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

The Faculty of Oregon State University has made this article openly available. Please share how this access benefits you. Your story matters.

| Citation          | Srain, B., Pantoja, S., Sepúlveda, J., Lange, C. B., Muñoz, P., Summons, R. E., McKay, J., and Salamanca, M. (2015) Inter-decadal changes in the intensity of the Oxygen Minimum Zone off Concepción, Chile (~ 36° S) over the last century, Biogeosciences Discussions, 12, 6003-6035, doi:10.5194/bgd-12-6003-2015 |
|-------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| DOI               | 10.5194/bgd-12-6003-2015                                                                                                                                                                                                                                                                                                  |
| Publisher         | Copernicus Publications                                                                                                                                                                                                                                                                                                      |
| Version           | Version of Record                                                                                                                                                                                                                                                                                                           |
| Terms of Use      | http://cdss.library.oregonstate.edu/sa-termsofuse                                                                                                                                                                                                               |
Inter-decadal changes in the intensity of the Oxygen Minimum Zone off Concepción, Chile (∼ 36° S) over the last century

B. Srain¹, S. Pantoja²,³, J. Sepúlveda⁴,*, C. B. Lange²,³, P. Muñoz⁵, R. E. Summons⁴, J. McKay⁶, and M. Salamanca²

¹Graduate Program in Oceanography, Department of Oceanography, University of Concepción, Concepción, Chile
²Department of Oceanography, University of Concepción, Concepción, Chile
³Center for Oceanographic Research in the eastern South Pacific (COPAS Sur-Austral), University of Concepción, Concepción, Chile
⁴Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, USA
⁵Facultad de Ciencias del Mar y Centro de Estudios Avanzados en Zonas Áridas (CEAZA), Universidad Católica del Norte, Coquimbo, Chile
⁶College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis, OR, USA
now at: Department of Geological Sciences and Institute of Arctic and Alpine Research, University of Colorado, Boulder, USA

Received: 13 March 2015 – Accepted: 24 March 2015 – Published: 24 April 2015

Correspondence to: S. Pantoja (spantoja@udec.cl)

Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

We reconstructed oxygenation changes in the Oxygen Minimum Zone of the upwelling ecosystem off Concepción (36° S), 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. 1935–1971 CE indicating a prolonged period of more reduced conditions in bottom waters and surface sediments. Significant positive correlations ($p < 0.05$; Spearman) between redox sensitive metals, algal sterols, biomarkers of anaerobic microorganisms, and archaeal glycerol dialkyl glycerol tetraether indicated a coupling among bottom water oxygen depletion, and increased primary and export production, suggesting that the period with low $O_2$ of ca. 35 years, follows low frequency inter-decadal variation of the Pacific Decadal Oscillation, which 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 anaerobic microbes allow us to suggest that the prokaryote community has been influenced by changes in oxygenation of the water column.

1 Introduction

Oxygen Minimum Zones (OMZs) are epipelagic and mesopelagic subsurface layers of suboxic waters (e.g., $\leq 22 \mu M O_2$) found along eastern boundary currents such as the Eastern Tropical North and South Pacific, and the Benguela current, as well as the Arabian Sea and the Equatorial Pacific, where upwelling of nutrient-rich waters promotes elevated primary production and $O_2$ consumption through microbial respiration (Wyrtyk, 1962; Helly and Levin, 2004; Paulmier and Ruiz-Pino, 2009). Due to the presence of strong redox gradients, reducing conditions and active microbial communities connecting the cycling of carbon, nitrogen, sulfur and other elements, OMZs are considered remnants of a past anoxic ocean due to their similarities with Archaean prokaryotic biota (Ulloa et al., 2012; Wright et al., 2012).
Waters overlaying the continental shelf of central 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 the shelf waters become oxygenated due to the input of Subantarctic waters (Ahumada and Chuecas, 1979; Sobbarzo et al., 2007). Inter-annual phenomena such as the El Niño Southern Oscillation (ENSO) can also impact 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 with variations in the Pacific Decadal Oscillation (PDO), characterized by an ENSO-like interdecadal variability in the Humboldt Current System. During the cold phase of the 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 oxygen consumption in the water column (Wyrtyk, 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 the PDO promote chemical and biological changes in the OMZ off central-southern Chile.

Past redox variations can be analyzed using trace elements in sediments since 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 uranium (U), molybdenum (Mo), and cadmium (Cd) useful paleoredox and paleoproductivity proxies (Algeo and Maynard, 2004; McManus et al., 2005; Riquier et al., 2005).

In the past decade, an abundant and diverse microbial community has been detected 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 com-
Community can be studied by analyzing their cell membrane lipids (biomarkers) preserved in the sedimentary record, as has been done for other OMZ areas of the world ocean (Schouten et al., 2000a; Arning et al., 2008; Rush et al., 2012).

We studied redox sensitive metals and organic biomarkers in a 110 year sedimentary record from the OMZ within the upwelling ecosystem off Concepción, central-southern Chile (36° S), to infer 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 has affected the prokaryote community.

2 Methods

2.1 Sampling

The study site (Station 18; 36°30.8′ S 73°7′ W) is located in the coastal upwelling ecosystem off central-south Chile at ca. 18 nautical miles from the coast of Concepción (Fig. 1). Sampling was carried out in the framework of the grant “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-long sediment core was collected at a 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 on board every 0.5 cm, whereas the rest of the core was sampled at 1 cm resolution. Samples were stored in glass petri plates and kept frozen at −18 °C until laboratory analysis. Water column was sampled monthly at Station 18 from January 2008 to November 2009 with Niskin bottles, and values of temperature, salinity, oxygen, and fluorescence of chlorophyll a were obtained using a Seabird 25 CTDO.
Fluorescence was transformed to 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

Redox potential was measured in the top 15 cm of the sediment core using a redox potential sensor (Hanna) with an accuracy of ±0.1 mV. Sedimentary organic carbon was determined by high temperature oxidation using a NA 1500 Carlo Erba elemental analyzer. Inorganic carbon was removed by putting the samples into an Ag cup and then fuming with concentrated HCl. After this, the samples were dried overnight at ca. 60 °C and then wrap the Ag cup into a tin cup for analysis.

2.3 Geochronology

$^{210}$Pb activities were determined in sediment core sections by Alpha spectrometry of its daughter $^{210}$Po using $^{209}$Po as a yield tracer (Flynn, 1968). The activities were quantified until 1σ error was achieved in a Canberra Quad Alpha Spectrometer. The ages (CE, common era) were established according the constant rate of supply model (CRS, Appleby and Oldfield, 1978), which considers the unsupported $^{210}$Pb inventories ($^{210}$Pb$_{xs}$). Geochronology of the sediment core was established through the best fit of curves of the ages obtained from the CRS model and three $^{14}$C control points from longer cores retrieved in 2006 at the same sampling site (Muñoz et al., 2012, core VG06-2). Radiocarbon ages were converted to calendar years before present using calibration curve MARINE09 (Reimer et al., 2009) and applying a DR = 137 ± 164 years and 2σ confidence interval (Table S1 in the Supplement).

2.4 Trace metal analysis

Trace metals molybdenum (Mo), uranium (U), and cadmium (Cd) were analyzed in an Agilent 7500ce Inductively Coupled Plasma-MS. Aluminum was determined in a Perkin Elmer Analyst 700 Atomic Absorption Spectrometer. Sediment samples
were prepared using sequential acid digestion (HNO₃, HCl, HClO₄, HF) until total dissolution. Analytical blanks were determined following the above procedure using 18.0 MΩ water and subtracted from sample measurements. Accuracy and precision of measurements were assessed by the analysis of the National Research Council of Canada reference material MESS-3. Excess metal (Meₓₛ) was calculated as 

\[ [\text{Me}_{\text{sample}}] - ([\text{Me}/\text{Al}]_{\text{earth}} \times [\text{Al}_{\text{sample}}]) \]  

(Me/Al)earth corresponds to an average ratio values for Biobío river (Fig. 1) in central-southern Chile (J. M. Muratli, personal communication, 2012).

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

The extraction of lipids (i.e., hopanes, hopanols, sterols, and mono-O-alkyl-glycerol ethers – MAGEs) from sediments was carried out according to Bligh and Dyer (1959), substituting chloroform with dichloromethane. 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 Na₂SO₄. Lipid extracts were then divided into four fractions by column chromatography using silica gel. Aliphatic hydrocarbons (F1) were eluted with 40 mL hexane, ketones (F2) were eluted with 50 mL toluene/hexane (1 : 3 v/v), alcohols (F3) eluted with 50 mL ethyl-acetate/hexane (1 : 9 v/v), and polar compounds (F4) eluted with 35 mL ethyl-acetate/methanol/hexane (4 : 4 : 1 v/v).

Samples were analyzed in an Agilent 6890 GC series coupled to an Agilent 5972 MS. The alcohol fraction (F3) was previously derivatized with 80 µL BSTFA (N,O-bis(trimethylsilyl) trifluoracetamide) and 40 µL TMCS (trimethylchlorosilane) at 70 °C for 1 h. 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. The GC oven temperature program was: 60 °C (2 min) to 150 °C at 15 °C min⁻¹, to 320 °C (held 34.5 min) at 4 °C 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°C (2 min) to 130°C at 20°C min⁻¹, to 310°C at 4°C min⁻¹. The MS was operated in electron impact mode (70 eV) with the ion source at 250°C. 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 individual alcohols and aliphatic hydrocarbons were based on those of internal standards 1-nonadecanol and squalene, and were transformed to contents by normalization by organic carbon content.

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, vol/vol), and dichloromethane. Lipid extracts were concentrated using a rotary evaporator and dried over a small Pasteur pipette filled with combusted glass wool and anhydrous Na₂SO₄. Lipids were separated into non-polar and polar fractions using a Pasteur pipette filled with activated Al₂O₃, after elution with hexane/dichloromethane (9:1, vol/vol) and dichloromethane/methanol (1:1 vol/vol), respectively. An aliquot of the polar fraction was dissolved in hexane/propanol (99:1 vol/vol) and filtered through a 0.45 µm PFTE filter. HPLC-MS analysis followed 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 vol/vol). GDGTs were separated using a Prevail Cyano column (2.1 × 150 mm, 3 mm; Grace, USA) maintained at 35°C and a flow rate of 0.25 mL/min. The elution program was: 5 min 100% eluent A (hexane/isopropanol, 99:1 vol/vol), followed by a linear gradient to 100% eluent B (hexane/isopropanol, 90:10 vol/vol) in 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), temperature ranged between 11 and 12°C in the upper 20 m of the water column, and between 10 and 11°C below 65 m depth (Fig. 2a). Surface salinity varied between 32 and 33 above 20 m, and was 34 below this depth (Fig. 2b). Chlorophyll a concentration varied between 0.3 and 1.4 mg m^{-3} with higher values in the top 20 m (Fig. 2c). Oxygen concentration varied between 170 and 205 µM in the top 20 m, and lower than 22 µM (suboxia) below 60 m depth (Fig. 2d).

During austral spring and summer (September to March) surface temperature ranged between 13 and 15°C, decreasing to 10°C below 84 m depth (Fig. 2a). Salinity varied between 31 and 34.5 in the whole water column (Fig. 2b). Chlorophyll a concentrations up to 53 mg m^{-3} were measured in surface waters (Fig. 2c). Oxygen concentration ranged between 114 and 217 µM in surface waters. Suboxic waters (i.e., < 22 µM) occur below ca. 20 m (Fig. 2d), which is significantly shallower than in austral fall-winter when dissolved O_{2} values lower than 22 µM below ca. 60 m depth.
3.2 Sedimentary redox potential and organic carbon

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. 2e), consistent with the occurrence of 5 µM O$_2$ in bottom waters of (Fig. 2d). A surface fluffy layer with a *Thioploca* mat was observed at the sediment–water interface. Organic carbon content varied between 2 to 4 wt.% (Fig. 2e).

3.3 Geochronology

$^{210}$Pb$_{xs}$ activity was detected down to 23 cm in the core where reached background values of $0.80 \pm 0.02$ dpm g$^{-1}$. The geochronology was estimated using CE ages from $^{210}$Pb$_{xs}$ inventories (Table S1) transformed to Cal BP years and calibrated ages from radiocarbon measurements values fitted a polynomial curve ($r^2 0.99$) allowing to adjust ages at the bottom of the core, that generates errors with the CRS model (Binford, 1990). A recent sedimentation rate of $0.24 \pm 0.02$ cm yr$^{-1}$ was established and an exponential decreased is observed due to sediment compaction (Fig. 2f). Thus, the core represents ca. 110 years of sedimentation at Site 18.

3.4 Redox sensitive trace metals

Redox sensitive metals are most enriched in the interval ca. 1935–1970 CE (Fig. 3a–c; black bar). Excess molybdenum (Mo$_{xs}$) content ranged between 2.5 and 6.5 ppm (Fig. 3a), showing a similar vertical distribution as uranium (U$_{xs}$) that ranged between 1.1 to 4.1 ppm (Fig. 3b), and Cd$_{xs}$, which ranged between 1.9 and 0.8 ppm (Fig. 3c). Enrichments of Mo$_{xs}$, U$_{xs}$, and Cd$_{xs}$ exhibited a significant correlation among each other ($R_s$: 0.6; $p < 0.05$) indicating lower O$_2$ depletion conditions in the 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), and presumably more oxygenated bottom waters and sediments.

3.5 Algal sterols

Sterols C27Δ5, C28Δ5, C29Δ5 and C30Δ22 were identified through the fragmentation pattern of their trimethylsilyl (TMS) derivatives. The presence of C27Δ5-sterol (m/z 458 [M]+) was confirmed due to the detection of fragments m/z 129, m/z 329 and 368. C28Δ5-sterol (m/z 472 [M]+) showed a base peak fragment at m/z 129, as well as m/z 343 and m/z 382. C29Δ5-sterol (m/z 486 [M]+) was identified by prominent m/z fragments at 357 and 396. Prominent fragments m/z 69, m/z 271, m/z 359 and m/z 500 [M]+ confirmed the presence of C30Δ22 dinosterol. The sterol content ranged between 1029 and 12 164 µg (g Corg)−1 with maximum values in surface sediments (Fig. 4a). Sterols correlated positively with Uxs (R_s: 0.4, p < 0.05).

3.6 Archaeal GDGTs

GDGTs were identified by their molecular ion and elution pattern: GDGT-0 (1302 [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). The concentration of GDGTs varied between 1094 and 5423 µg (g Corg)−1 (Fig. 4b), with elevated values at the base core and between ca. 1947 and 1975 CE (Fig. 4b). A positive correlation was found between GDGTs concentration and Uxs content (R_s: 0.6; p < 0.05).

3.7 Geohopanoid composition and abundance

C27-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 at the ring system (Table 1). Three diploptene isomers were identified according
with their mass spectra, hop-13,18-ene, neohopene, and hop-22,29-ene (Fig. 5a, Table 1). The C_{30} hopene diploptene was identified based on its molecular ion (m/z 410 [M^+]) and diagnostic ions m/z 395, 299 and 191 (Fig. 5a, Table 1). A homologous series of C_{31} to C_{35} hopanes with the \(\alpha\beta\) configuration were identified through m/z 191 in the hydrocarbon fraction (Fig. 5a). Homohopanes C_{31}, C_{33}, C_{34}, and C_{35} were present as epimers S and R (Fig. 5a, Table 1), whereas C_{32} hopane occurred as epimer R (Fig. 5a; Table 1). C_{27} norhopene, and hopanes C_{30} and C_{31} were the only compounds with \(\beta\beta\) configuration (Fig. 5a, Table 1). C_{31} hopane showed the highest relative abundance in the homohopane homologous series, with S and R 17\(\alpha\),21\(\beta\) homohopane as predominant compound, followed by C_{33} and C_{34} (Fig. 5a).

17\(\beta\),21\(\beta\) hopanol (C_{30}), 17\(\beta\),21\(\beta\) homohopanol (C_{31}), 17\(\beta\),21\(\beta\) bishomohopanol (C_{32}), and 17\(\beta\),21\(\beta\) trishomohopanol (C_{33}) were identified detecting m/z 191 and their molecular ions ([M]^+ m/z 500, m/z 514, m/z 528, and m/z 542) (Fig. 5b, Table 1). The most abundant hopanol was homologue C_{32} (Fig. 5b).

C_{27}-trisnorhopene ranged between 0.03 and 1.1 \(\mu\)g (g C_{org})^{-1}. Maximum values occurred between ca. 1935 and 1970 CE (Fig. 4c), whereas minimum values were observed during periods 1905–1928 CE and 1980–2005 CE (Fig. 4c). C_{27}-trisnorhopene correlated positively with U_{xs} and Cd_{xs} (R_s: 0.5; \(p < 0.05\)). Content profile of C_{31} hopanol varied between 1.1 and 3.7 \(\mu\)g (g C_{org})^{-1}, and reached the highest value during period 1935–1970 CE (Fig. 4d). Positive correlations between C_{31} hopanol, Mo_{xs}, and Cd_{xs} were observed (R_s: 0.6 and 0.4 respectively; \(p < 0.05\)). In contrast, C_{32} hopanol anticorrelated with C_{31} hopanol and U_{xs} (R_s: −0.5, \(p < 0.05\); Fig. 4e).

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

Mass spectra of MAGEs showed a base peak fragment of m/z 205 characteristics of monoalkyl glycerol-TMS compounds, which corresponds to cleavage between carbons 1 and 2 of the glycerol moiety, and fragment m/z 445 [M + H-CH_{3}]^{+} that corresponds
to a 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]$^+$.

The 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 during the period 1901–1928 CE with an average concentration of 50 µg (g C$_{org}$)$^{-1}$ (Fig. 4f). From ca. 1935 CE, MAGEs concentrations increased reaching the highest content in surface sediments (Fig. 4f). MAGEs correlated positively with Mo$_{xs}$ ($R_S$: 0.4, $p<0.05$) and Cd$_{xs}$ ($R_S$: 0.6, $p<0.05$).

4 Discussion

4.1 Patterns of redox depositional conditions, primary and exported production

We interpret variations in contents of sedimentary redox sensitive metals as changes in oxygenation of bottom waters and surface sediments. This interpretation is coincident with previous observations by Muñoz et al. (2012) for the same sampling site, and authigenic enrichments of Mo over the Oregon shelf associated with O$_2$ depletion and increased primary productivity (Erhardt et al., 2014). U and Mo authigenic enrichment occur under O$_2$-depleted conditions (Eriksson and Helz, 2000; Siebert et al., 2003; Algeo and Tribovillard, 2009). Cd is an element that becomes enriched in sediments in the presence of pore water sulfide as export production increases (Tribovillard et al., 2004, 2006). We interpret Cd enrichment in sediments as indicative of higher export production from the water column.

Variations in the abundance of total algal sterols (sum of C$_{27}^{\Delta 5}$, C$_{28}^{\Delta 5}$, C$_{29}^{\Delta 5}$ and C$_{30}^{\Delta 22}$) are considered to represent changes in primary and export production to the sediment. Changes in the abundance of isoprenoidal GDGTs are used as an indication of variations in ammonia oxidation by marine pelagic archaea (De Long et al., 1998; Schouten et al., 2000b; Turich et al., 2007; Lincoln et al., 2014). The preservation of
C_{27}-trisnorhopene is favored in anoxic and euxinic environments, and during upwelling events (Granatham et al., 1980; Schouten et al., 2001), and is considered an indicator of anaerobic microbial degradation (Volkman et al., 1983; Duan et al., 1996; Duan, 2000; Peters et al., 2005).

Fluctuations in bacterial hopanes and hopanols are related to variations in bacterial groups (Ourisson and Albrecht, 1992; Innes et al., 1998; Rohmer et al., 1984; Talbot et al., 2007). MAGEs C_{16}, C_{17}, and C_{18} mono-O-alkyl glycerol ethers are present in fermentative and sulfate reducing bacteria (Langworthy et al., 1983; Langworthy and Pond, 1986; Ollivier et al., 1991), although this biological source does not appear to be unique (Hernández-Sanches et al., 2014). That said, the statistical relationship found between MAGEs (R_s < 0.05) and reducing conditions in the core collected from 18 St. is explained as changes in abundance and occurrence of bacteria involved in microaerophilic and anaerobic metabolism, in response to variations in water column oxygenation over the continental shelf off Concepción.

The downcore distribution of inorganic and organic proxies reveal a period of ca. 35 years between ca. 1935 and 1970 CE (Figs. 3 and 4; black bar) when 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 higher. Taken together, these patterns allow us to infer that water column O_2 was comparatively lower than during those periods immediately above and below, in association with enhanced primary production reflected in increase of sterols and GDGTs contents (Fig. 4a). Likewise, two periods with relatively more ventilated and oxygenated conditions are evident between ca. 1901 and 1919 CE, and between ca. 1979 and 2005 CE (Figs. 4 and 5). Both of these periods were 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 (Fig. 4c, d and f), and lower organic matter fluxes evidenced by low contents of sedimentary sterols (Fig. 4a) and GDGTs (Fig. 4b).

We suggest that from ca. 1935–1970 CE there was higher export production, and that this export is responsible for the increase in phytoplankton sterols (Fig. 4a), con-
current with an increase in Cd (Fig. 3) and GDGTs (Fig. 4b). An enhanced sinking of organic matter leads to a subsequent increase in 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 sediments. Higher GDGTs content during this same time period (Fig. 4b) may reflect better preservation favored by severe O$_2$ depletion. The positive correlation between sterols, GDGTs, and U enrichments support this conclusion, since U enrichment occurs under low O$_2$ concentration and/or high organic matter deposition (Dezileau et al., 2002; Tribovillard et al., 2006; Muñoz et al., 2012). Schouten et al. (2004) and Zonneveld et al. (2010) reported that GDGTs preservation is lower in oxygenated than in suboxic-anoxic settings.

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). The hopanol content was dominated by C$_{32}$ hopanol whose predominance in recent sediments has been previously reported (Buchholz et al., 1993; Innes et al., 1997, 1998; Talbot et al., 2003).

An increase in C$_{31}$ hopanol content between ca. 1935 and 1970 CE (Fig. 4d) is indicative of low oxygen if analyzed in light of the positive correlation between Mo$_{xs}$ and Cd$_{xs}$ (R$_s$: 0.6 and 0.4 respectively; $p < 0.05$). The content of C$_{32}$ hopanol, a diagenetic product of BHTs (Innes et al., 1998; Talbot et al., 2003), mostly produced by heterotrophic aerobic bacteria (Rohmer et al., 1984), exhibited a slight decrease (Fig. 4e) concurrent with the enrichment of C$_{31}$ hopanol (Fig. 4d) and redox sensitive metals (Fig. 3). Observed changes in abundance and distribution of C$_{31}$ and C$_{32}$ hopanols in concomitance with past variations of oxygen 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 abundance and structural diversity of BHPs, the biological sources of hopanoids, increase with decreasing oxygen in the water column of

6017
the Peruvian margin, Arabian Sea, Cariaco Basin, and in the Eastern Tropical North Pacific.

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

The sedimentary content of MAGEs was also higher in the period 1935–1970 CE and in the topmost sediments (Fig. 4f). 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 as well for coastal waters of Chile (Canfield et al., 2010) and Peru (Finster and Kjeldsen, 2010).

4.3 Forcing of variations in the intensity of OMZ in central-southern Chile

The combined records of redox-sensitive metals and biomarkers suggest the occurrence of enhanced reducing conditions, both in the water column and at the sediment–water interface, from ca. 1935 until 1970 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 cycle, with alternating phases of decreased (1901–1930 and 1979–1997 CE) and enhanced upwelling (ca. 1935 to 1970 CE). The PDO is a recurring pattern of ocean–atmosphere variability in which the Pacific central gyre cools down while the eastern margin warms up, with phases that last between two and three decades (Mantua et al., 1997, 2002). The 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). During cool or negative phase, the western Pacific becomes
warmer while parts of the eastern Pacific become colder. The reverse pattern occurs during warm or positive phase.

Periods of favorable upwelling conditions off central Chile may have been triggered by an enhanced thermal contrast between the sea-surface and land during negative phases of the PDO (Bakun, 1990; Vargas et al., 2007). Negative correlations between PDO index values with algal sterols (Figs. 4a and g; $R_s$: $-0.3$; $p < 0.05$) and GDGTs (Figs. 4b and 5g; $R_s$: $-0.2$, $p < 0.05$) suggest an inverse relationship between the PDO and primary and export production at the study site, at least during the last 110 years. Interdecadal variations of enhanced coastal-upwelling conditions, recorded in sediments obtained from Mejillones Bay (23° S) during the last century, have been previously reported by Vargas et al. (2007). These authors suggested that decreased anomalous sea surface temperatures during interdecadal ENSO-like conditions might have exacerbated the land–sea thermal contrast, which in turn intensified the wind stress responsible of upwelling events.

Negative correlations between sedimentary $C_{27}$-trisnorhopene, $C_{31}$ hopanol, MAGEs, and PDO values ($R_s = -0.3$, $-0.4$, $0.3$, $-0.2$, respectively; $p < 0.05$) and a positive correlation between $C_{32}$ hopanol ($R_s = 0.3$) and PDO suggest that this wide-basin climatic anomaly has an impact on local oceanographic conditions off Concepción that in turn modulate the structure of the prokaryotic 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) showed an inverse correlation with PDO index ($R_s$: $-0.4$ with $C_{31}$ hopanol, $-0.3$ with MAGEs, $p < 0.05$). 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 oxygen. Reverse conditions must have dominated during negative PDO phases, with more upwelling and primary production.

Previous studies in the Pacific Basin have evidenced connections between the PDO and variations in marine ecosystems, including perturbations in commercially impor-
Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Abstract

Introduction

Conclusions

References

Tables

Figures

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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° S) as proxies for...
changes in the intensity of the Oxygen Minimum Zone over the past century, and how these changes may have affected the microbial planktonic community. Our conclusions are summarized as follows:

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

2. Inorganic and organic sedimentary proxies reveal that enhanced O$_2$-depleted conditions dominated from ca. 1935 to 1970 CE and were synchronously with more favorable upwelling conditions.

3. We suggest that variations in the Pacific Decadal Oscillation could be the physical mechanism controlling interdecadal variations of redox conditions in the coastal upwelling ecosystem off Concepción, influencing the composition of the microbial community, and that negative phases of the PDO correlate with decreased oxygenation on the inner continental shelf off Concepción.

The Supplement related to this article is available online at doi:10.5194/bgd-12-6003-2015-supplement.

Author contributions. The study was initiated and designed by B. Srain and S. Pantoja. B. Srain carried out field work and sample preparation. B. Srain, J. Sepúlveda, and J. McKay performed chemical analysis, and P. Muñoz and M. Salamanca did 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 and C. B. Lange.

Acknowledgements. This research was funded by the Center for Oceanographic Research in the eastern South Pacific (COPAS, grant # PFB-31), the Gordon and Betty Moore Foundation (MI_LOCO Project, Oregon_Concepción, grant # 1661), the COPAS Sur-Austral Program.
(PFB-31), and the MIT International Science and Technology Initiatives (MIT-MISTI-Chile). Additionally, Fondecyt grant #1061214 funded radiocarbon analysis. B. Srain acknowledges a student fellowship from the Ministry of Education’s MECESUP grant UCO0602, the Department of Atmospheric, Earth and Planetary Sciences of MIT, the Fulbright Chilean Commission, and the MI_LOCO Project for supporting a research visit to MIT. S. Pantoja acknowledges support from the Hanse Wissenschaftskolleg, Delmenhorst (Germany). We acknowledge the support provided by the COPAS Oceanographic Time Series St. 18 off Concepción. We are grateful to the crew of the L/C Kay-Kay II for help during sampling, the personnel of the Marine Organic Geochemistry Laboratory at UDEC and Geobiology Laboratory at MIT for analytical assistance. We thank Renato Quiñones for providing sedimentary redox data.

References

Adkison, M. D., Peterman, R. M., Lapointe, M. F., Gillis, D. M., and Korman, J.: Alternative models of climatic effects on sockeye salmon Oncorhynchus nerka) productivity in Bristol Bay, Alaska and Fraser River, British Columbia, Fish. Oceanogr., 5, 137–152, 1996.

Ahumada, R. and Chuecas, L.: Algunas características hidrográficas de la Bahía Concepción (36°40’ S–73°02’ W) y áreas adyacentes, Chile, Gayana Miscelánea (Chile), 8, 1–56, 1979.

Algeo, T. J. and Maynard, J. B.: Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems, Chem. Geol., 206, 289–318, 2004.

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

Arning, E. T., Birgel, D., Schulz-Vogt, H. N., Holmkvist, L., Jorgensen, B. B., Larson, A., and Peckman, J.: Lipid biomarker patterns of phosphogenic sediments from upwelling regions, Geomicrobiol. J., 25, 69–82, 2008.

Appleby, P. G. and Oldfield, F.: The calculation of lead-210 dates assuming a constant rate of supply of unsupported $^{210}$Pb to the sediment, Catena, 5, 1–8, 1978.

Bakun, A.: Global climate change and intensification of coastal ocean upwelling, Science, 247, 198–201, 1990.

Berndmeyer, C., Thiel, V., Schmale, O., and Blumenberg, M.: Biomarkers for aerobic methanotrophy in the water column of the stratified Gotland Deep (Baltic Sea), Org. Geochem., 55, 103–111, 2013.
Binford, M.: Calculation and uncertainty analysis of $^{210}$Pb dates for PIRLA project lake sediments cores, J. Paleolimnol., 3, 253–267, 1990.
Bligh, E. G. and Dyer, W. J.: A rapid method of total lipid extraction and purification, Can. J. Biochem. Physiol., 37, 911–917, 1959.
Blanco, J. L., Carr, M. E., Thomas, A. C., and Strub, P. T.: Hydrographic conditions off northern Chile during the 1996–1998 La Niña and El Niño events, J. Geophys. Res., 107, 3-1–3-3, 2002.
Blumenberg, M., Krüger, M., Nauhaus, K., Talbot, H. M., Oppermann, B. I., Seifert, R., Pape, T., and Michaelis, W.: Biosynthesis of hopanoids by sulfate-reducing bacteria (genus Desulfovibrio), Environ. Microbiol., 8, 1220–1227, 2006.
Buchholz, B., Laczko, E., Pfennig, N., Rohmer, M., and Neunlist, S.: Hopanoids of a recent sediment from Lake Constance as eutrophication markers, FEMS Microbiol. Ecol., 102, 217–223, 1993.
Canfield, D. E.: Models of oxic respiration, denitrification and sulfate reduction in zones of coastal upwelling, Geochim. Cosmochim. Ac., 70, 5753–5765, 2006.
Canfield, D. E., Stewart, F. J., Thamdrup, B., De Brabandere, L., Dalsgaard, T., DeLong, E. F., Revsbech, N. P., and Ulloa, O.: A cryptic sulfur cycle in oxygen-minimum-zone waters off the Chilean coast, Science, 330, 1375–1378, 2010.
Carr, M. E., Strub, P. T., Thomas, A., and Blanco, J. L.: Evolution of 1996–1999 La Niña and El Niño conditions off the western coast of South America: a remote sensing perspective, J. Geophys. Res., 107, 29-1–29-16, 2002.
Cloern, J. M., Jassby, A. D., Thompson, J. K., and Hieb, K. A.: A cold phase of the East Pacific triggers new phytoplankton blooms in San Francisco Bay, P. Natl. Acad. Sci. USA, 104, 18561–18565, 2007.
DeLong, E. F., King, L. L., Massana, R., Cittone, H., Murray, A., Schleper, C., and Wakeham, S. G.: Dibiphytanyl ether lipids in nonthermophilic crenarchaeotes, Appl. Environ. Microb., 64, 1133–1138, 1998.
Deutsch, C., Brix, H., Ito, T., Frenzel, H., and Thompson, L.: Climate-forced variability of ocean hypoxia, Science, 333, 336–339, 2011.
Dezileau, L., Bareilleb, G., and Reyss, J. L.: Enrichissement en uranium authigène dans les sédiments glaciaires de l’océan Austral, CR Geosci., 334, 1039–1046, 2002.
Duan, Y.: Organic geochemistry of recent marine sediments from the Nansha Sea, China, Org. Geochem., 31, 159–167, 2000.
Duan, Y., Luo, B., Xu, Y., and Ma, L.: Composition and geochemical significance of biomarkers in marine sediments from Nansha Islands waters, the South China Sea, Chin. J. Oceanol. Limn., 27, 258–263, 1996.

Erhardt, A. M., Reimers, C. E., Kadko, D., and Paytan, A.: Records of trace metals in sediments from the Oregon shelf and slope: investigating the occurrence of hypoxia over the past several thousand years, Chem. Geol., 382, 32–43, 2014.

Erickson, B. E. and Helz, G. R.: Molybdenum (VI) speciation in sulfidic waters: stability and lability of thiomolybdates, Geochim. Cosmochim. Ac., 64, 1149–1158, 2000.

Escribano, R., Daneri, G., Farias, L., Gallardo, V. A., González, H. E., Gutiérrez, D., Lange, C. B., Morales, C. E., Pizarro, O., Ulloa, O., and Braun, M.: Biological and chemical consequences of the 1997–1998 El Niño in the Chilean coastal upwelling system: a synthesis, Deep-Sea Res. Pt. II, 51, 2389–2411, 2004.

Farías, L., Fernández, C., Faúndez, J., Cornejo, M., and Alcaman, M. E.: Chemolithoautotrophic production mediating the cycling of the greenhouse gases N₂O and CH₄ in an upwelling ecosystem, Biogeosciences, 6, 3053–3069, doi:10.5194/bg-6-3053-2009, 2009.

Finster, K. W. and Kjeldsen, K. U.: Desulfovibrio oceani subsp. oceani sp. nov., subsp. nov., and Desulfovibrio oceani subsp. galateae subsp. nov., novel sulfate-reducing bacteria isolated from the oxygen minimum zone off the coast of Peru, A. Van Leeuwen. J. Microb., 97, 221–229, 2010.

Fischer, W. W., Summons, R. E., and Pearson, A. P.: Targeted genomic detection of biosynthetic pathways: anaerobic production of hopanoid biomarkers by a common sedimentary microbe, Geobiology, 3, 33–40, 2005.

Flynn, W. W.: The determination of low levels of polonium-210 in environmental materials, Anal. Chim. Acta, 43, 221–227, 1968.

Grantham, P. J. and Douglas, A. G.: The nature and origin of sesquiterpenoids in some Tertiary fossil resins, Geochim. Cosmochim. Ac., 44, 1801–1810, 1980.

Gutiérrez, D., Gallardo, V. A., Mayor, S., Neira, C., Vásquez, C., Sellanes, J., Rivas, M., Soto, A., Carrasco, F., and Baltazar, M.: Effects of dissolved oxygen and fresh organic matter on the bioturbation potential of macrofauna in sublittoral sediments off central Chile, during the 1997–98 El Niño, Mar. Ecol.-Prog. Ser., 202, 81–99, 2000.

Hanson, R. S. and Hanson, T. E.: Methanotrophic bacteria, Microbiol. Rev., 60, 439–471, 1996.

Helly, J. J. and Levin, L. A.: Global distribution of naturally occurring marine hypoxia on continental margins, Deep-Sea Res. Pt. I, 51, 1159–1168, 2004.
Hernandez-Sanchez, M. T., Homoky, W. B., and Pancost, R. D.: Occurrence of 1-O-monoalkyl glycerol ether lipids in ocean waters and sediments, Org. Geochem., 66, 1–13, 2014.

Hinrichs, K.-U., Hmelo, L. R., and Sylva, S. P.: Molecular fossil record of elevated methane levels in late pleistocene coastal waters, Science, 299, 1214–1217, 2003.

Hollowed, A. B., Hare, S. R., and Wooster, W.S.: Pacific-Basin climate variability and patterns of Northeast Pacific marine fish production, Progress in Oceanography, 49, 257–282, 2001.

Huguet, C., Hopmans, E. C., Febo-Ayala, W., Thompson, D. H., Sinninghe Damsté, J. S., and Schouten, S.: An improved method to determine the absolute abundance of glycerol dibiphytanyl glycerol tetraether lipids, Org. Geochem., 37, 1036–1041, 2006.

Innes, H. E., Bishop, A. N., Head, I. M., and Farrimond, P.: Preservation and diagenesis of hopanoids in recent lacustrine sediments of Priest Pot, England, Org. Geochem., 26, 565–576, 1997.

Innes, H. E., Bishop, A. N., Fox, P. A., Head, I. M., and Farrimond, P.: Early diagenesis of bacterio-hopanoids in recent sediments of Lake Pollen, Norway, Org. Geochem., 29, 1285–1295, 1998.

Johnson, G. C. and McPhaden, M. L.: Interior pycnocline flow from the subtropical to the equatorial Pacific Ocean, J. Phys. Oceanogr., 29, 3073–3089, 1999.

Kharbush, J. J., Ugalde, J. A., Shane, L. H., Allen, E. E., and Aluwihare, L. I.: Composite bacterial hopanoids and their microbial producers across oxygen gradients in the water column of the California Current, Appl. Environ. Microb., 79, 7491–7501, 2013.

Kawasaki, T., Tanaka, S., Toba, Y., and Taniguchi, A.: Long-term Variability of Pelagic Fish Population and their environment, Pergamon Press, Tokyo, Japan, 402 pp, 1991.

Langworthy, T. A. and Pond, J. L.: Archaebacterial ether lipids and chemotaxonomy, Syst. Appl. Microbiol., 7, 253–257, 1986.

Langworthy, T. A., Holzer, G., Zeikus, J. G., and Tornabene, T. G.: Iso- and anteiso-branched glycerol diethers of the thermophilic anaerobe Thermodesulfotobacterium commune, Syst. Appl. Microbiol., 4, 1–17, 1983.

Levin, L. A., Rathburn, A. E., Neira, C., Sellanes, J., Muñoz, P., Gallardo, V., and Salamanca, M.: Benthic processes on the Perú margin: a transect acros the oxygen minimum zone during the 1997–1998 El Niño, Prog. Oceanogr., 53, 1–27, 2002.

Levipan, H. A., Alarcón, W. O., and Saldías, G. S.: Fingerprinting analysis of the prokaryote community along a marine-freshwater transect in central-southern Chile, Ann. Microbiol., 62, 1121–1140, 2012.

6025
Lincoln, S. A., Brenner, W., Eppley, J. M., Church, M. J., Summons, R. E., and DeLong, E. F.: Planktonic Euryarchaeota are significant source of archaeal tetraether lipids in the ocean, P. Natl. Acad. Sci. USA, 111, 9858–9863, 2014.

Mantua, N. J., Hare, S. R., Zhang, Y., Wallace, J. M., and Francis, R. C.: A Pacific decadal climate oscillation with impacts on salmon, B. Am. Meteorol. Soc., 78, 1069–1079, 1997.

Mantua, N. J. and Hare, S. R.: The Pacific Decadal Oscillation, J. Oceanogr., 58, 35–44, 2002.

McManus, J., Berelson, W. M., Klinkhammer, G. P., Hammond, D. E., and Holm, C.: Authigenic uranium: relationship to oxygen penetration depth and organic carbon rain, Geochim. Cosmochim. Ac., 69, 95–108, 2005.

Molina, M., Belmar, L., and, Ulloa, O.: High diversity of ammonia-oxidizing archaea in permanent and seasonal oxygen-deficient waters of the eastern South Pacific, Environ. Microbiol., 12, 2450–2465, 2010.

Muñoz, P., Dezileau, L., Cardenas, L., Sellanes, J., Lange, C. B., Inostroza, J., Muratli, J. J., and Salamanca, M.: Geochemistry of trace metals in shelf sediments affected by seasonal and permanent low oxygen conditions off central Chile, SE Pacific (∼36°S), Cont. Shelf Res., 33, 51–68, 2012.

Neira, C., Sellanes, J., Soto, A., Gutierrez, D., and Gallardo, V. A.: Meiofauna and sedimentary organic matter off Central Chile: response to changes caused by the 1997–1998 El Niño, Oceanol. Acta, 24, 313–328, 2001.

Ollivier, B., Hatchikian, C. E., Prensier, G., Guezenneec, J., and Garcia, J. L.: Desulfohalobium retbaense gen. nov. sp. nov., a halophilic sulfatereducing bacterium from sediments of a hypersaline lake in Senegal, Int. J. Syst. Bacteriol., 41, 74–81, 1991.

Ourisson, G. and Albrecht, P.: Hopanoids. 1. Geohopanoids: the most abundant natural products on Earth?, Accounts Chem. Res., 25, 398–402, 1992.

Parsons, T. R., Maita, Y., and Lalli, C. M.: A Manual of Chemical and Biological Methods for Seawater Analysis, Pergamon Press, Oxford, UK, 1984.

Paulmier, A. and Ruiz-Pino, D.: Oxygen minimum zones (OMZs) in the modern ocean, Prog. Oceanogr., 80, 113–128, 2009.

Peterman, R. M., Pyper, B. J., Lapointe, M. F., Adkison, M. D., and Walters, C. J.: Patterns of covariation in survival rates of British Columbia and Alaskan sockeye salmon (Oncorhynchus nerka) stocks, Can. J. Fish. Aquat. Sci., 55, 2503–2517, 1998.
Peters, K. E., Walters, C. C., and Moldowan, J. M.: The Biomarker Guide, 2nd edn., Volume II, Biomarkers and Isotopes in Petroleum Systems and Earth History, Cambridge University Press, UK, 684 pp., 2005.

Reimer, P. J., Baillie, M. G. L., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Bronk Ramsey, C., Buck, C. E., Burr, G. S., Edwards, R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Hajdas, I., Heaton, T. J., Hogg, A. G., Hughen, K. A., Kaiser, K. F., Kromer, B., McCormac, F. G., Manning, S. W., Reimer, R. W., Richards, D. A., Southon, J. R., Talamo, S., Turney, C. S. M., van der Plicht, J., and Weyhenmeyer, C. E.: IntCal09 and Marine09 radiocarbon age calibration curves, 0–50,000 years calBP, Radiocarbon, 51, 1111–50, 2009.

Riquier, L., Tribovillard, N., Averbuch, O., Joachimski, M. M., Racki, G., Devleeschouwer, X., El Albani, A., and Riboulleau, A.: Productivity and bottom water redox conditions at the Frasnian–Famennian boundary on both sides of the Eovariscan Belt: constraints from trace-element geochemistry, in: Understanding Late Devonian and Permian–Triassic Biotic and Climatic Events: Towards an Integrated Approach: Developments in Palaeontology and Stratigraphy, edited by: Over, D. J., Morrow, J. R., and Wignall, P. B., Elsevier Pub. Co., Amsterdam, Netherlands, 199–224, 2005.

Rohmer, M., Bouvier-Nave, P., and Ourisson, G.: Distribution of hopanoid triterpenes in prokaryotes, J. Gen. Microbiol., 130, 1137–1150, 1984.

Rush, D., Hopmans, E. C., Wakeham, S. G., Schouten, S., and Sinninghe Damsté, J. S.: Occurrence and distribution of ladderane oxidation products in different oceanic regimes, Biogeosciences, 9, 2407–2418, doi:10.5194/bg-9-2407-2012, 2012.

Saenz, J., Summons, R., Eglinton, T. I., and Wakeham, S. G.: Distribution of bacteriohopanepolyols in marine anoxic environments: new constraints on the provenance of hopanoids in the marine geologic record, Org. Geochem., 42, 1322–1351, 2011.

Santoro, A. E., Buchwald, C., McIlvin, M. R., and Casciotti, K. L.: Isotopic signature of N2O produced by marine ammonia-oxidizing archaea, Science, 333, 1282–1285, 2011.

Sarmiento, J. L., Hughes, T. M. C., Stouffer, R. J., and Manabe, S.: Simulated response of the ocean carbon cycle to anthropogenic climate warming, Nature, 393, 245–249, 1998.

Schouten, S., Hopmans, E. C., Pancost, R. D., and Sinninghe Damsté, J. S.: A molecular and stable carbon isotopic study of lipid in late quaternary sediments from the Arabian Sea, Org. Geochem., 31, 509–532, 2000a.

Schouten, S., Hopmans, E. C., Pancost, R. D., and Sinninghe Damsté, J. S.: Widespread occurrence of structurally diverse tetraether membrane lipids: evidence for the ubiquitous
presence of low-temperature relatives of hyperthermophiles, P. Natl. Acad. Sci. USA, 97, 14421–14426, 2000b.

Schouten, S., de Loureiro, M. R. B., Sinninghe Damsté, J. S., and de Leeuw, J. W.: Molecular biogeochemistry of Monterrey sediments, Napoles Beach, California. I: distributions of hydrocarbons and organic sulfur compounds, in: The Monterrey Formation: From Rocks to Molecules, edited by: Isaacs, C. M. and Rullkötter, J., Columbia University Press, New York, 150–174, 2001.

Schouten, S., Hopmans, E. C., and Sinninghe Damstei, J. S.: The effect of maturity and depositional redox conditions on archaeal tetraether lipid palaeothermometry, Org. Geochem., 35, 567–571, 2004.

Scranton, M. I. and Brewer, P. G.: Occurrence of methane in the near-surface waters of the western subtropical North Atlantic, Deep-Sea Res., 24, 127–138, 1977.

Siebert, C., Nägler, T. F., von Blanckenburg, F., and Kramers, J. D.: Molybdenum isotope records as a potential new proxy for paleoceanography, Earth Planet. Sc. Lett., 211, 159–171, 2003.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Schouten, S., Fuerst, J. A., Jetten, M. S. M., and Strous, M.: The occurrence of hopanoids in planctomycetes: implications for the sedimentary biomarker record, Org. Geochem., 35, 561–566, 2004.

Sobarzo, M., Bravo, L., Donoso, D., García-Vargas, J., and Schneider, W.: Coastal upwelling and seasonal cycles that influence the water column over the continental shelf off central Chile, Progress in Oceanography, 75, 363–382, 2007.

Srain, B., Sepúlveda, J., Pantoja, S., Summons, R. E., Quiñones, R. A., Levipan, H. A.: Archaeal and bacterial assemblages in the Oxygen Minimum Zone of the upwelling ecosystem off Central Chile as determined by organic biomarkers, International Journal of Biodiversity, Oceanology and Conservation, 79, 2015.

Stevens, H. and Ulloa, O.: Bacterial diversity in the oxygen minimum zone of the eastern tropical South Pacific, Environ. Microbiol., 10, 1244–1259, 2008.

Talbot, H. M. and Farrimond, P.: Bacterial populations recorded in diverse sedimentary bio-hopanoid distributions, Org. Geochem., 38, 1212–1225, 2007.

Talbot, H. M., Watson, D. F., Murrell, J. C., Carter, J. F., and Farrimond, P.: Analysis of intact bacteriohopanepolys from methanotrophic bacteria by reversed-phase high-performance liquid chromatography-atmospheric pressure chemical ionisation mass spectrometry, J. Chromatogr. A, 921, 175–185, 2001.
Talbot, H. M., Watson, D. F., Pearson, E. J., and Farrimond, P.: Diverse biohopanoid compositions of non-marine sediments, Org. Geochem., 34, 1353–1371, 2003.

Tribovillard, N., Riboulleau, A., Lyons, T., and Baudin, F.: Enhanced trapping of molybdenum by sulfurized organic matter of marine origin as recorded by various Mesozoic formations, Chem. Geol., 213, 385–401, 2004.

Tribovillard, N., Algeo, T. J., Lyons, T., and Riboulleau, A.: Trace metals as paleoredox and paleoproductivity proxies: an update, Chem. Geol., 232, 12–32, 2006.

Turich, C., Freeman, K. H., Bruns, M. A., Conte, M., Jones, A. D., and Wakeham, S. G.: Lipids of marine Archaea: patterns and provenance in the water-column and sediments, Geochim. Cosmochim. Ac., 71, 3272–3291, 2007.

Ulloa, O., Canfield, D. E., DeLong, E. F., Letelier, R. M., and Stewart, F. J.: Microbial oceanography of anoxic oxygen minimum zones, P. Natl. Acad. Sci. USA, 109, 15996–16003, 2012.

Vargas, G., Pantoja, S., Rutillant, J., Lange, C. B., and Ortlieb, L.: Enhancement of coastal upwelling and interdecadal ENSO-like variability in the Peru–Chile Current since late 19th century, Geophys. Res. Lett., 34, L13607, doi:10.1029/2006GL028812, 2007.

Volkman, J. K., Alexander, R., Kagi, R. I., and Rullkötter, J.: GC-MS characterisation of C27 and C28 triterpanes in sediments and petroleum, Geochim. Cosmochim. Ac., 47, 1033–1040, 1983.

White, W. B. and Cayan, D. R.: Quasi-periodicity and global symmetries in interdecadal upper ocean temperature variability, J. Geophys. Res., 103, 21335–21354, 1998.

Wright, J. D., Kishori, M., Konwar, M., and Hallam, S. J.: Microbial ecology of expanding oxygen minimum zones, Nat. Rev. Microbiol., 10, 381–394, 2012.

Wyrtki, K.: The oxygen minima in relation to ocean circulation, Deep-Sea Res., 9, 11–23, 1962.

Yasuda, T. and Hanawa, K.: Decadal changes in the mode waters in the midlatitude North Pacific, J. Phys. Oceanogr., 27, 858–870, 1997.

Zonneveld, K. A. F., Versteegh, G. J. M., Kasten, S., Eglinton, T. I., Emeis, K.-C., Huguet, C., Koch, B. P., de Lange, G. J., de Leeuw, J. W., Middelburg, J. J., Mollenhauer, G., Prahl, F. G., Retemeyer, J., and Wakeham, S. G.: Selective preservation of organic matter in marine environments; processes and impact on the sedimentary record, Biogeosciences, 7, 483–511, doi:10.5194/bg-7-483-2010, 2010.
Table 1. Compounds identified in the m/z 191 mass chromatogram of aliphatic hydrocarbon and alcohol fractions from shelf sediments off Concepción (36° S).

| Symbol | Component                          | Number of carbon atoms | Molecular weight |
|--------|-----------------------------------|------------------------|------------------|
|        | Hopanes                           |                        |                  |
| 1      | 17α-22,29,30-trinorhopane         | 27                     | 370              |
| 2      | 22,29,30-trinor-hop-17(21)-ene    | 27                     | 368              |
| 3      | 17β-22,29,30-trinorhopane         | 27                     | 370              |
| 4      | 17α,21a-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              |
|        | Hopenals                          |                        |                  |
| 17     | 17β,21β-hopanol                  | 30                     | 500              |
| 18     | 17β,21β-homohopanol              | 31                     | 514              |
| 19     | 17β,21β-bishomohopanol           | 32                     | 528              |
| 20     | 17β,21β-trishomohopanol          | 33                     | 542              |
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. Oceanographic variability in the water column off Concepción (36° S) from January 2008 to January 2009: (a) temperature (°C); (b) salinity (psu); (c) chlorophyll (mg m⁻³); (d) dissolved O₂ (µM); and (e) redox potential (Eh) and organic carbon content (Wt.%) in the sediment core recovered from Station 18 in February 2009 (austral summer). Data collected by the Center for Oceanographic Research in the eastern South Pacific at the Oceanographic Time Series Station 18 (www.copas.udec.cl/eng/research/serie/). Data for (e) was provided by R. Quiñones. (f) Geochronology estimated from ²¹⁰Pbxs inventories (black line) and ¹⁴C measurements ± standard deviation. All ages are expressed as years before present (1950). Dotted line shows the predicted values from the curve (r² = 0.99).
Figure 3. Downcore excess content of redox sensitive metals (a) Mo, (b) U, and (c) Cd. Shaded area and black bars corresponds 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.
Figure 4. Downcore content of (a) sterols, (b) archaeal GDGTs, (c) $C_{27}$-TNH, geo-hopanoid, (d) $C_{31}$ hopanol, (e) geo-hopanoid $C_{32}$ hopanol, (f) MAGEs, and (g) Pacific Decadal Oscillation index (http://jisao.washington.edu/pdo/PDO.latest). Units are micrograms per gram organic carbon. Shaded area and vertical bars, and chronology as in Fig. 3.
Figure 5. Representative GC-MS chromatograms of \( m/z \) 191 of (a) aliphatic hydrocarbons, and (b) TMS-derivatized alcohols from shelf sediments off Concepción (36° S). Numbers identify molecules as listed in Table 1, and S, R are epimers of the hopane series.