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

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ABSTRACT

Hypoxic (<62 μmol/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 $\delta^{13}C$, 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.

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 μmol 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 μmol 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).

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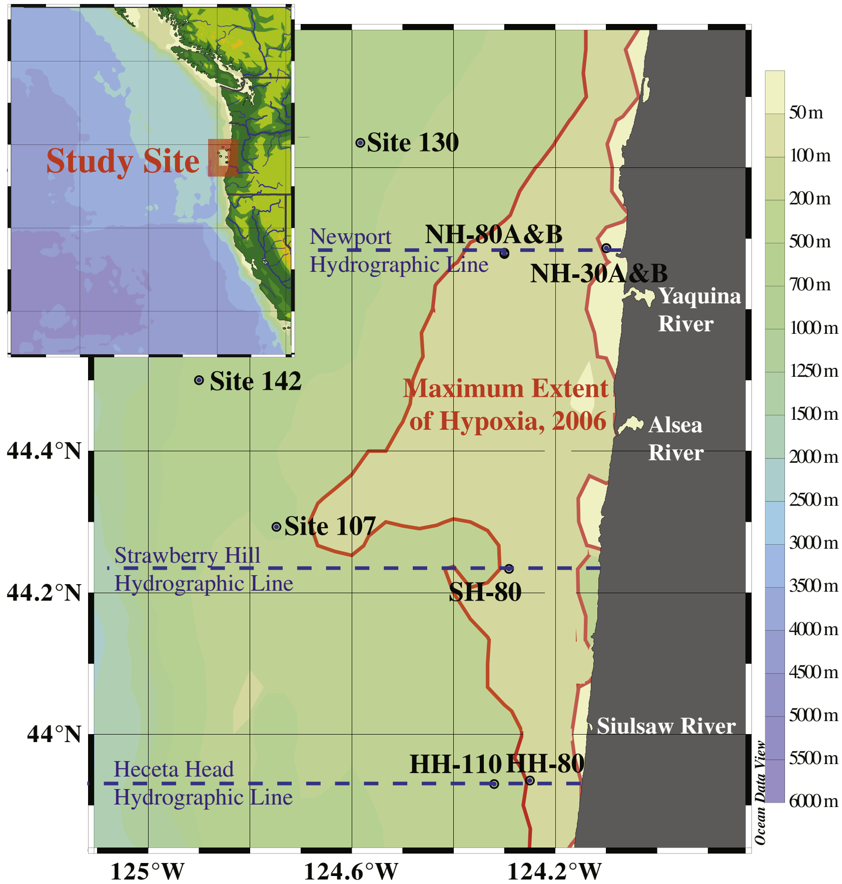

Fig. 1. Study region and sampling locations along the central Oregon coast described in this study. The maximum extent of hypoxia from 2006 is delineated in solid red. The three hydrographic lines are notated in dashed blue.

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 ($MoO_xS_{4x}^{2-}$) under anoxic conditions or to molybdenum sulfide (MoS_4^{2-}) under euxinic conditions and is removed to the sediment resulting in authigenic enrichment of Mo (Crusius et al., 1996;