Inter-decadal changes in intensity of the Oxygen Minimum Zone off Concepción, Chile (~36°S) over the last century

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Abstract

We reconstructed oxygenation changes in the upwelling ecosystem off Concepción (36ºS), Chile, using inorganic and organic proxies in a sediment core covering the last ca. 110 years of sedimentation in this area. Authigenic enrichments of Mo, U and Cd were observed between ca. 1935 and 1971 CE implying a prolonged period with predominantly more reduced conditions in bottom waters and surface sediments. Significant positive correlations between redox-sensitive metals, algal sterols, biomarkers of micro-aerophilic and anaerobic microorganisms, and archaeal glycerol dialkyl glycerol tetraethers point to a tight coupling among bottom water O_2 depletion and increased primary and export production. The time interval with low O_2 of ca. 35 years seems to follow low frequency inter-decadal variation of the Pacific Decadal Oscillation, and may have resulted in O_2 depletion over the entire continental shelf off Concepción. Taken together with the concurrent increase in sedimentary molecular indicators of micro-aerophilic and anaerobic microbes, allow us to suggest that changes in oxygenation of the water column are reflected by changes in microbial community. This study can inform our understanding of ecological consequences to projected trends in ocean deoxygenation.

Key words: Oxygen Minimum Zone, upwelling, organic biomarkers, redox sensitive metals, microbial community, Pacific Decadal Oscillation, Chile

1. Introduction

Oxygen Minimum Zones (OMZs) are epipelagic and mesopelagic subsurface layers of suboxic waters (e.g., ≤ 22 μM O_2) found along Eastern Boundary currents, Arabian Sea

and Equatorial Pacific, where upwelling of nutrient-rich waters promotes elevated primary production and O_2 consumption through microbial respiration (Wyrtky, 1962; Helly and Levin, 2004; Paulmier and Ruiz-Pino, 2009). Due to strong redox gradients and reducing conditions, an active microbial community connects cycling of carbon, nitrogen, sulfur and other elements (Lam et al., 2009; Canfield et al., 2010; Naqvi et al., 2010; Ulloa et al., 2012; Wright et al., 2012). Waters overlying the continental shelf of central-southern Chile become seasonally depleted in O_2 during austral spring and summer when the area is fed by the poorly oxygenated Peru–Chile Countercurrent. In austral autumn and winter shelf waters are oxygenated due to the input of Subantarctic waters (Ahumada and Chuecas, 1979; Sobarzo et al., 2007). Inter-annual phenomena such as El Niño Southern Oscillation (ENSO) can also affect oxygenation of south Pacific waters (Blanco et al., 2002; Carr et al., 2002; Levin et al., 2002). In central-southern Chile, the upper edge of the OMZ deepens during El Niño thus allowing greater oxygenation of bottom waters (Gutiérrez et al., 2000; Neira et al., 2001; Escribano et al., 2004). Analyzing a sedimentary record from northern Chile, Vargas et al. (2007) related changes in coastal upwelling and biological production to variations in the Pacific Decadal Oscillation (PDO), characterized by an ENSO-like interdecadal variability in the Humboldt Current System. During the cool phase of PDO, primary production intensifies in response to upwelling and fertilization of the upper ocean (Mantua et al., 1997, 2002; Cloern et al., 2007), leading to enhanced O_2 consumption in the water column (Wyrtky, 1962; Sarmiento et al., 1998; Helly and Levin, 2004). Since patterns of biological production and oxygenation of the water column during PDO cycles resemble those of ENSO (Vargas et al., 2007), we hypothesize that variations at the scale of PDO promote chemical and biological changes in the OMZ off central-southern Chile.

1.1. Trace metals as redox proxies

Past redox variations can be analyzed using trace elements in sediments since some redox-sensitive metals are less soluble under reducing conditions resulting in authigenic enrichment in low oxygen and high organic matter environments (Algeo and Maynard, 2004; McManus et al., 2005). This chemical behavior makes molybdenum (Mo), uranium (U), and cadmium (Cd) valuable paleoredox and paleoproductivity proxies (Calvert and Pedersen, 1993; Morford and Emerson, 1999; Crusius et al., 1996; Algeo and Maynard, 2004).

Mo occurs primarily as soluble MoO_4^{2-} in oxygenated marine waters and its reduction to particle reactive thiomolybdates ($MoO_xS_{4x}^{2-}$) under anoxia or molybdenum sulfide (MoS_4^{2-}) under euxinia, result in authigenic enrichment of sedimentary Mo (Crusius et al., 1996; Helz et al., 1996; Zheng et al., 2000; Vorlicek and Helz, 2002), thus indicative of O_2-depleted environments. Uranium is mainly present as U (VI) that binds to carbonate ions, forming $UO_2(CO_3)_3^{4-}$ in seawater. Reduction of U (VI) to U (IV) occurs under suboxic conditions and at similar redox potentials that allow Fe(III) reduction to Fe(II) (Cochran et al., 1986; Klinkhammer and Palmer, 1991 ; Chaillou et al., 2002; McManus et al., 2005, 2006). Higher content of U relative to Mo indicates anoxic depositional conditions (Algeo and Maynard, 2004; Tribovillard et al., 2006) whereas equal contents of U, V and Mo indicate euxinic conditions in overlying water column (Algeo and Maynard, 2004; Tribovillard et al., 2006).

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Cadmium is delivered to marine sediment mainly in association with sinking organic matter (Piper and Perkins, 2004). If sediments are reduced then Cd is authigenically enriched, likely as sulfide (Rosenthal et al., 1995; Gobeil et al., 1997; Morford and Emerson, 1999; Morford et al., 2001).

1.2. Lipid biomarkers

In the past decade, a diverse and active microbial community has been identified in OMZ waters off central and northern Chile (Stevens and Ulloa, 2008; Farías et al., 2009; Quiñones et al., 2009; Canfield et al., 2010; Molina et al., 2010; Levipan et al., 2012; Srain et al., 2015). Temporal and compositional variations in this microbial community can be studied by analyzing their cell membrane lipids (biomarkers) preserved in the sedimentary record, as demonstrated in other OMZ areas of the ocean (Schouten et al., 2000a; Arning et al., 2008; Rush et al., 2012).

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Lipid biomarkers are organic molecules occurring in recent and geological materials that have chemical structures that record their biological origin (Brassell, 1992; Schouten et al., 2000a; Hinrichs et al., 2003; Coolen et al. 2008; Talbot et al., 2014). Biomarkers are relatively resistant to degradation and they can be indicators of a broad group of organisms or of a specific genus or species, and as such, of their growing environment (Table 1) (Brassell et al., 1986; Brocks and Pearson, 2005). Abundant sedimentary sterols $C_{27}\Delta^5$, $C_{28}\Delta^5$, $C_{29}\Delta^5$ and $C_{30}\Delta^{22}$ (Volkman et al., 2003) are indicative of algal primary and export production. The content and composition of isoprenoidal

glycerol dialkyl glycerol tetraethers (GDGTs) are used as indicators of ammonia oxidation by marine pelagic archaea (De Long et al., 1998; Schouten et al., 2000b; Turich et al., 2007; Lincoln et al., 2014), which are capable of nitrifying under low-O_2 conditions (Brandhorst, 1959; Carlucci & Strickland 1968; Ward & Zafiriou 1988; Ward et al. 1989; Lipschultz et al. 1990).

Changes in sedimentary contents of bacterial hopanes and hopanols are related to variations in bacterial groups (Rohmer et al., 1984; Ourisson and Albrecht, 1992; Innes et al., 1998; Talbot et al., 2007). Occurrence of C_{27}-trisnorhopene is favored in anoxic and euxinic environments, and during upwelling events (Grantham et al., 1980; Schouten et al., 2001), and considered as an indicator of anaerobic microbial degradation (Volkman et al., 1983; Duan et al., 1996; Duan, 2000; Peters et al., 2005). C_{16}, C_{17}, and C_{18} mono-O-alkyl glycerol ethers (MAGEs) are present in fermentative and sulfate reducing bacteria (Langworthy et al., 1983; Langworthy and Pond, 1986; Ollivier et al., 1991), although these biological sources do not appear to be unique (Hernández-Sanchez et al., 2014).

We studied redox-sensitive metals and organic biomarkers in ca. 110-year sedimentary record from the OMZ within the upwelling ecosystem off Concepción, central-southern Chile (36° S), to infer temporal changes in biological production and oxygenation of the water column. Our goal was to assess whether the intensity of the OMZ has varied over the past century in response to ocean/atmosphere circulation patterns, and whether this is reflected in changes in microbial community

2. Methods

2.1 Sampling

The study site (Station 18; 36º30.8' S 73º7' W) is located in the coastal upwelling ecosystem off central-southern Chile at ca. 18 nautical miles from the coast of Concepción (Fig. 1). Sampling was carried out as part of the "Microbial Initiative in Low Oxygen off Concepción and Oregon" (http://mi_loco.coas.oregonstate.edu), and the Oceanographic Time Series Program (Station 18) of the Center for Oceanographic Research in the eastern South Pacific (COPAS) at University of Concepción (www.copas.udec.cl/eng/research/serie).

A 25 cm sediment core was collected at a water depth of 88 m during austral summer (February 2009) using a GOMEX box corer onboard R/V Kay-Kay II. The top 5 cm were sectioned onboard every 0.5 cm, whereas the rest of the core was sampled at 1cm resolution. Samples were stored in glass petri plates and kept frozen at -18 ºC until laboratory analysis. The water column was sampled monthly at Station 18 from January 2008 to November 2009 with Niskin bottles, and temperature, salinity, O_2, and fluorescence of chlorophyll *a* data were obtained using a Seabird 25 CTDO. Fluorescence data were transformed to concentration of chlorophyll *a* according to Parsons et al. (1984). All water column data were obtained from the database of the COPAS Center.

2.2 Sedimentary redox potential and organic carbon content

Redox potential was measured in the top 15 cm of the sediment core using a redox potential sensor (Hanna) with an accuracy of ± 0.1mV. Sedimentary organic carbon content was determined by high temperature oxidation using a NA 1500 Carlo Erba elemental analyzer. Prior to organic carbon analysis, inorganic carbon was removed by placing samples into silver cups with a drop of Milli-Q water and then fuming over night with concentrated HCl. Samples were dried at 60°C for analysis.

2.3 Geochronology

Sedimentary ^{210}Pb activities were determined by Alpha spectrometry of its daughter ^{210}Po using ^{209}Po as a yield tracer (Flynn, 1968). Activities were quantified until 1 σ error was achieved in a Canberra Quad Alpha Spectrometer. Ages (CE, Common Era) were established according to Constant Rate of Supply model (CRS, Appleby and Oldfield, 1978), which considers unsupported ^{210}Pb inventories (^{210}Pbxs). Geochronology of our sediment core was determined through radiocarbon measurements on fish scales and the best fit age curves resulting from CRS model and three ^{14}C control points from a longer core (VG06-2) retrieved in 2006 from the same sampling site (Muñoz et al., 2012 and Supplement). Resulting ages were converted to calendar years before present using calibration curve MARINE09 (Reimer et al., 2009) and applying a regional marine reservoir correction (ΔR) of 137±164 years, 2σ confidence interval (Table S1; Fig. 2).

2.4 Trace metal analysis

Trace metals Mo, U, and Cd were analyzed with an Agilent 7500ce Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), and aluminum (Al) was determined in a Perkin Elmer Analyst 700 Atomic Absorption Spectrometer. Sediment samples and analytical blanks (18.0 MΩ deionized water) were sequentially digested with suprapure HNO_3, HCl, $HClO_4$, and HF. Accuracy and precision of measurements were assessed by analyzing reference material MESS-3 from the National Research Council of Canada. Excess metal (Me_{xs}) was calculated as $[Me_{sample}] - ((Me/Al)_{earth} \times [Al_{sample}])$. $(Me/Al)_{earth}$ corresponds to an average ratio for the Biobío and Itata rivers (Fig. 1) in central-southern Chile (J. M. Muratli, personal communication, 2012) (Table S2).

2.5 Gas chromatography-mass spectrometry (GC-MS) of biomarkers

Extraction of lipid biomarkers (i.e., hopanes, hopanols, sterols, and mono-O-alkyl-glycerol ethers – MAGEs) from sediments was carried out according to a modified Bligh and Dyer (1959) procedure, substituting dichloromethane for chloroform. Freeze-dried sediment samples (1–5 g) were sequentially extracted by ultra-sonication with 30 mL dichloromethane/methanol (1:3 v/v, 2X), (1:1 v/v, 1X), and dichloromethane (2X). The lipid extract was concentrated with a rotary evaporator and dried with anhydrous Na_2SO_4. Lipid extracts were then separated into four fractions by column chromatography (30 cm length, 1 cm ID) filled with ca. 7 g deactivated silica gel. Aliphatic hydrocarbons (F1) were eluted with 40mL hexane, ketones (F2) were eluted with 50 mL toluene/hexane (1:3 v/v), alcohols (F3) with 50 mL ethyl-acetate/hexane (1:9 v/v), and polar compounds (F4) were eluted with 35 mL ethyl-acetate/methanol/hexane (4:4:1v/v). The alcohol fraction (F3) was derivatized with 80 µL BSTFA (N,O- bis(trimethylsilyl) trifluoracetamide) and 40 µL TMCS

(trimethylchlorosilane) at 70 ºC for 1 h before analysis. Samples were analyzed in an Agilent 6890 GC series coupled to an Agilent 5972 MS. Hopanols, sterols and MAGEs were analyzed with a 30 m DB-5 column (0.5 mm ID, 0.25 µm film thickness) using He as carrier gas. Oven temperature program included: 60 ºC (2min) to 150 ºC at 15 ºC min^{-1}, to 320 ºC (held 34.5min) at 4 ºC min^{-1}. Hopanes were analyzed in the aliphatic hydrocarbon fraction (F1) using a 30 m HP- 5 column (0.32 mm ID, 0.25 µm film thickness). GC oven temperature program was: 80 ºC (2min) to 130 ºC at 20 ºC min^{-1}, to 310 ºC at 4º C min^{-1}. The MS was operated in electron impact mode (70 eV) with the ion source at 250 ºC. Mass spectra were acquired in both full scan mode (m/z range 40–600, scan rate 2.6 s^{-1}) and selective ion-monitoring mode (SIM, m/z 191 for hopanes and hopanols). Concentrations of alcohols and aliphatic hydrocarbons were based on those of internal standards 1-nonadecanol and squalene.

2.6 Analysis of glycerol dialkyl glycerol tetraethers (GDGTs) by High Performance Liquid Chromatography – Atmospheric Pressure Chemical Ionization – Mass Spectrometry (HPLC-APCI-MS)

Sedimentary material was sequentially extracted by ultrasonication (3X) with methanol, dichloromethane-methanol (1:1, v/v), and dichloromethane. Lipid extracts were concentrated using a rotary evaporator and dried over a small Pasteur pipette filled with combusted glass wool and anhydrous Na_2SO_4. Lipids were separated into non-polar and polar fractions using a Pasteur pipette filled with activated Al_2O_3, after elution with hexane/dichloromethane (9:1, v/v) and dichloromethane/methanol (1:1 v/v), respectively. An aliquot of the polar fraction was dissolved in hexane/propanol (99:1 v/v), and filtered through a 0.45 µm PFTE filter. HPLC-MS analysis followed

methodologies described by Hopmans et al. (2000) and Liu et al. (2012), using an Agilent Technologies 1200 Series HPLC equipped with an auto-sampler and a binary pump, linked to a Q-TOF 6520 mass spectrometer via an atmospheric pressure chemical ionization interface (Agilent Technologies). Samples were dissolved in 200 μL hexane/isopropanol (99:1 v/v). GDGTs were separated using a Prevail Cyano column (2.1×150mm, 3mm; Grace, USA) and maintained at 35 ºC and a flow rate of 0.25mL min^{-1}. The elution program was: 5 min 100 % eluent A (hexane/isopropanol, 99:1, v/v), followed by a linear gradient to 100 % eluent B (hexane/isopropanol, 90:10 v/v) for 35 min, and then held at 100 % eluent B for 5 min. Quantification of core GDGTs was achieved by co-injection of samples with a C_{46}GDGT as internal standard (Huguet et al., 2006).

2.7 Statistical analysis

Homogeneity of variances was assessed using the Levene's test, whereas normality was determined using a Shapiro–Wilk test. Non-parametric Spearman correlations were calculated between selected variables in order to determine statistical associations with significance < 0.05 (Software Statistica, version 12).

3. Results

3.1 Oceanographic setting of the study site

During austral fall and winter (April to August), water temperature ranged between 11 and 12 ºC in the upper 20 m of the water column, and between 10 and 11 ºC below 65

m depth (Fig. S1a). Surface salinity varied between 32 and 33 above 20 m, and was 34 below this depth (Fig. S1b). Chlorophyll a concentration varied between 0.3 and 1.4 mg m^{-3} with higher values in the top 20 m (Fig. S1c). Oxygen concentration varied between 170 and 205 µM in the top 20 m, and dropped to values lower than 22 µM (suboxia) below 60 m depth (Fig. S1d). During austral spring and summer (September to March) surface temperature ranged between 13 and 15 ºC, decreasing to 10 ºC below 84 m depth (Fig. S1a). Salinity varied between 31 and 34.5 in the whole water column (Fig. S1b). Chlorophyll a concentrations up to 53 mg m^{-3} were measured in surface waters (Fig. S1c). Oxygen concentration ranged between 114 and 217 µM in surface waters. Suboxic waters (i.e., < 22 µM) occur below ca. 20 m (Fig. S1d), which is significantly shallower than in austral fall-winter.

Redox potential decreased from −176 mV at the water-sediment interface to −325 mV below 3 cm, indicating predominance of reducing conditions in near-surface sediments at the time of sampling during austral summer (Fig. S1e), consistent with the occurrence of 5 µM O_2 in bottom waters (Fig. S1d). A surface fluff layer with a *Thioploca* mat was observed at the sediment-water interface. Organic carbon content varied between 0.07 and 0.1 g $(gdw)^{-}$ (Fig. S1e).

3.2 Geochronology

Background $^{210}Pb_{xs}$ activity of 0.80 ± 0.02 dpm g^{-1} was reached at 23 cm in the core. Geochronology from both $^{210}Pb_{xs}$ inventories and radiocarbon ages (Fig. 2; Table S1) fitted an exponential decrease (r^2 0.99) due to sediment compaction (Fig. 2), allowing adjusting older ages (Binford, 1990). A recent sedimentation rate of 0.24 ± 0.02 cm yr^{-1}

was estimated, representing ca. 110 years of sedimentation in our sediment core at Station 18.

3.3 Redox sensitive trace metals

Redox sensitive metals are enriched in the interval ca. 1935–1971 CE (Fig. 3a–c; black bar). Mo_{xs} content ranged between 2.5 and 6.5 ppm (Fig. 3a), showing a similar vertical distribution as U_{xs} (1.1-4.1 ppm; Fig. 3b), and Cd_{xs} (0.8-1.9 ppm; Fig. 3c). Enrichments of Mo_{xs}, U_{xs}, and Cd_{xs} exhibited a significant correlation among each other (R_s: $p < 0.05$; Table 2; Fig. S2) indicating more reducing conditions in bottom waters and sediments at this time. In comparison, the periods 1905–1919 CE and 1979–2005 CE showed lower contents of redox-sensitive metals (Fig. 3a–c; white bars), pointing to presumably more oxygenated bottom waters and sediments.

3.4 Algal sterols

Sterols $C_{27}\Delta^5$, $C_{28}\Delta^5$, $C_{29}\Delta^5$ and $C_{30}\Delta^{22}$ were identified through the fragmentation pattern of their trimethylsilyl (TMS) derivatives. The presence of $C_{27}\Delta^5$-sterol cholesterol (m/z 458 $[M]^+$) was confirmed by detection of ions m/z 129, m/z 329 and 368. The $C_{28}\Delta^5$-sterol (m/z 472 $[M]^+$) showed ions of m/z 129, as well as m/z 343 and m/z 382. The $C_{29}\Delta^5$-sterol (m/z 486 $[M]^+$) was identified by prominent ions m/z 357 and 396. Prominent ions m/z 69, m/z 271, m/z 359 and m/z 500 $[M]^+$ confirmed the presence of $C_{30}\Delta^{22}$ dinosterol. Sterol contents ranged between 1,029 and 12,164 μg (g $C_{org})^{-1}$ with maximum values in surface sediments (Fig. 4a). Sterols correlated positively with U_{xs} (R_s: $p < 0.05$; Table 2; Fig. S3).

3.5 Archaeal GDGTs

GDGTs were identified by their molecular ion and elution pattern: GDGT-0 (1302 15 $[M + H]^+$), GDGT-I (1300 $[M + H]^{+)}$, GDGT-II (1298 $[M + H]^+$), GDGT-III (1296 $[M + H]^+$), and GDGT-V and GDGT-V' (1292 $[M + H]^+$ known as crenarchaeol and crenarchaeol regioisomer). Content of GDGTs varied between 1094 and 5423 μg (g $C_{org})^{-1}$ (Fig. 4b), with elevated values at the base core and between ca. 1947 and 1975 CE (Fig. 4b). GDGTs and U_{xs} contents correlated positively (R_s: $p < 0.05$; Table 2; Fig. S4).

3.6 Hopanoid composition and abundance

C_{27}-trisnorhopene (22,29,30 trinorhop-17,(21)-ene) was identified based on its molecular ion fragment m/z 368 $[M^+-2H^+]$ and fragments m/z 191 and 231 indicating unsaturation in the ring system (Table 3). Three diploptene isomers were identified according to their mass spectra, hop-13,18-ene, neohopene, and hop-22,29-ene (Table 3; Fig. S5a). C_{30} hopene diploptene was identified based on its molecular ion (m/z 410 $[M^+]$) and diagnostic ions m/z 395, 299 and 191 (Table 3; Fig. S5a). A homologous series of C_{31} to C_{35} hopanes with $\alpha\beta$ configuration were identified through m/z 191 in the hydrocarbon fraction (Fig. S5a). Homohopanes C_{31} , C_{33} , C_{34} , and C_{35} were present as epimers S and R (Fig. 5a, Table 3), whereas C_{32} hopane occurred as the single epimer R (Table 3; Fig. S5a). C_{27} norhopene, and hopanes C_{30} and C_{31} were the only compounds with $\beta\beta$ configuration (Table 3; Fig. S5a). C_{31} hopane showed the highest

relative abundance in the homohopane homologous series, with S and R 17α,21β homohopane as the predominant one, followed by hopanes C_{33} and C_{34} (Fig. S5a).

17β,21β hopanol (C_{30}), 17β,21β homohopanol (C_{31}), 17β,21β bishomohopanol (C_{32}), and 17β,21β trishomohopanol (C_{33}) were identified by the characteristic ion m/z 191 and by their molecular ions ($[M]^+$ m/z 500, m/z 514, m/z 528, and m/z 542) (Table 3; Fig. S5b). Homologue C_{32} was the most abundant hopanol (Fig. S5b). C_{27}-trisnorhopene ranged between 0.03 and 1.1 μg $(g\ C_{org})^{-1}$. Maximum values occurred between ca. 1935 and 1971 CE (Fig. 4c), whereas minimum values were observed during intervals 1905–1928 CE and 1980–2005 CE (Fig. 4c). C_{27}-trisnorhopene correlated positively with U_{xs} and Cd_{xs} (R_s : $p < 0.05$; Table 2; Fig. S6). The profile of C_{31} hopanol content varied between 1.1 and 3.7 μg $(g\ C_{org})^{-1}$, and reached the highest value during 1935–1971 CE (Fig. 4d). Positive correlations among C_{31} hopanol, Mo_{xs}, and Cd_{xs} were observed (R_s: $p < 0.05$; Table 2; Fig. S7). In contrast, C_{32} hopanol anticorrelated with C_{31} hopanol, U_{xs}, and Cd_{xs} (R_s: $p < 0.05$; Table 2; Fig. 4e; Fig. S8).

3.7 Mono-O-alkyl glycerol ethers (MAGEs) indicators of fermentative and sulfate reducing bacteria

Mass spectra of MAGEs showed a base peak ion of m/z 205 characteristics of monoalkyl glycerol-TMS compounds, which corresponds to cleavage between carbons 1 and 2 of glycerol moiety, and fragment m/z 445 $[M+H-CH_3]^+$ due to loss of methyl group. We identified C_{16}-MAGE with molecular ion m/z 460 $[M]^+$, C_{17}-MAGE with m/z 474 $[M]^+$, and C_{18}-MAGE with m/z 488 $[M]^+$. Content of MAGEs (sum of C_{16}, C_{17}, and C_{18} MAGEs) varied between 9 and 628 μg $(g\ C_{org})^{-1}$ (Fig. 4f). MAGEs content

remained low (50 μg ($g C_{org}$)$^{-1}$) during 1901–1928 CE (Fig. 4f). From ca. 1935 CE, MAGEs contents increased reaching the highest value in surface sediments (Fig. 4f). MAGEs correlated positively with Mo_{xs} and Cd_{xs} (R_s: $p < 0.05$; Table 2; Fig. S9).

4 Discussion

4.1 Patterns of redox depositional conditions, and primary and export production

We interpret variations in contents of sedimentary redox-sensitive metals as changes in oxygenation of bottom waters and surface sediments. This interpretation agrees with previous observations by Böning et al. (2009) and Muñoz et al. (2012) for the continental shelf off Concepción, as well as with authigenic enrichments of U and Mo over the Oregon shelf and Peru upwelling region associated with O_2 depletion and increased primary production (Scholz et al., 2011, Erhardt et al., 2014).

Higher excess amounts of Mo, Cd and U during the period between 1935 and 1971 (Fig., 3a, b, c) indicate more reduced depositional conditions. Favorable conditions for Mo and Cd authigenic enrichments are observed in bottom water and surface sediments during the upwelling season when high primary production, low water column O_2, and severe low redox-potential in surface sediments occur (Figs. S1c, d, and e; www.copas.udec.cl/eng/research/serie). However, downcore distribution of these trace metals could also reflect subtle changes in intensity of O_2 depletion over the continental shelf off central-southern Chile. Thus, from ca. 1932 to 1951 CE, an increase in excess

Mo and Cd indicates redox potential favorable to sulfate reduction and HS^- production at least in bottom waters (euxinic conditions). Since ca. 1957 to 1969 CE, an increase in excess U content, coincident with a decrease in excess Mo and Cd, could indicate a transition to anoxia from previous euxinic conditions since U enrichment begins when the redox potential reaches that for Fe-oxide reduction (Cochran et al., 1986; Klinkhammer and Palmer, 1991). The observed temporal variations in the redox-potential evidenced by those subtle changes in trace metals enrichment could result in readjustment of the microbial community to changing redox potential of the water column. However, correspondence of these conditions with changes in organic biomarker patterns is not necessarily detected in sediments since we assume that sediment diagenesis is constant for organics but not for redox-sensitive metals once they reach the sediments.

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Downcore distribution of inorganic and organic proxies reveal a period of ca. 35 years between ca. 1935 and 1971 CE (Figs. 3 and 4; black bar) when values of redox-sensitive metals (Fig. 3), sterols (Fig. 4a), GDGTs (Fig. 4b), C_{27} trisnorhopene (Fig. 4c), C_{31} hopanol (Fig. 4d), and MAGEs (Fig. 4f) were elevated. Taken together, these patterns allow us to infer that water column O_2 was comparatively lower than during the periods immediately before and after, in association with enhanced primary production based on the observed increases of sterols and GDGTs concentrations (Fig. 4a). The two periods with relatively more oxygenated conditions (ca. 1901 and 1919 CE, and ca. 1979 and 2000 CE; Figs. 3 and 4) are characterized by low metal enrichments (Fig. 3), a lower content of bacterial biomarkers related to oxygen depleted conditions such as C_{27} trisnorhopene, C_{31} hopanol, and MAGEs (Table 2; Figs. 4c, d and f), and lower organic matter export as evidenced by low contents of sedimentary sterols (Fig. 4a) and GDGTs

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(Fig. 4b).

We suggest that for the period 1935–1971 CE algal export production was elevated, and that this export is responsible for the increase in phytoplankton sterols (Fig. 4a), which was concurrent with an increase in Cd (Fig. 3) and GDGTs (Fig. 4b). An enhanced sinking of organic matter leads to a subsequent increase in the rate of O_2 consumption by microbial degradation, potentially depleting O_2 in the water column (Helly and Levin, 2004; Canfield, 2006) and sediments. Such conditions lead to Mo, U and Cd enrichment in sediments. Higher GDGTs abundance during this time (Fig. 4b) may reflect a better preservation of archaeal biomarkers favored by O_2 depletion as demonstrated by Schouten et al. (2004) and Zonneveld et al. (2010). The positive correlations between sterols, GDGTs, and U enrichments (Table 2) support this conclusion, since U enrichment occurs in environments with low O_2 concentration and/or high organic matter deposition (Dezileau et al., 2002; Böning et al., 2009; Tribovillard et al., 2006; Muñoz et al., 2012).

4.2 Changes in microbial communities in response to redox variation

Hopanols C_{31} and C_{32} are used to analyze changes in the bacterial community structure because they are the diagenetic products of bacteriohopanetetrols (BHPs), which in turn can have different bacterial sources (Talbot et al., 2003). Hopanol content was dominated by C_{32} hopanol, as found previously in recent sediments (Buchholz et al., 1993; Innes et al., 1997, 1998; Talbot et al., 2003). C_{31} hopanol content was more elevated between ca. 1935 and 1971 CE (Fig. 4d) with peaks at the beginning and end of the low-O_2 period, and exhibited positive correlation with Mo_{xs} and Cd_{xs} (R_s: $p <$

0.05; Table 2). Content of C_{32} hopanol (Fig. 4e), a diagenetic product of BHTs (Innes et al., 1998; Talbot et al., 2003), mostly produced by heterotrophic aerobic bacteria (Rohmer et al., 1984), displays a common peak with C_{31} hopanol (Fig. 4d) between 1920 and 1935, and they are decoupled, concurrent with enrichment of redox-sensitive metals (Figs. 3a, b and c). Observed changes in abundance and distribution of C_{31} and C_{32} hopanols, in concomitance with past variations of O_2 in the water column at the study site, are consistent with previous findings by Saenz et al. (2011) and Kharbush et al. (2013). These authors found that the composition and abundance of BHPs, the biological sources of hopanoids, change with decreasing O_2 in the water column of the Peruvian margin, Arabian Sea, Cariaco Basin, and in the Eastern Tropical North Pacific.

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Trisnorhopanes are bacterial lipid markers associated with upwelling and anoxic depositional environments, although their biological sources have not yet been identified (Schouten et al., 2001; Peters et al., 2005). The highest C_{27} trisnorhopene (Fig. 4c) content occurred during the proposed period of high primary production and O_2 depletion (1935−1971 CE), suggesting a relationship between its abundance and upwelling-favorable conditions and anaerobic bacterial activity, as previously suggested for other areas of the world (Grantham et al., 1980; Duan et al., 1996; Duan, 2000; Schouten et al., 2001).

Sedimentary content of MAGEs was also higher in the period 1935–1971 CE and in the topmost sediments (Fig. 4f), resembling C_{16}-MAGE (Fig. 5 of Arning et al., 2008) at the same sampling site (Station 18), assuming similar sedimentation rate as in our core. MAGEs have been detected in sediments from upwelling regions of Namibia, Peru, and central-southern Chile and are attributed to the occurrence of sedimentary

sulfate reducing bacteria (Arning et al., 2008). The presence of sulfate reducing bacteria has been previously documented in coastal waters off Chile (Canfield et al., 2010) and Peru (Finster and Kjeldsen, 2010).

4.3 Forcing mechanisms and variations in OMZ intensity in central-southern Chile

Combined records of redox-sensitive metals and biomarkers suggest the occurrence of enhanced reducing conditions at the sediment– water interface and likely in the water column, from ca. 1935 until 1971 CE (Figs. 3 and 4), that roughly coincide with a cool (negative) phase of the Pacific Decadal Oscillation (PDO) (Fig. 4g). This suggests a link between changes in continental shelf oxygenation off Concepción and the PDO, with alternating phases of decreased (1901–1930 and 1979–1997 CE) and enhanced upwelling (ca. 1935 to 1971 CE). PDO is a recurring pattern of ocean– atmosphere variability with phases that last between two and three decades (Mantua et al., 1997, 2002). During cool or negative phases, the western Pacific becomes warmer while parts of the eastern Pacific become colder. The reverse pattern occurs during warm or positive phase. PDO plays a major role in decadal-scale oceanographic variability in the Pacific Ocean (Mantua et al., 1997, 2002; White and Cayan, 1998; Johnson and McPhaden, 1999).

Negative correlations between sedimentary C_{27}-trisnorhopene, C_{31} hopanol, MAGEs, and PDO values (Table 2; Fig. S10) and a positive correlation between C_{32} hopanol (Table 2; Fig. S10) and PDO suggest that this basin-wide climatic anomaly has an impact on local oceanographic conditions off Concepción, which in turn modulate

the structure of the microbial community. Bacterial C_{31} hopanol and MAGEs derive from microorganisms associated with marked chemoclines and redox gradients (Rohmer et al., 1984; Innes et al., 1997, 1998; Talbot et al., 2003, 2007; Kool et al., 2014). Thus, positive PDO phases (warm) were likely associated with a decrease in wind-driven upwelling, greater oxygenation, decreased primary productivity, and a concomitant decrease of microorganisms associated with low O_2. Reverse conditions must have dominated during negative PDO phases, with enhanced upwelling and primary production. An increase in coastal upwelling off Concepción, as expected during cool (negative) PDO phases, could contribute to accumulation of atmospheric greenhouse gases as reported for upwelling ecosystems at seasonal scales (Bakun and Weeks, 2004; Naqvi et al., 2010).

5. Conclusions

Our main goal was to assess the use of redox-sensitive metals and organic biomarkers in the sedimentary record on the shelf off Concepción, Chile (36^{o} S) as proxies for changes in the intensity of the OMZ over the past century. Our conclusions are as follows:

1. Sedimentary redox-sensitive metals and organic biomarkers indicate interdecadal variations in intensity (oxygenation) of the OMZ during the last 110 years.

2. Inorganic and organic sedimentary proxies reveal that enhanced O_2-depleted conditions dominated from ca. 1935 to 1971 CE in synchronicity with

enhanced productivity and microbial activity, likely due to more favorable conditions for the development of upwelling events.

3. We suggest that variations in the PDO could be the physical mechanism controlling interdecadal variations in redox conditions and composition of microbial community in the coastal upwelling ecosystem off Concepción. Negative (positive) phases of PDO correlate with decreased (enhanced) oxygenation on the continental shelf off Concepción.

Author contributions. The study was initiated and designed by B. Srain, S. Pantoja and J. Sepúlveda. B. Srain carried out field work and sample preparation. B. Srain, J. Sepúlveda, and J. McKay performed geochemical analysis, and P. Muñoz and M. Salamanca completed geochronology. All data analysis, including statistical analysis, was done by B. Srain advised by S. Pantoja, C. B. Lange, J. Sepúlveda and R. E. Summons. All authors contributed to data interpretation and general discussion. B. Srain wrote the manuscript with major inputs from S. Pantoja, J. Sepúlveda, C. B. Lange and R. E. Summons.

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Figure captions

Figure 1. Location of sampling site Station 18 in the upwelling ecosystem off Concepción, central-southern Chile. Bathymetry in shades of blue, scale on right-hand side.

Figure 2. Geochronology estimated from $^{210}Pb_{xs}$ inventories (black line) and ^{14}C measurements ± standard deviation. Ages are years before present (1950). Dotted line shows fitted values from curve ($r^2 = 0.99$).

Figure 3. Downcore excess content (ppm) of redox-sensitive metals a) Mo, b) U, and c) Cd. Shaded area and black bar correspond to a period of ca. 35 years of enhanced authigenic precipitation of redox-sensitive metals compared to periods of higher oxygenation (white bars) and low authigenic precipitation. CE = Common Era. Samples for interval 1957−1969 were lost.

Figure 4. Downcore contents of a) sterols, b) archaeal GDGTs, c) 17α-22,29,30-trinorhopene (C_{27}-TNH), d) 17β,21β-homohopanol (C_{31} hopanol), e) 17β,21β-bishomohopanol (C_{32} hopanol), f) MAGEs, and g) Pacific Decadal Oscillation (PDO) index (http://jisao.washington.edu/pdo/PDO.latest). Units are micrograms per gram dry weight. Shaded area and black bar as in Fig. 3. Gaps in the record indicate that biomarker content was under detection limit.

Figures

Figure 1

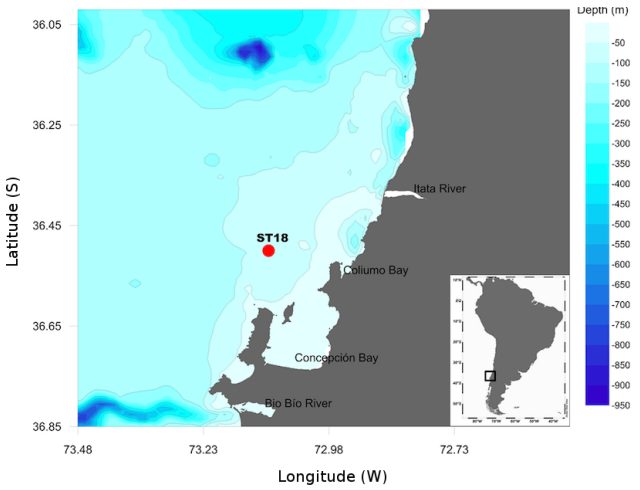


Figure 2

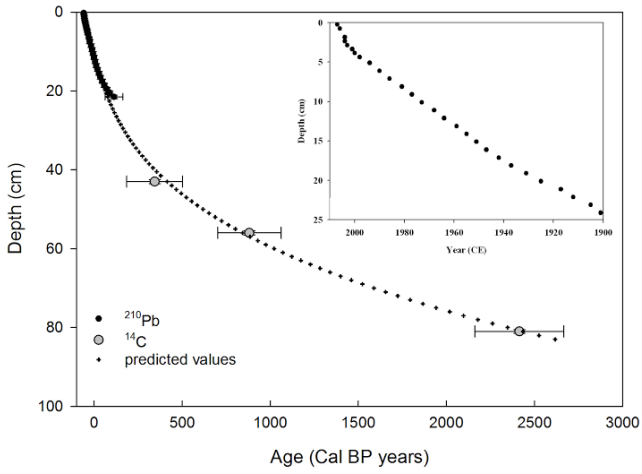


Figure 3

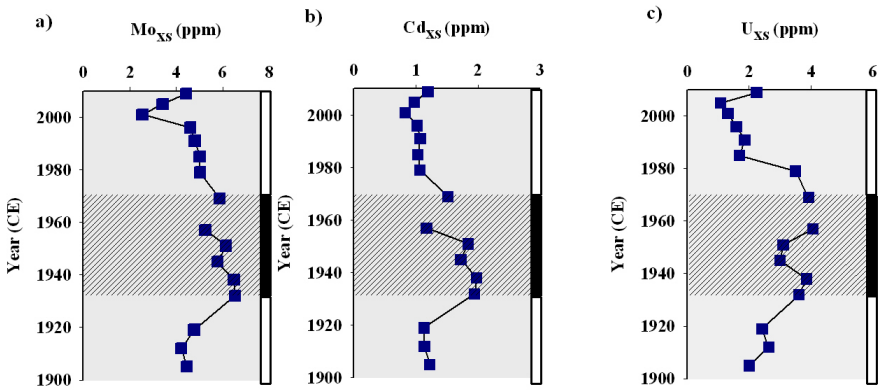
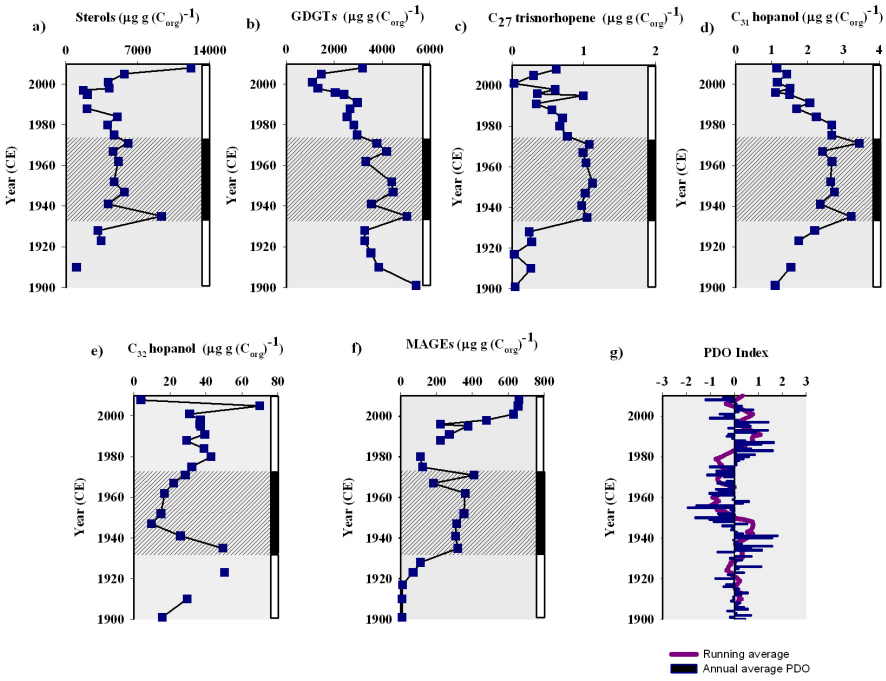


Figure 4



Tables

Table 1. Lipid biomarkers used in this study and their paleobiological interpretation

Biomarker	Biological and/or environmental interpretation	References
Hopanoids hydrocarbons		
C_{30} hopanes	Diverse bacterial lineages, few eukaryotic species (e.g. some cryptogams, ferns, mosses, lichens, filamentous fungi, protists)	Rohmer et al., 1984
Extended C_{31} to C_{35} hopanes (homohopanes)	Diagnostic for Bacteria. Its biosynthesis is restricted to facultative anaerobes and strict anaerobes involved in anaerobic methane cycling (Thiel et al., 2003)	Rohmer et al., 1984; Ourisson and Albrecht, 1992
22,29,30-trinor-hop-17(21)-ene (C_{27}-trisnorhopene)	Detected in anoxic and euxinic sediments, and during upwelling events, and considered indicator of anaerobic microbial degradation	Grantham et al., 1980; Volkman et al., 1983; Peters and Moldowan, 1993; Schouten et al., 2001
Hopanols		
17β,21β-hopanol (C_{30})	Diverse bacterial lineages. Diagenetic product of hexafunctionalized bacteriohopanepolyols	Rohmer et al., 1984; Venkatesan et al., 1990; Innes et al., 1997, 1998; Talbot et al., 2001; Farrimond et al., 2002
17β,21β-homohopanol (C_{31})	Diverse bacterial lineages. Diagenetic product of pentafunctionalized bacteriohopanepolyols	Rohmer et al., 1984; Venkatesan et al., 1990; Innes et al., 1997, 1998; Talbot et al., 2001; Farrimond et al., 2002
17β,21β-bishomohopanol (C_{32})	Diverse bacterial lineages. Diagenetic product of bacteriohopanetetrols	Rohmer et al., 1984; Venkatesan et al., 1990; Innes et al., 1997, 1998; Talbot et al., 2001; Farrimond et al., 2002
Sterols		
$C_{27}\Delta^5$	Bacillariophyceae, Bangiophyceae Dinophyceae, marine Eustigmatophyceae, Haptophyceae. Indicator of primary production and algal bloom.	Volkman, 2003
$C_{29}\Delta^5$	Diverse microalgae lineages (Bacillariophyceae, Chlorophyceae, Chrysophyceae, Euglenophyceae, Haptophyceae, Pelagophyceae, Raphidophyceae, Xanthophyceae). Indicator of primary production and algal bloom	Volkman, 2003
$C_{30}\Delta^{22}$	Dinophyceae	Volkman, 2003
MAGEs		
C_{16}-MAGE to C_{18}-MAGE	Fermentative and sulfate reducing bacteria. Biological source does not appear unique. Considered indicators of suboxic/anoxic water column and sediments	Langworthy et al., 1983; Langworthy and Pond, 1986; Ollivier et al., 1991; Hernández-Sanchez et al., 2014
GDGTs		
GDGT-0 to GDGT-V	Marine archaea (Thaumarchaeota and Euryarchaeota). Considered indicators of ammonia oxidation by Thaumarchaeota and archaeal secondary production	DeLong et al., 1998; Schouten et al., 2000b; Turich et al., 2007; Lincoln et al., 2014

	Mo_{xs}	U_{xs}	Cd_{xs}	Sterols	GDGTs	C_{27} trisnorhopane	C_{31} hopanol	C_{32} hopanol	MAGEs	PDO Index
Mo_{xs}		**0.6**	**0.6**	0.2	0.3	0.2	**0.6**	-0.3	**0.6**	**-0.3**
U_{xs}	**0.6**		**0.6**	**0.4**	**0.6**	**0.5**	0.4	**-0.5**	**0.4**	-0.3
Cd_{xs}	**0.6**	**0.6**		0.1	0.3	**0.6**	**0.4**	**-0.4**	**0.5**	**-0.3**
Sterols	0.2	**0.4**	0.1		0.3	0.4	0.1	**-0.3**	**-0.4**	**-0.3**
GDGTs	0.3	**0.6**	0.3	0.3		0.3	**0.6**	**-0.4**	**0.4**	**-0.2**
C_{27} trisnorhopane	0.2	**0.5**	**0.6**	0.4	0.3		**0.5**	-0.3	0.4	**-0.4**
C_{31} hopanol	**0.6**	0.4	**0.4**	0.1	**0.6**	**0.5**		**-0.4**	**0.4**	**-0.3**
C_{32} hopanol	-0.3	**-0.5**	**-0.4**	**-0.3**	**-0.4**	-0.3	**-0.4**		-0.4	**0.3**
MAGEs	**0.6**	**0.4**	**0.5**	**-0.4**	**0.4**	0.4	**0.4**	-0.4		**-0.2**
PDO index	**-0.3**	-0.3	**-0.3**	**-0.3**	**-0.2**	**-0.4**	**-0.3**	**0.3**	**-0.2**	

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Table 2. Spearman rank order correla

	Mo_{xs}	U_x
Mo_{xs}		**0.**
U_{xs}	**0.6**	
Cd_{xs}	**0.6**	**0.**
Sterols	0.2	**0.**
GDGTs	0.3	**0.**
C_{27} trisnorhopane	0.2	**0.**
C_{31} hopanol	**0.5**	0.
C_{32} hopanol	-0.3	**-0.**
MAGEs	**0.6**	0.
PDO index	**-0.3**	-0.

Eliminado:

Table 3. Molecules identified in m/z 191 mass chromatogram of aliphatic hydrocarbon and alcohol fractions from shelf sediments off Concepción (36ºS).

Hopanoid hydrocarbons			
ID	**Molecule**	**Number of carbon atoms**	**Molecular weight**
1	17α-22,29,30-trinorhopane	27	370
2	22,29,30-trinor-17(21)-ene	27	368
3	17β-22,29,30-trinorhopane	27	370
4	17α,21α-30-norhopane	29	398
5	17β,21β-norhopene	27	368
6	17β,21β-hopane	30	412
7	Neohop-13(18)-ene	30	410
8	17α,21β-hopene	30	410
9	Hop-22(29)-ene	30	410
10	17α,21β-homohopane (R)	31	426
11	Diploptene	30	410
12	17α,21β-bishomohopane (R)	32	440
13	17β,21β-homohopane	31	426
$14_{S/R}$	17α,21β-trishomohopane (S-R)	33	454
$15_{S/R}$	17α,21β-tetrahomohopane (S-R)	34	468
$16_{S/R}$	17α,21β-pentakishomohopane (S-R)	35	482
Hopanols			
17	17β,21β-hopanol	30	500
18	17β,21β-homohopanol	31	514
19	17β,21β-bishomohopanol	32	528
20	17β,21β-trishomohopanol	33	542