the base to the top of the core, with an excursion to 5% at the core top. Within each core, a gradual increase upcore is observed at all three sites, though this increase is more pronounced at Site 107. These TOC values are consistent with recorded values (1.09–2.99%) for deep-water sediments off the Washington Coast, a similar oceanographic environment (Dickens et al., 2004). TOC for the 80 m water depth cores reported by Reimers et al. (2012) are much lower than at the slope locations analyzed for this study. The southern site, HH-80, has the highest values, peaking at 0.7% at 8 cm depth (Reimers et al., 2012). TOC at the remaining two locations ranges between 0.1 and 0.2%, with the northern site having slightly higher TOC. These trends generally correspond to the percent fines for each of these locations, with Site HH-80 also having a greater percentage of fines (Reimers et al., 2012). Overall, these results highlight increases in TOC with water depth, a trend consistent with carbon transport from shelf to slope.

4. Discussion

4.1. Metal proxies

Trace metals in the cores collected within the shelf area impacted by the current reoccurring water column hypoxia (at 30 and 80 m depth) with the exception of the upper 10 cm in core NH-30B do not show any pronounced enrichment in redox sensitive metal (relative to shale) (Fig. 4). The observed enrichment in the U/Al and V/Al records at site NH-30B are not recorded in the Mo/Al ratios and may indicate suboxic conditions with U enrichment occurring at the Fe redox boundary (Algeo and Tribouillard, 2009). The shallow water depth at the 30 m cores, in combination with the strong wave action in this region, likely

precludes significant oxygen depletion. However, the lack of redox sensitive metal enrichment at the 80 m water depth sites indicates that seasonal hypoxia was not persistent enough to enhance trace metal accumulation, at least for the past few centuries. The low sedimentation rates (1–2 mm/year) relative to bioturbation depths (estimated at >10 cm, Wheatcroft and Sommerfield, 2005; Wheatcroft et al., 2013) will tend to obscure the record of the most recent (last decade) hypoxia but longer-term trends or hypoxia of longer duration should be captured.

Temporal trends vary regionally. No temporal trends are observed in the northern sites while a decrease in metal content with time toward the present is seen at the southern sites (particularly HH-110). The metal enrichments at the bottom of the cores at the southern sites point to a period with lower oxygen at the southern part of the region more than 200 years ago. However, these conditions are restricted to the southern reaches of the current hypoxia zone and are not similar to present conditions in terms of spatial extent. These trends may be related to millennia scale changes in PDO (see below).

Trace metals at the slope sites show measurable enrichment relative to shale (Fig. 5), however only the most northern site located at a depth of 298 m (Site 130) records a temporal trend toward increasing metal enrichment. This enrichment corresponds to increases in TOC, $\delta^{13}\text{C}$ and N:C, suggesting that the reduction in oxygen content at this site is potentially associated with higher marine productivity. Notably, the water mass at this depth may be the source of upwelling waters to the shelf area.

We interpret the metal enrichment trends as reflecting redox conditions. However, Mo, U and V enrichments in marine sediments can also result from changes in TOC and grain size (Kennedy et al., 2002). In Algeo and Lyons (2006), a clear relationship is observed between TOC and trace metals concentrations, and they suggest that trace metals are directly associated with organic material such that increased organic matter preservation may increase metal concentrations. The higher trace metal concentrations at our deeper sites relative to the shallow sites may be influenced by TOC, which is lower in abundance at the shallow sites. However, the sites at 30 m have higher metal enrichments and lower TOC than those at 80 m and within a particular core TOC does not appear to be related to trace metal concentrations. Indeed, plots of TOC versus Mo/Al ratios for the three outer shelf/slope locations where data is available (Fig. 5) do not show any relationship between these variables.

Quantitative grain size information is not available for all cores; however samples from the shallow sites are dominantly sand while the deeper sites are clay dominated. Within a particular core, core log descriptions note little variability in grain size. While grain size control of the metal abundances cannot be excluded, there is no evidence for variations in grain size significant enough to account for the changes

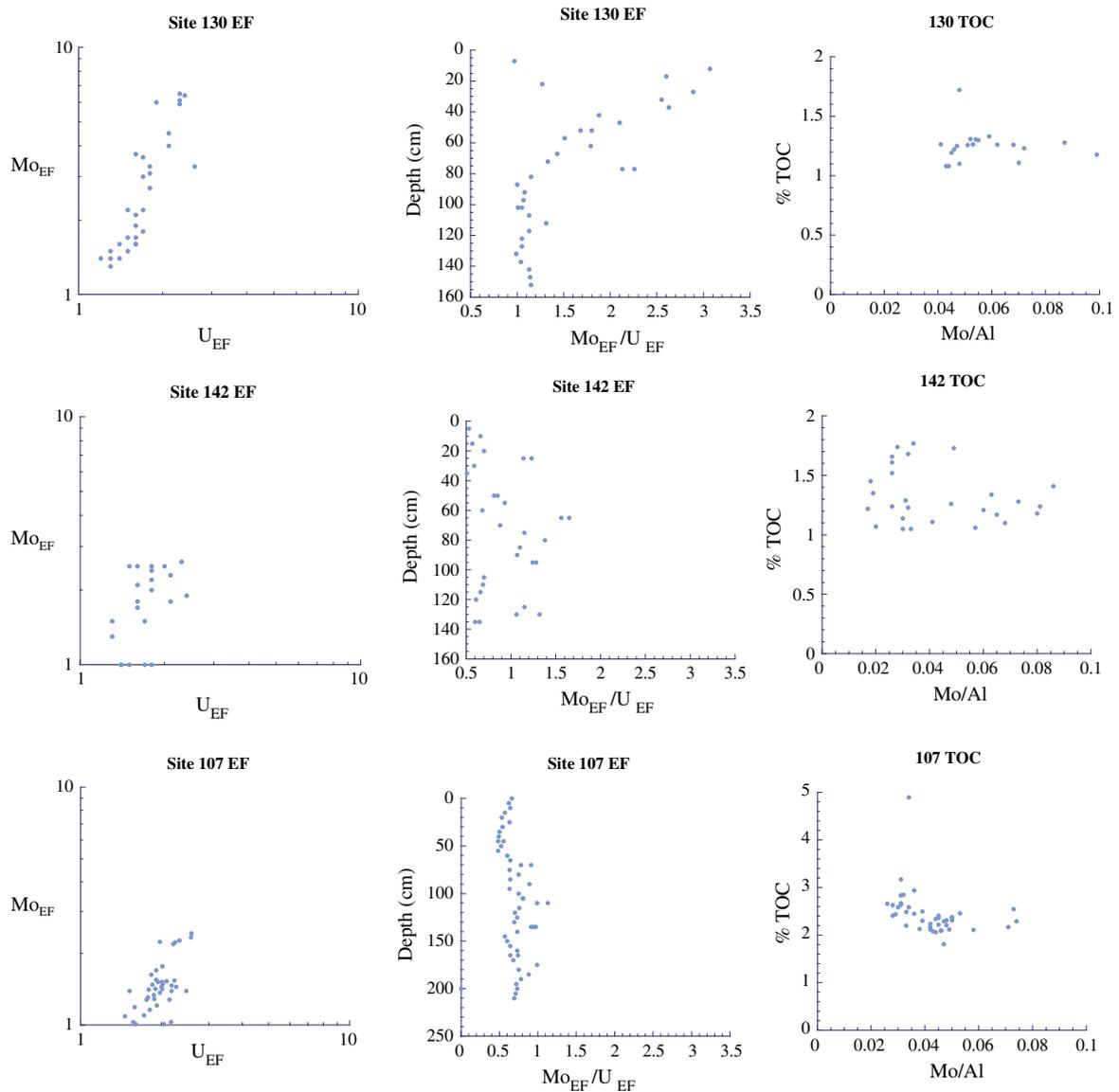


Fig. 4. Relationships between Mo and U enrichment factors for slope cores. Column A represents Mo_{EF} versus U_{EF} , column B represents the Mo_{EF}/U_{EF} by depth, and column C shows the relationship between TOC and Mo/Al ratios.

in metal ratios observed in the few cores for which trends in TOC are recorded (decreasing trend in the southern shore and shelf sites and increasing in the slope northern site). Accordingly, oxygen levels remain the most likely driver for any observed spatial or temporal changes in trace metal abundance in cores used for this study.

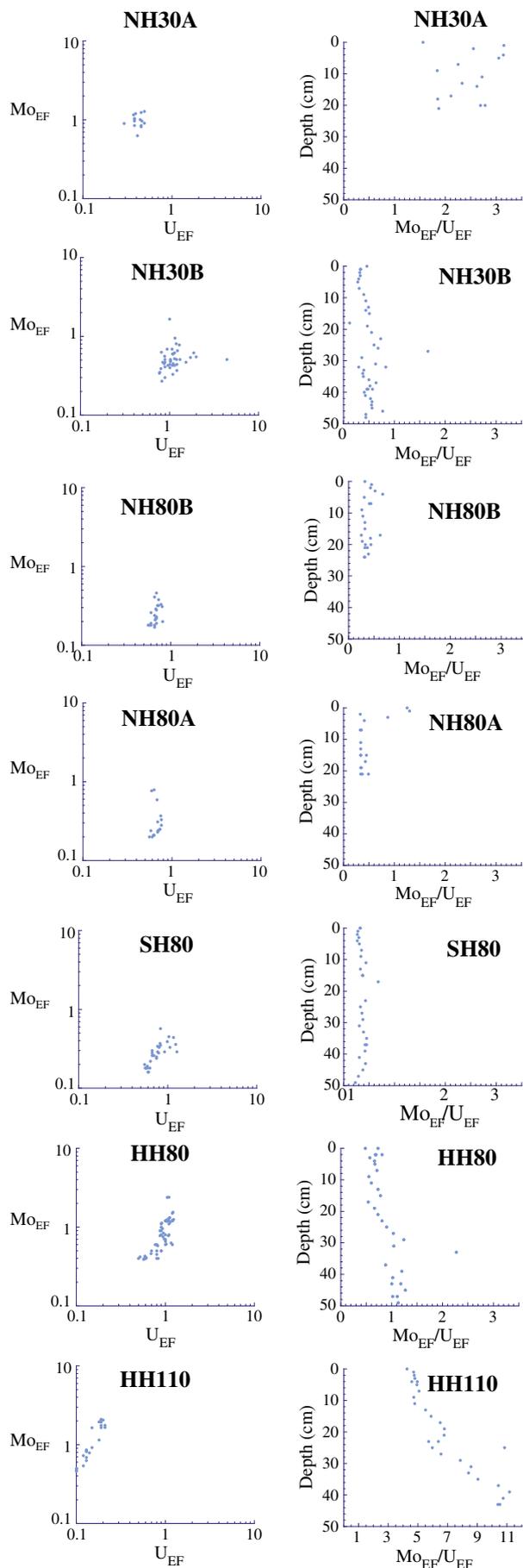
Comparison of Mo versus U enrichment factors (Mo_{EF} versus U_{EF} , Figs. 4 and 5) provides insight into the potential for particle shuttling (i.e. Algeo and Tribouillard, 2009) as a controlling factor of metal enrichment. This mechanism can be assessed through the analysis of Mo_{EF}/U_{EF} ratios. For the majority of the shelf cores, U_{EF} tend to be greater than Mo_{EF} , with Mo_{EF}/U_{EF} ratios averaging 0.5 and even less for cores SH80, NH80A&B, and NH30B. These results suggest that for the time interval represented by the cores the water column in this area was not stratified and the water was overall oxic (although short intervals of lower oxygen which are not captured in the sediment cannot be excluded). Indeed this is expected based on the seafloor topography and high wave intensity of the Oregon coast.

Site 142 and 107 both show trace metal enrichments relative to average shale values (up to $\sim 2\times$ shale levels) with a slightly larger U enrichment compared to Mo throughout the cores, potentially indicative of consistent suboxic conditions during the time interval represented

by the sediments. The temporal trends in each core differ, however. Site 142 (456 m water depth) exhibits a high degree of variability and no long-term trends are observed. This is consistent with the work of Pierce et al. (2012) who found that over the past 50 years water at the depths corresponding to Site 142 (~ 450 m) had oxygen concentrations of $<60 \mu\text{mol kg}^{-1}$ (i.e. hypoxic) though not anoxic and no measurable changes in oxygen concentrations were recorded over the last 50 years.

Site 107 (817 m water depth, within the OMZ) also shows little change in trace metal enrichment in our records. This is in contrast to instrumental records which show decreasing oxygen and enhancement of the OMZ over the past 50 years at this depth (Pierce et al., 2012). It is possible that these latest trends (e.g. last 50 years) are not resolved in the sediments due to the low sedimentation rates and the bioturbation depths of ~ 10 cm. Overall, our data indicates that no significant long-term (100 s to 1000s of years) changes in the oxygen levels at the slope sites between 450 and 800 m have occurred.

The shallower slope location, Site 130 at 298 m water depth, is within the California Undercurrent. We see a pronounced increase in Mo enrichment upcore, reaching the highest values for any core we studied. This enrichment likely results from changing redox conditions at this depth. Specifically, waters from this depth are a dominant source for



upwelling along the Oregon margin, and changes in the oxygenation at this depth will directly affect oxygen availability on the shelf with implications to the severity of anoxia during upwelling events. This is consistent with the observations of [Pierce et al. \(2012\)](#) showing this depth to be highly sensitive to change in the last 50 years. Robust age control of this core is needed to evaluate the relationship of changes in water chemistry at this depth to the observed regional anoxia history.

The long-term trend observed at Site 130 is the opposite of that seen at Sites HH-80 and HH-110, indicating latitudinal differences across the region. When considering the results in cores within the shelf area, we see that Site HH-110 along the southern transect (HH hydrographic line) is the only shelf location to show any enrichment above average shale values, and this enrichment is restricted to the bottom of the core (below 20 cm). The regional differences may be related to the spatial structure of coastal circulation and are consistent with the southern Heceta Bank region having weaker circulation with longer water residence time and this may be more prone to hypoxia ([Grantham et al., 2004](#); [Barth et al., 2005](#)). This may explain the more frequent hypoxia and higher productivity in the south compared to the northern Newport line in historical records ([Grantham et al., 2004](#); [Barth et al., 2005](#)). The Mo_{EF}/U_{EF} ratios and overall metal enrichments are decreasing toward the top of the core, indicating a change over time toward greater oxygenation. This suggests that the current anoxia is not a manifestation of a long-term change in conditions but is a rather new trend. The metal enrichment below 20 cm at Site HH-110, however, indicates that low oxygen conditions have occurred in this area in the past (more than 200 years ago based on the age model for this core).

The above interpretation is based primarily on the U and Mo data, which show similar trends. V concentrations in the two sites that record pronounced temporal trends (Site 130 and HH-110) do not change much and all slope locations have an enrichment value of approximately 2.6. The cause for the stability of the V record is unknown, but may be related to the high V in riverine particulate sediments obscuring any authigenic enrichment ([Emerson and Huested, 1991](#)). A riverine influence on V is also consistent with the highest V enrichment being observed at the shallowest water locations.

We compared the trends in the metal ratios for the two cores with robust age models (HH-80 and HH-110) to a smoothed tree ring derived record of the PDO (i.e. [MacDonald and Case, 2005](#)) to determine if the PDO is influencing the oxygen levels at these sites ([Fig. 6](#)). Given that the age models are derived from sedimentation rates based on ^{210}Pb from the upper sections of the cores, a direct comparison or attempt to identify individual PDO cycles is beyond the reach of this dataset. However, longer-term trends in PDO may be identified. [Fig. 6](#) shows the large-scale trends in the PDO, namely a shift at approximately 180 years ago from a weakly negative PDO index to a strongly positive one. This transition also appears in the Mo/Al record for cores HH-80 and HH-110 at roughly the same time considering the age model errors (shifting from enriched to not enriched levels). Both cores show a change in the slope of the Mo/Al temporal trend, along with decreased variability after this transition (though it is most obvious HH-110). No higher resolution cycles are observed in the record.

The limited published data relating oxygenation and PDO cycles do not extend back far enough in time to capture millennial scale changes. Instrumental records of oxygen concentrations extending 50+ years at Station P, located further offshore at 50°N, 145°W ([Whitney et al., 2007](#)), do not show a relation between oxygen and PDO ([Mecking et al., 2008](#)). These data indicate that PDO is not a dominant driver for hypoxia on the Oregon shelf on decadal time scales but it may be a driver on millennial scale. More data is needed to confirm this relationship.

Fig. 5. Relationships between Mo and U enrichment factors for shelf cores. Column A represents Mo_{EF} versus U_{EF} , while column B represents the Mo_{EF}/U_{EF} by depth.

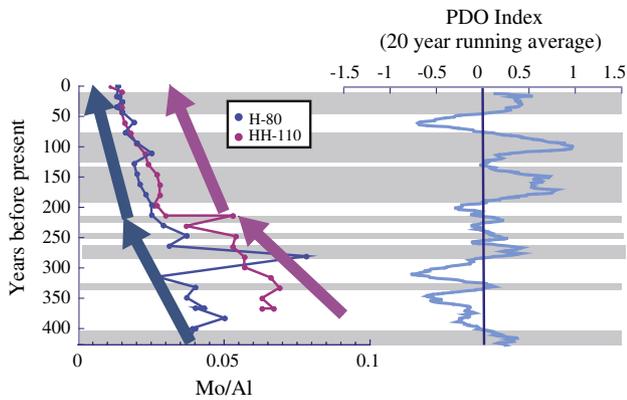


Fig. 6. Mo/Al ratios plotted in comparison to a 20-year running average of the PDO index of MacDonald and Case (2005). Mo/Al ratios are plotted using the age model derived for site HH-110 from this study and for site HH-80 from Wheatcroft et al. (2013). A 20-year running average of the PDO was used to minimize ENSO and seasonal variations. The gray bars denote time periods of a positive PDO index.

4.2. Carbon and nitrogen measurements

Organic matter $\delta^{13}\text{C}$ and C:N ratios can be used to identify sources of organic matter to the sediment (Hastings et al., 2012). Overall, our $\delta^{13}\text{C}$ values at all sites ranged between -23.5% and -22% . As average marine organic matter values range from -18% to -20% (Meyers, 1994 and references therein) and terrestrial organic matter ranges from -24% to -30% (Opsahl and Zepp, 2001), the organic matter in these samples is likely a mixture of terrestrial and marine sources. As expected, overall trends show lower (more terrestrial) values at shallower water depths compared to offshore sites. Cores 130 and 142 show gradually increasing $\delta^{13}\text{C}$ values through time suggesting increased influence of marine organic matter, while at Core 107 there is variability within a slightly decreasing $\delta^{13}\text{C}$ upcore. These data support a potential increase in marine productivity through the time interval studied, particularly at Site 130. These changes, coupled with the increase in Mo/Al and U/Al ratios at Site 130 described above, point toward a potential relationship between increase in marine productivity and increased hypoxic conditions at this site.

The carbon isotope data interpretations are consistent with the C:N ratios for these sites. Values between 4 and 10 are consistent with marine sources while vascular land plants have C:N ratios of 20 or greater (Premuzic et al., 1982; Jasper and Gagosian, 1993; Meyers, 1994; Prah et al., 1994). C:N ratios above ~ 10 can indicate a terrestrial influence. All samples from Core 130 fall above a C:N ratio of 10, while C:N ratios for Cores 142 and 107 average around 10. This implies that Core 130, at a relatively shallower water depth of 298 m compared to the other two studied cores, as expected has more terrestrial material. This site also shows a general trend toward increased marine influence upcore, consistent with the $\delta^{13}\text{C}$ record and implying a change in the relative contribution of marine and terrestrial sources at this site. C:N ratios for Core 142 are consistently between 10 and 11, implying minor terrestrial influence and show a slight trend toward more marine influence through time. Core 107, the deepest site at 817 m water depth, appears to have little terrestrial influence throughout the core (C:N < 10).

Hastings et al. (2012) used $\delta^{13}\text{C}$ and C:N ratios, in combination with lignin phenols, to illustrate the mixing between terrestrial and marine organic matter on the continental shelf in the same core array used in Wheatcroft et al. (2013). While the center of terrestrial accumulation was located near the outflow of the Umpqua River, the mixed signature (marine and terrestrial) was evident across the region. Plots of C:N and lignin phenols versus $\delta^{13}\text{C}$ for the sites studied by Hastings et al. (2012) place all data along a mixing line between marine organic matter and vascular plants. Even the upper-slope muds, the most distal

environment, had some terrestrial contribution (Hastings et al., 2012). Given the overlap between some of the northern samples in Hastings et al. (2012) and this study, the observed influence of terrestrial matter throughout the shelf, and slope environment supports our conclusion of small but measurable terrestrial influence at our deeper water locations.

Measurements of TOC from the three slope cores can be compared to previously published results of TOC from the three 80 m water depth sites (Reimers et al., 2012) and the more southern core array (Hastings et al., 2012) to determine a more complete picture of regional and downcore trends. The three slope sites in this study show a general gradient related to water depth for TOC, with the deepest water site having the highest TOC. This is consistent with results from the Washington and southern Oregon margins showing the greatest TOC on the slope with generally decreasing values approaching land (Prah et al., 1994; Hastings et al., 2012). This trend with water depth indicates some combination of winnowing of fines, dilution from increased lithogenic material, changes in preservation, and changes in productivity. The same depth related trends are also captured in the trace metal ratios. Because the trace metal ratios provide some control over lithology (by normalizing to Al), we believe that the downslope TOC variations are not solely due to dilution effects. Enhanced preservation is the likely driver as less degradation of organic material is expected to accrue closer to the OMZ due to limited oxygen contact time (Hartnett et al., 1998).

Temporal trends showing a slight increase in TOC at Sites 130 and 142 similar to trends in $\delta^{13}\text{C}$ from the same locations reflect an increase in marine organic deposition likely related to an increase in marine productivity. In contrast, the deepest water and most southern site, Site 107, does not show this trend. While TOC increases from the base to the top of this core, $\delta^{13}\text{C}$ decreases and hypoxia indicators do not change, both inconsistent with an increase in marine productivity. The strong increase in TOC at the top of this core may have a terrestrial origin based on the $\delta^{13}\text{C}$ results.

The $\delta^{13}\text{C}$, C:N ratio, and TOC spatial variations described above are consistent with the regional changes observed in the trace metal data. Specifically, increases in marine productivity may have contributed to declines in oxygen concentrations at Site 130 in the California Undercurrent and these changes to the source of upwelling water may have impacted the shelf. Although hints for corresponding changes in metal enrichments in some of the shelf sediments are seen (e.g. peaks in the upper parts of cores NH-30B and to a lesser extent in NH-30A), the limited age control on these records precludes conclusions that directly link these observations to present day events.

5. Conclusions

Redox sensitive trace metal analysis combined with $\delta^{13}\text{C}$, C:N ratios, and TOC accumulation provide a more complete picture of the long term evolution of hypoxic/anoxic conditions off the Oregon coast. Overall, the northern shelf locations do not show significant metal enrichment over the past millennia, indicating that this environment has likely remained dominantly oxygenated for the past several hundred years. The present day hypoxic conditions may be a new phenomena not recorded at these sites for millennia. The most southern locations, particularly at 110 m water depth, have significant metal enrichment at the base of cores (corresponding to ~ 200 years ago) suggesting that this area is the most sensitive region for hypoxia. The enrichment declines upcore indicating an apparent increase in oxygen through time. This increase is counter to current observations suggesting that the current conditions are a relatively recent trend and not the culmination of a gradual change in conditions. This change may be related to millennial scale changes in PDO although more data are needed to support this conclusion.

When considering sediments from locations at the source of the upwelled waters (298 cm water depth) in this region, an overall increase in Mo enrichment upcore is observed, suggesting a depletion of oxygen over time. Changes in $\delta^{13}\text{C}$ and C:N ratios coincide with changes

in metal enrichment, indicating that increases in marine productivity are contributing to the reduction of oxygen levels. Given that this trend is only observed at this location, however, it remains unclear that long-term productivity changes are the primary driver of the current regional hypoxia.

Overall, our results support the hypothesis that current hypoxic conditions are driven by recent climatic changes triggering fluctuations in productivity and circulation patterns (upwelling intensity) that have not been present in the region as a whole during recent centuries to millennia. Such conditions, however, may have been present more than 200 years ago at the southern reaches of the currently impacted area. Additional cores from the southern area spanning a longer time frame are needed in order to confirm this observation.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2014.05.029>.

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