

# 1 Organic carbon production, mineralization and 2 preservation on the Peruvian margin

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## 10 11 **Abstract**

12 Carbon cycling in Peruvian margin sediments (11°S and 12°S) was examined at 16 stations  
13 from 74 m water depth on the middle shelf down to 1024 m using a combination of in situ  
14 flux measurements, sedimentary geochemistry and modelling. Bottom water oxygen was  
15 below detection limit down to ca. 400 m and increased to 53  $\mu\text{M}$  at the deepest station.  
16 Sediment accumulation rates decreased sharply seaward of the middle shelf and subsequently  
17 increased at the deep stations. The organic carbon burial efficiency (CBE) was unusually low  
18 on the middle shelf (< 20 %) when compared to an existing global database, for reasons  
19 which may be linked to episodic ventilation of bottom waters by oceanographic anomalies.  
20 Deposition of reworked, degraded material originating from sites higher up on the slope is  
21 proposed to explain unusually high sedimentation rates and CBE (> 60 %) at the deep  
22 oxygenated sites. In line with other studies, CBE was elevated under oxygen-deficient waters  
23 in the mid-water OMZ. Organic carbon rain rates calculated from the benthic fluxes alluded to  
24 efficient mineralization of organic matter in the water column compared to other oxygen-  
25 deficient environments. The observations at the Peruvian margin suggest that a lack of oxygen  
26 does not greatly affect the degradation of organic matter in the water column but promotes the  
27 preservation of organic matter in marine sediments.

## 1 **1 Introduction**

2 The Peruvian upwelling forms part of the boundary current system of the Eastern Tropical  
3 South Pacific and is one of the most biologically productive regions in the world (Pennington  
4 et al., 2006). Respiration of organic matter in subsurface waters leads to the development of  
5 an extensive and perennial oxygen minimum zone (Walsh, 1981; Quiñones et al. 2010).  
6 Bottom water dissolved oxygen (O<sub>2</sub>) concentrations have been measured to be below the  
7 analytical detection limit from the shelf down to 400 m (Bohlen et al., 2011). Sediments  
8 within this depth interval display organic carbon contents in excess of 15 % (Reimers and  
9 Suess, 1983a; Suess et al., 1987; Arthur et al., 1998); much higher than the average  
10 continental margin of < 2 % (Seiter et al., 2004). Oxygen-deficient margins like Peru have  
11 thus been proposed to be sites of enhanced carbon preservation and petroleum-source rock  
12 formation (Demaison and Moore, 1980).

13 An understanding of the factors that enhance carbon preservation and burial in marine  
14 sediments is critical to interpret the sedimentary record and constrain global carbon sources  
15 and sinks over geological time scales (Berner, 2004; Wallmann and Aloisi, 2012). Pioneering  
16 workers argued that carbon preservation is strongly driven either by the absence of O<sub>2</sub> in the  
17 bottom water (Demaison and Moore, 1980) or by higher primary production (Pedersen and  
18 Calvert, 1990). Since then, much work on the biogeochemical characteristics of sediments has  
19 been undertaken to better disentangle these factors (Hedges and Keil, 1995; Arthur et al.,  
20 1998; Hedges et al., 1999; Keil and Cowie, 1999; Vanderwiele et al., 2009; Zonneveld et al.,  
21 2010; and many others). These studies do broadly indicate that organic matter under oxic  
22 bottom waters is in a more advanced state of degradation compared to oxygen-deficient  
23 waters. Investigations in the water column have also shown that respiration of organic carbon  
24 is significantly reduced in oxygen-deficient waters, leading to elevated carbon fluxes to the  
25 sediments (Martin et al., 1987; Devol and Hartnett, 2001; Van Mooy et al., 2002).

26 Rates of carbon burial and mineralization on the Peruvian margin have been studied as part of  
27 the Collaborative Research Center 754 (Sonderforschungsbereich, SFB 754,  
28 [www.sfb754.de/en](http://www.sfb754.de/en)) "Climate-Biogeochemistry Interactions in the Tropical Ocean" (first  
29 phase 2008-2011 and second phase 2012-2015). The overall aim of the SFB 754 is to  
30 understand the physical and biogeochemical processes that lead to the development and  
31 existence of oxygen-deficient regions in the tropical oceans. In this paper, in situ benthic  
32 fluxes and sedimentary geochemical data collected during two campaigns to the Peruvian

1 margin at 11°S and 12°S are used to summarize our current understanding of carbon cycling  
2 in this setting. We address the following questions:

3 1) What is the rate of organic carbon mineralization and burial in the sediments down through  
4 the OMZ? Do these data point toward diminished rates of organic carbon mineralization in  
5 the water column?

6 2) Which factors determine the carbon burial efficiency at Peru and is there any marked  
7 difference for stations underlying oxic and anoxic bottom waters?

8

## 9 **2 Study Area**

10 Equatorward winds engender upwelling of nutrient-rich Equatorial subsurface water along  
11 the Peruvian coast (Fiedler and Talley, 2006). Upwelling is most intense between 5 and 15°S  
12 where the shelf narrows (Quiñones et al. 2010). The sampling transects at 11°S and 12°S are  
13 located within the same upwelling cell (Suess et al., 1987). Highest rates of primary  
14 productivity ( $1.8 - 3.6 \text{ g C m}^{-2} \text{ d}^{-1}$ ) are 6 months out of phase with upwelling intensity due to  
15 the deepening of the mixed layer during the upwelling period (Walsh, 1981; Echevin et al.,  
16 2008; Quiñones et al. 2010). Austral winter and spring is the main upwelling period with  
17 interannual variability imposed by the El Niño Southern Oscillation (ENSO) (Morales et al.,  
18 1999). The lower vertical limit of the OMZ is around 700 m water depth off Peru ( $\text{O}_2 < 20$   
19  $\mu\text{mol kg}^{-1}$ ; Fuenzalida et al. 2009). The mean depth of the upper boundary of the OMZ on the  
20 shelf at 11°S and 12°S is around 50 m (Gutiérrez et al., 2008), but deepens to ca. 200 m or  
21 more during ENSO years (e.g. Levin et al., 2002). At these times, dissolved  $\text{O}_2$  on the shelf  
22 can vary between 0 and 100  $\mu\text{M}$  within a matter of days to weeks as opposed to several  
23 months during weaker ENSO events (Gutiérrez et al., 2008; Noffke et al., 2012).

24 Sediments at 11 and 12°S are generally diatomaceous, rapidly accumulating muds (Suess et  
25 al., 1987, and many others). Grain size analysis shows that clay/silt fractions are highest on  
26 the shelf and in mid-waters ( $> 80 \%$ ), whereas the sand content is highest (40 %) in deeper  
27 waters (Mosch et al., 2012). The sediments can thus be described as sandy mud to slightly  
28 sandy mud (Flemming, 2000). The distribution of sediment on the margin is influenced by,  
29 resuspension, winnowing and lateral particle transport due to high bottom currents and  
30 breaking of internal waves on the slope (Arthur et al., 1998; Levin et al., 2002; Mosch et al.,  
31 2012). Surface particulate organic carbon (POC) content is high in mid-waters (15 to 20 %)   
32 with lower values (5 to 10 %) on the shelf and in deep waters (Böning et al., 2004).  $\delta^{13}\text{C}$

1 analysis and other geochemical indicators confirm that the organic matter at this latitude is  
2 almost entirely of marine origin (Arthur et al., 1998; Reimers and Suess, 1983b; Levin et al.,  
3 2002; Gutiérrez et al., 2009).

4 The sediments down to around 400 m are notably cohesive, ranging from dark olive green to  
5 black in colour with no surface-oxidized layer (Bohlen et al., 2011; Mosch et al., 2012). The  
6 surface is colonized by dense, centimetre-thick mats of gelatinous sheaths containing  
7 microbial filaments of the large sulfur oxidizing bacteria *Thioploca* spp. (Henrichs and  
8 Farrington, 1984; Arntz et al., 1991). These bacteria glide vertically through the sediments to  
9 access sulfide which they oxidize using nitrate stored within intracellular vacuoles (Jørgensen  
10 and Gallardo, 2006). The bacterial density varies with time on the shelf depending on the  
11 bottom water redox conditions (Gutiérrez et al., 2008). Spionid polychaetes (ca. 2 cm length)  
12 have been observed in association with the mats (Mosch et al., 2012). The biomass of  
13 macrofauna generally tends to be highest in the OMZ but with low species richness,  
14 dominated by polychaetes and oligochaetes (Levin et al., 2002). At the lower boundary of the  
15 OMZ, high abundances of epibenthic megafauna such as ophiuroids as well as echinoderms,  
16 pennatulaceans, porifera, crustaceans, gastropods and echinoderms have been observed  
17 (Levin et al., 2002; Mosch et al., 2012). Sediments here are olive green throughout with a thin  
18 upper oxidized layer light green/yellow in colour (Bohlen et al., 2011; Mosch et al., 2012).

19 For the purposes of this study, we divide the Peruvian margin into 3 zones broadly reflecting  
20 bottom water O<sub>2</sub> distributions and sedimentary POC content: (i) the middle and outer shelf (<  
21 ca. 200 m, POC 5 to 10 %, O<sub>2</sub> < detection limit (dl, 5 μM) at time of sampling) where non-  
22 steady conditions are occasionally driven by periodic intrusion of oxygenated bottom waters,  
23 (ii) the OMZ (ca. 200 to 450 m, POC 10 – 20 %, O<sub>2</sub> predominantly < dl), and (iii) the deep  
24 stations below the OMZ with oxygenated bottom water (POC ≤ ca. 5 % and O<sub>2</sub> > dl).

### 25 **3 Material and methods**

#### 26 **3.1 Flux measurements and sediment sampling**

27 We present data from six stations along 11°S sampled during expedition M77 (cruise legs 1  
28 and 2) in November/December 2008 and ten stations along 12°S during expedition M92 (leg  
29 3) in January 2013 (Fig. 1). Both campaigns took place during austral summer, i.e. the low  
30 upwelling season, and under neutral or negative ENSO conditions  
31 (<http://www.cpc.ncep.noaa.gov>). With the exception of the particulate phases, the

1 geochemical data and benthic modelling results from the 11°S transect have been published  
2 previously (Bohlen et al., 2011; Scholz et al., 2011; Mosch et al., 2012; Noffke et al., 2012).  
3 Data from 12°S are new to this study.

4 In situ fluxes were measured using data collected from Biogeochemical Observatories, BIGO  
5 (Sommer et al., 2008). BIGO landers contained two circular flux chambers (internal diameter  
6 28.8 cm, area 651.4 cm<sup>2</sup>). One lander at 11°S, BIGO-T, contained only one benthic chamber.  
7 Each chamber was equipped with an optode to monitor dissolved O<sub>2</sub> concentrations. A TV-  
8 guided launching system allowed guided placement of the observatories on the sea floor. Two  
9 hours (11°S) and 4 hours (12°S) after the landers were placed on the sea floor, the chamber(s)  
10 were slowly driven into the sediment (~ 30 cm h<sup>-1</sup>). During this initial period, the water inside  
11 the flux chamber was periodically replaced with ambient bottom water. After the chamber  
12 was driven into the sediment (~10 cm), the chamber water was again replaced with ambient  
13 bottom water to flush out solutes that might have been released from the sediment during  
14 chamber insertion. The water volume enclosed by the benthic chamber ranged from 7.8 to  
15 18.5 L and was mixed using a 5-cm stirrer bar at 140 rpm located 10-15 cm above the  
16 sediment surface. During the BIGO-T experiments, the chamber water was replaced with  
17 ambient bottom water half way through the deployment period to restore outside conditions  
18 and then re-incubated.

19 Four (11°S) or eight (12°S) sequential water samples were removed periodically with glass  
20 syringes (volume of each syringe ~ 47 ml) to determine fluxes of solutes across the sediment-  
21 water interface. For BIGO-T, 4 water samples were taken before and after replacement of the  
22 chamber water. The syringes were connected to the chamber using 1 m long Vygon tubes  
23 with an internal volume of 6.9 ml. Prior to deployment, these tubes were filled with distilled  
24 water, and great care was taken to avoid enclosure of air bubbles. Concentrations were  
25 corrected for dilution using measured chloride concentrations in the syringes and bottom  
26 water. Water samples for gas measurements (12°S) were taken at four regular time intervals  
27 using 80 cm-long glass tubes (internal volume ca. 15 ml). An additional syringe water  
28 sampler (four or eight sequential samples) was used to extract ambient bottom water samples  
29 from 30 – 40 cm above the seafloor. The benthic incubations were conducted for time periods  
30 ranging from 17.8 to 33 hours. Immediately after retrieval of the observatories, the water  
31 samples were transferred to the onboard cool room set to the average bottom water  
32 temperature on the margin (8°C) for further processing and sub-sampling. Benthic fluxes

1 were estimated from linear regressions of the concentration-time data and corrected for the  
2 volume to surface area ratio of the chamber. The volume was estimated on board using the  
3 mean height of water above the sediments in the recovered chambers.

4 Sediment samples for analysis were taken using multiple-corers (MUC) deployed adjacent to  
5 the BIGO sites. Retrieved cores were immediately transferred to the cool room and processed  
6 within a few hours. Sub-sampling for redox sensitive constituents was performed under  
7 anoxic conditions using an argon-filled glove bag. Sediment samples for porosity analysis  
8 were transported to the on shore laboratory in air-tight containers at 8°C. Samples for  
9 porewater extraction were transferred into tubes pre-flushed with argon and subsequently  
10 centrifuged at 4500 rpm for 20 minutes. Prior to analysis, the supernatant was filtered with  
11 cellulose acetate Nuclepore® filters (0.2 µm) inside the glove bag. The centrifugation tubes  
12 with the remaining solid phase of the sediment were stored at -20 °C for further analysis on  
13 shore. Additional samples for bottom water analysis were taken from the water overlying the  
14 sediment cores.

### 15 **3.2 Analytical details**

16 Dissolved oxygen concentrations in the water column were measured using a Seabird SBE43  
17 sensor mounted on a SeaBird 911 CTD rosette system. These optodes, plus the ones inside the  
18 chambers, were initially calibrated by vigorously bubbling unfiltered seawater from the  
19 bottom water at each station with air or argon for 20 minutes. The sensors were further  
20 calibrated against discrete samples collected from the water column on each CTD cast and  
21 analyzed on board using Winkler titration with a detection limit of ca. 5 µM. We broadly  
22 define O<sub>2</sub> concentrations below the detection limit of the Winkler analysis as anoxic, whilst  
23 noting that sub-micromolar levels have been measured in the OMZ using microsensors  
24 (Kalvelage et al., 2013).

25 Ammonium (NH<sub>4</sub><sup>+</sup>) was measured on board using standard photometric techniques with a  
26 Hitachi U2800 photometer (Grasshoff et al., 1999). The detection limit was 1 µM and the  
27 precision of the analyses was 5 µM (NH<sub>4</sub><sup>+</sup>). Total alkalinity (TA) was determined by direct  
28 titration of 1 ml porewater with 0.02 M HCl using a mixture of methyl red and methylene  
29 blue as an indicator and bubbling the titration vessel with Ar gas to strip CO<sub>2</sub> and hydrogen  
30 sulfide. The analysis was calibrated using IAPSO seawater standard, with a precision and  
31 detection limit of 0.05 meq l<sup>-1</sup>. Ion chromatography (Methrom 761) was used to determine

1 sulfate ( $\text{SO}_4^{2-}$ ) in the onshore laboratory with a detection limit of  $< 100 \mu\text{M}$  and precision of  
2  $200 \mu\text{M}$ . Major cations were determined by ICP-AES with a detection limit and precision as  
3 given by Haffert et al. (2013).

4 Partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) was analyzed in the benthic chambers at  $12^\circ\text{S}$  by passing the  
5 sample from the glass tubes (without air contact) through the membrane inlet of a quadrupole  
6 mass spectrometer (GAM200 IPI Instruments, Bremen). The samples were analyzed  
7 sequentially, flushing with distilled water between samples. Standards of 300, 500, 1000 and  
8 5000 ppm  $\text{CO}_2$  were prepared by sparging filtered seawater from the bottom water from each  
9 station using standard bottles of  $\text{CO}_2$  of known concentration at in situ temperature for 30  
10 minutes. Calibration was performed before and after analysis of the samples from each site.  
11 The relative precision of the measurement was  $<3 \%$ .

12 Wet sediment samples for analysis of POC and particulate organic nitrogen (PON) were  
13 freeze-dried in the home laboratory and analyzed using a Carlo-Erba element analyzer (NA  
14 1500). POC content was determined after acidifying the sample with  $\text{HCl}$  (0.25 N) to release  
15 the inorganic components as  $\text{CO}_2$ . Weight percent of total carbon was determined using  
16 samples without acidification. Inorganic carbon was determined by weight difference between  
17 the total and organic carbon. The precision and detection limit of the POC analysis was 0.04  
18 and 0.05 dry weight percent (% C), respectively. The precision and detection limit of the  
19 inorganic carbon analysis was 2 and 0.1 % C, respectively. Porosity was determined from the  
20 weight difference of the wet and freeze-dried sediment. Values were converted to porosity  
21 (water volume fraction of total sediment) assuming a dry sediment density of  $2 \text{ g cm}^{-3}$   
22 (Böning et al., 2004) and seawater density of  $1.023 \text{ g cm}^{-3}$ . The analysis of total aluminium  
23 (Al) concentrations in digestion solutions was carried out using an inductively coupled plasma  
24 optical emission spectrometer (ICP-OES, VARIAN 720-ES) following the procedure  
25 described by Scholz et al. (2011).

26 Additional samples from adjacent MUC liners taken from the same cast were used for the  
27 determination of down-core profiles of unsupported (excess)  $^{210}\text{Pb}_{\text{xs}}$  activity by gamma  
28 counting. This approach includes monitoring of the main peaks of anthropogenic deposition  
29 of  $^{241}\text{Am}$  during the 1950s (test of nuclear weapons) as an independent time marker. Between  
30 5 and 34 g of freeze-dried and ground sediment, each averaging discrete 2-cm depth intervals,  
31 was embedded into a 2-phase epoxy resin (West System Inc.), all in the same counter-specific  
32 calibrated disc geometry (2 inch diameter). Following Mosch et al. (2012), a low-background

1 coaxial Ge(Li) planar detector (LARI, University of Göttingen) was used to measure total  
 2  $^{210}\text{Pb}$  via its gamma peak at 46.5 keV and  $^{226}\text{Ra}$  via the granddaughter  $^{214}\text{Pb}$  at 352 keV. Prior  
 3 to analysis,  $^{226}\text{Ra}$  and  $^{214}\text{Pb}$  in the gas-tight embedded sediment were allowed to equilibrate  
 4 for at least three weeks. To determine  $^{210}\text{Pb}_{\text{xs}}$ , the measured total  $^{210}\text{Pb}$  activity of each sample  
 5 was corrected by subtracting its individual  $^{226}\text{Ra}$  activity, assuming post-burial closed-system  
 6 behaviour. Uncertainty of the  $^{210}\text{Pb}_{\text{xs}}$  data was calculated from the individual measurements of  
 7  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  activities using standard propagation rules. The relative error of the  
 8 measurements ( $2\sigma$ ) ranged between 8 and 58 %.

### 9 **3.3 Calculation of dissolved inorganic carbon (DIC) fluxes**

10 DIC concentrations in the benthic chambers at 12°S were calculated from the concentrations  
 11 of TA and  $\text{pCO}_2$  using the equations and equilibrium coefficients given by Zeebe and Wolf-  
 12 Gladrow (2001).  $\text{pCO}_2$  and TA concentrations increased linearly with time inside the  
 13 chambers. Since four samples for  $\text{pCO}_2$  were taken using the glass tubes versus eight samples  
 14 for TA analysis in the syringes, each successive pair of TA data were averaged for calculating  
 15 DIC. A constant salinity (35 psu), total boron concentration (0.418 mM) and seawater density  
 16 ( $1.025 \text{ kg L}^{-1}$ ) were assumed. For the shelf stations where sulfide was released from the  
 17 sediment (Sommer et al., unpub. data), corrections were made for the contribution of  $\text{HS}^-$  to  
 18 TA using the relevant equilibrium constants (Zeebe and Wolf-Gladrow, 2001). DIC fluxes  
 19 were calculated from the concentrations as described above.

### 20 **3.4 Determination of sediment accumulation rates**

21 Particle-bound  $^{210}\text{Pb}_{\text{xs}}$  is subject to mixing in the upper sediment layers by the movement of  
 22 benthic fauna. The distribution of  $^{210}\text{Pb}_{\text{xs}}$  can thus be used to determine bioturbation  
 23 coefficients as well as sedimentation rates using a reaction-transport model. We simulated the  
 24 activity of  $^{210}\text{Pb}_{\text{xs}}$  in  $\text{Bq g}^{-1}$  using a steady state numerical model that includes terms for  
 25 sediment burial, mixing (bioturbation), compaction and radioactive decay:

$$(1-\varphi(x))\cdot\rho\cdot\frac{\partial^{210}\text{Pb}_{\text{xs}}(x)}{\partial t} = \frac{\partial\left((1-\varphi(x))\cdot\rho\cdot D_B(x)\cdot\frac{\partial^{210}\text{Pb}_{\text{xs}}(x)}{\partial x}\right)}{\partial x} - \frac{\partial\left((1-\varphi(x))\cdot\rho\cdot v_s(x)\cdot^{210}\text{Pb}_{\text{xs}}(x)\right)}{\partial x} + (1-\varphi(x))\cdot\rho\cdot\lambda\cdot^{210}\text{Pb}_{\text{xs}}(x) \quad (1)$$

26 In this equation,  $t$  (yr) is time,  $x$  (cm) is depth below the sediment–water interface,  $\varphi(x)$   
 27 (dimensionless) is porosity,  $v_s(x)$  ( $\text{cm yr}^{-1}$ ) is the burial velocity for solids,  $D_B(x)$  ( $\text{cm}^2 \text{ yr}^{-1}$ ) is



1 the bioturbation coefficient,  $\lambda$  ( $0.03114 \text{ yr}^{-1}$ ) is the decay constant for  $^{210}\text{Pb}_{\text{xs}}$  and  $\rho$  is the bulk  
 2 density of solid particles ( $2.0 \text{ g cm}^{-3}$ ).

3 Porosity was described using an exponential function assuming steady-state compaction:

$$\varphi(x) = \varphi(L) + (\varphi(0) - \varphi(L)) \cdot \exp\left(-\frac{x}{z_{\text{por}}}\right) \quad (2)$$

4 where  $\varphi(0)$  is the porosity at the sediment-water interface,  $\varphi(L)$  is the porosity of compacted  
 5 sediments and  $z_{\text{por}}$  (cm) is the attenuation coefficient. These parameters were determined from  
 6 the measured data at each station (Table S2).

7 Sediment compaction was considered by allowing the sediment burial velocity to decrease  
 8 with sediment depth:

$$v_s(x) = \frac{\omega_{\text{acc}} \cdot (1 - \varphi(L))}{1 - \varphi(x)} \quad (3)$$

9 where  $\omega_{\text{acc}}$  corresponds to the sediment accumulation rate of compacted sediments.

10 The decrease in bioturbation intensity with depth was described with a Gaussian-type  
 11 function (Boudreau, 1996):

$$D_B(x) = D_B(0) \cdot \exp\left(-\frac{x^2}{2 \cdot x_s^2}\right) \quad (4)$$

12 where  $D_B(0)$  ( $\text{cm}^2 \text{ yr}^{-1}$ ) is the bioturbation coefficient at the sediment-water interface and  $x_s$   
 13 (cm) is the bioturbation halving depth.

14 The flux continuity at the sediment surface serves as the upper boundary condition:

$$F(0) = (1 - \varphi(0)) \cdot \rho \cdot \left( v_s(0) \cdot ^{210}\text{Pb}_{\text{xs}}(0) - D_B(0) \cdot \left. \frac{\partial ^{210}\text{Pb}_{\text{xs}}(x)}{\partial x} \right|_0 \right) \quad (5)$$

15 where  $F(0)$  is the steady-state flux of  $^{210}\text{Pb}_{\text{xs}}$  to the sediment surface ( $\text{Bq cm}^{-2} \text{ yr}^{-1}$ ). The influx  
 16 of  $^{210}\text{Pb}_{\text{xs}}$  was determined from the measured integrated activity of  $^{210}\text{Pb}_{\text{xs}}$  multiplied by  $\lambda$ :

$$F(0) = \lambda \cdot \rho \int_0^\infty ^{210}\text{Pb}_{\text{xs}}(x) \cdot (1 - \varphi(x)) \, dx \quad (6)$$

17  $^{210}\text{Pb}_{\text{xs}}$  was present down to the bottom of the core at the 74 m station ( $12^\circ\text{S}$ ), implying rapid  
 18 burial rates. Here,  $F(0)$  was adjusted until a fit to the data was obtained.

19 A zero gradient (Neumann) condition was imposed at the lower boundary at 50 cm (100 cm  
 20 for the shallowest stations at  $12^\circ\text{S}$ ). At this depth, all  $^{210}\text{Pb}_{\text{xs}}$  will have decayed for the burial  
 21 rates encountered on the Peruvian margin. The model was initialized using low and constant  
 22 values for  $^{210}\text{Pb}_{\text{xs}}$  in the sediment column. Solutions were obtained using the numerical solver  
 23 NDSolve in MATHEMATICA 9 with a mass conservation  $> 99 \%$ .

1 The adjustable parameters ( $\omega_{acc}$ ,  $D_B(0)$ ,  $x_s$ ) were constrained by fitting the  $^{210}\text{Pb}_{xs}$  data.  
2 Unsupported  $^{210}\text{Pb}$  measurements were not made at the 101 and 244 m station (12°S) and  
3 sedimentation rates here were estimated from adjacent stations. Parameters and boundary  
4 conditions for simulating  $^{210}\text{Pb}_{xs}$  at 12°S are given in Table S2 and in Bohlen et al. (2011) for  
5 11°S. For some cores, the subsampling strategy revealed the detection of the anthropogenic  
6 enrichment peak of nuclide  $^{241}\text{Am}$  (co-analysed on 60 keV). This provides an independent  
7 time marker in the profiles and potential validation of the radiometric age model deduced  
8 from the  $^{210}\text{Pb}_{xs}$ -based sediment accumulation rates.

### 9 **3.5 Diagenetic modelling of POC degradation**

10 A steady-state 1–D numerical reaction–transport model was used to simulate the degradation  
11 of POC in surface sediments at all stations. The model developed for 12°S is based on that  
12 used to quantify benthic N fluxes at 11°S by Bohlen et al. (2011) with modifications to  
13 account for benthic denitrification by foraminifera (Glock et al., 2013).

14 The basic model framework follows Eq. (1). Solutes were transported by molecular diffusion,  
15 sediment accumulation (burial) and non–local transport by burrowing organisms  
16 (bioirrigation). Solid transport by burial and bioturbation was parameterized using the results  
17 of the  $^{210}\text{Pb}_{xs}$  model. Model sensitivity analysis based on solute fluxes showed that  
18 bioirrigation rates were very low in oxygenated sediments below the OMZ.

19 The model includes a comprehensive set of redox reactions that are ultimately driven by POC  
20 mineralization. POC was degraded by aerobic respiration, denitrification, iron oxide  
21 reduction, sulfate reduction and methanogenesis. Manganese oxide reduction was not  
22 considered due to negligible total manganese in the sediment (Scholz et al., 2011). The rate of  
23 each carbon degradation pathway was determined using Michaelis–Menten kinetics based on  
24 traditional approaches (e.g. Boudreau, 1996). DIC is produced by POC degradation only, that  
25 is, carbonate dissolution or precipitation are not included (see Results).

26 The total rate of POC degradation was constrained using a nitrogen-centric approach based on  
27 the relative rates of transport and reactions that produce/consume  $\text{NH}_4^+$ . The procedure  
28 follows a set of guidelines that is outlined fully in Bohlen et al. (2011). The modelled POC  
29 mineralization rates for 11°S were constrained using both porewater concentration data and in  
30 situ flux measurements of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_4^+$ . Dissolved  $\text{O}_2$  flux data were used as an  
31 additional constraint at the deeper stations. The POC degradation rates at 12°S were further

1 constrained from the measured DIC fluxes. The model output includes concentration profiles,  
2 benthic fluxes and reaction rates which are assumed to be in steady state. Note, however, that  
3 the bottom waters on the middle shelf at 12°S were temporarily depleted in  $\text{NO}_3^-$  and  $\text{NO}_2^-$  at  
4 the time of sampling. Although this leads to uncertainties in the rate of nitrate uptake by  
5 *Thioploca*, POC degradation rates remain well-constrained from the DIC fluxes.

6 The model was solved in the same way as described for  $^{210}\text{Pb}_{\text{xs}}$ . The sediment depth ranged  
7 from 50 to 100 cm depending on the station (Boudreau, 1996). Measured solute  
8 concentrations and known or estimated particulate fluxes to the sea floor served as upper  
9 boundary conditions (Bohlen et al., 2011). At the lower boundary, a Neumann (zero flux)  
10 boundary was generally implemented. A steady-state solution was obtained (invariant  
11 concentrations with time and sediment depth) with a mass conservation > 99 %.

### 12 **3.6 Pelagic modelling of primary production**

13 Primary production was estimated using the high-resolution physical-biogeochemical model  
14 (ROMS-BioEBUS) in a configuration developed for the Eastern Tropical Pacific (Montes et  
15 al., 2014). It consists of the hydrodynamic model ROMS (Regional Ocean Model System;  
16 Shchepetkin and McWilliams (2003)) coupled with the BIOgeochemical model developed for  
17 the Eastern Boundary Upwelling Systems (BioEBUS, Gutknecht et al., 2013). BioEBUS  
18 describes the pelagic distribution of  $\text{O}_2$  and the N cycle under a range of redox conditions  
19 with twelve compartments: phytoplankton and zooplankton split into small (flagellates and  
20 ciliates, respectively) and large organisms (diatoms and copepods, respectively), detritus,  
21  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , dissolved organic N and a parameterization to determine nitrous oxide  
22 ( $\text{N}_2\text{O}$ ) production (Suntharalingam et al., 2000; 2012).

23 The model configuration covers the region between 4°N and 20°S and from 90°W to the west  
24 coast of South America. The model horizontal resolution is  $1/9^\circ$  (ca. 12 km) and has 32  
25 vertical levels that are elongated toward the surface to provide a better representation of shelf  
26 processes. The model was forced by heat and freshwater fluxes derived from COADS ocean  
27 surface monthly climatology (Da Silva et al., 1994) and by the monthly wind stress  
28 climatology computed from QuikSCAT satellite scatterometer data (Liu et al., 1998). The  
29 three open boundary conditions (northern, western and southern) for the dynamic variables  
30 (temperature, salinity and velocity fields) were extracted from the Simple Ocean Data  
31 Assimilation (SODA) reanalysis (Carton and Giese, 2008). Initial and boundary conditions

1 for biogeochemical variables were extracted from the CSIRO Atlas of Regional Seas (CARS  
2 2009; for  $\text{NO}_3^-$  and  $\text{O}_2$ ) and SeaWiFS (O'Reilly et al., 2000; for chlorophyll *a*). Other  
3 biogeochemical variables were computed following Gutknecht et al. (2013) and Montes et al.  
4 (2014). Monthly chlorophyll climatology from SeaWiFS was used to generate phytoplankton  
5 concentrations which were then extrapolated vertically from the surface values using the  
6 parameterization of Morel and Berthon (1989). Based on Koné et al. (2005), a cross-shore  
7 profile following in situ observations was applied to zooplankton, with higher concentrations  
8 near the coast.

9 The simulation period was 18 years. The first 13 years considered the hydrodynamics only  
10 and then the biogeochemical model was coupled for the following five years. The coupled  
11 model reached a statistical equilibrium after four years. The data presented here correspond to  
12 the final simulation year. Details of model configuration and validation are described by  
13 Montes et al. (2014).

14 Primary production (PP) was computed as the sum of the production supported by  $\text{NO}_3^-$  and  
15  $\text{NO}_2^-$  uptake and regenerated production of  $\text{NH}_4^+$  uptake by nano- and microphytoplankton  
16 (Gutknecht et al., 2013). Rates (in N units) were calculated for the station locations listed in  
17 Table 1 by integrating over the euphotic zone. The atomic Redfield C:N ratio (106/16,  
18 Redfield et al., 1963) was used to convert PP into carbon units.

## 19 **4 Results**

### 20 **4.1 Sediment appearance**

21 Bottom sediments at 12°S were very similar to those at 11°S (see Section 2). The sediments  
22 down to ca. 300 m were cohesive, dark-olive anoxic mud (Gutiérrez et al., 2009; Bohlen et  
23 al., 2011; Mosch et al., 2012). Porosity was high on the shelf and in the OMZ (>0.9)  
24 decreasing to <0.8 at the deepest stations (Fig. S1 and Table 1). Porewater had a strong sulfidic  
25 odour, especially in the deeper layers. Shelf and OMZ sediments were colonized by mats of  
26 large filamentous bacteria, presumably *Thioploca* spp. (Gallardo, 1977; Henrichs and  
27 Farrington, 1984). Surface coverage by bacterial mats was 100 % on the shelf and decreased  
28 to roughly 40 % by 300 m where the bacteria formed patches several decimetres in diameter.  
29 Mat density was much lower at 11°S, not exceeding 10 % coverage (Mosch et al., 2012).  
30 *Thioploca* trichomes extended 2 cm into the overlying water to access bottom water  $\text{NO}_3^-$  (c.f.  
31 Huettel et al., 1996) and were visible down to a depth of ca. 20 cm at the mat stations.

1 Polychaetes and oligochaetes were also present on the shelf, but not at the deeper stations  
2 within the OMZ. Despite anoxic bottom waters, no mats were visible at St. 8 (409 m, 12°S).  
3 Sediments here consisted of hard grey clay underlying a 2 – 3 cm porous surface layer that  
4 was interspersed with cm-sized phosphorite nodules. The upper layer contained large numbers  
5 of live foraminifera that were visible to the naked eye (J. Cardich et al., unpub. data). Similar  
6 foraminiferal ‘sands’ containing phosphorite granules were noted at 11°S, in particular below  
7 the OMZ (Mosch et al., 2012). Phosphorite sands on the Peruvian margin are found in areas  
8 of enhanced sediment reworking by bottom currents and the breaking of internal waves on the  
9 seafloor (Suess, 1981; Glenn and Arthur, 1988; Mosch et al., 2012). Below the OMZ,  
10 macrofauna were more prevalent and included harpacticoids, amphipods, oligochaetes and  
11 large polychaetes.

## 12 **4.2. Sediment mixing and accumulation rates**

13 At most stations,  $^{210}\text{Pb}_{\text{xs}}$  distributions decreased quasi-exponentially and showed little  
14 evidence of intense, deep mixing by bioturbation (Fig. 2 and Bohlen et al., 2011); a feature  
15 that is supported by the lack of large bioturbating organisms in and below the OMZ. The  
16 highest bioturbation coefficient determined by the model was  $4 \text{ cm}^2 \text{ yr}^{-1}$  for St. 3 at 12°S  
17 (Table S2).

18 Mass accumulation rates (MAR) derived from  $^{210}\text{Pb}_{\text{xs}}$  modelling (Fig. 3a) were similar to  
19 values reported previously (Reimers and Suess, 1983c). Rates were extremely high at the  
20 shallowest stations ( $1200$  and  $1800 \text{ g m}^{-2} \text{ yr}^{-1}$  at 11 and 12°S, respectively). These are a factor  
21 of 2 – 3 times higher than measured elsewhere on the transects and 3 – 4 times higher than the  
22 global shelf average of  $500 \text{ g m}^{-2} \text{ yr}^{-1}$  (Burwicz et al., 2011). They corresponded to  
23 sedimentation rates ( $\omega_{\text{acc}}$ ) of  $0.45$  and  $0.3 \text{ cm yr}^{-1}$  (Table 2). Beyond the middle shelf, MAR  
24 decreased sharply to  $132$  and  $44 \text{ g m}^{-2} \text{ yr}^{-1}$  at St. 2 (11°S) and St. 8 (12°S), respectively. These  
25 latter values are associated with measurable  $^{210}\text{Pb}_{\text{xs}}$  in the upper 3 cm only and thus indicative  
26 of sediment winnowing or resuspension as mentioned above. A relatively low MAR of  $128 \text{ g}$   
27  $\text{m}^{-2} \text{ yr}^{-1}$  was also determined for St. 4 at 12°S compared to the neighbouring stations. MAR  
28 and  $\omega_{\text{acc}}$  tended to be higher at the deep oxygenated stations compared to the OMZ stations,  
29 with  $\omega_{\text{acc}}$  of  $0.06 \text{ cm yr}^{-1}$  at St. 10 (12°S) and  $0.05 \text{ cm yr}^{-1}$  at St. 5 (11°S). Aluminium  
30 accumulation showed similar trends to MAR, with highest values on the shelf and a  
31 pronounced increase below the OMZ (Fig. 3b). For some cores, peaks in  $^{241}\text{Am}$  activities

1 could be detected which provide independent validation of  $\omega_{acc}$  derived from the  $^{210}\text{Pb}_{xs}$   
2 systematics (Fig. 2 and Appendix A).

### 3 **4.3 Geochemistry**

4 Dissolved  $\text{O}_2$  concentrations in the water column reveal the vertical extent of the OMZ and  
5 the presence of oxygen-deficient water overlying the upper slope sediments at both latitudes  
6 (Fig. 1). Qualitatively, geochemical solute profiles in the sediments from 11 and 12°S are  
7 typical for continental margin settings (Bohlen et al., 2011; Fig. 4). The model was able to  
8 accurately simulate the geochemical profiles along both transects (Fig. 4 and Bohlen et al.,  
9 2011). Sediment porewater concentrations of  $\text{NH}_4^+$  and alkalinity were highest on the shelf  
10 and decreased with water depth. Conversely,  $\text{SO}_4^{2-}$  depletion was more extensive at the  
11 shallower stations.  $\text{SO}_4^{2-}$  also showed a much stronger depletion on the shelf at 12°S  
12 compared to 11°S, leading to the formation of a methanogenic layer below 65 cm. These  
13 trends confirm general expectations that less reactive organic material reaches the sea floor as  
14 water depth increases (e.g. Suess, 1980; Levin et al., 2002).

### 15 **4.4 Organic carbon distributions and burial rates**

16 Surface POC content at 12°S was lowest (ca. 5 %) on the middle shelf and below the OMZ  
17 (Fig. 4). At these stations, POC decreased in the upper 10 cm and reached asymptotic values  
18 at around 10 cm where refractory component dominated the mixture (Reimers and Suess,  
19 1983a). PON showed the same qualitative trends. Maximal POC contents of ca. 17 % were  
20 measured inside the OMZ and are typical for the Peruvian margin (Suess, 1981). Here, POC  
21 showed a marked change at around 15 to 20 cm depth (Fig. 4). This may reflect the regime  
22 shift in the Peruvian OMZ during the Little Ice Age circa 1820 AD caused by a northward  
23 displacement of the Intertropical Convergence Zone (Gutiérrez et al., 2009). These features  
24 were also present at St. 4 and 5 on the outer shelf. The steady-state model does not capture  
25 centennial changes in OMZ conditions suggested by the POC profiles. Very similar trends  
26 were observed at 11°S, implying that organic matter distributions are qualitatively and  
27 quantitatively driven by the same first-order processes at both latitudes.

28 POC accumulation rates for the middle shelf and deep stations were calculated from the mass  
29 accumulation rates and POC content at 10 cm (Table 2). Due to recent variations in POC  
30 content for the OMZ stations, the average POC content in the upper 10 cm was used instead.

1 For St. 8 at 12°S (409 m), POC accumulation was calculated at 3 cm since the underlying  
2 sediment was old, non-accumulating clay. Highest carbon accumulation rates were calculated  
3 for the middle shelf at 12°S ( $60 \text{ g m}^{-2} \text{ yr}^{-1}$ ; Table 2). POC accumulation generally decreased  
4 with increasing water depth at 12°S with relatively low values at St. 4 ( $11 \text{ g m}^{-2} \text{ yr}^{-1}$ ) and St. 8  
5 ( $2 \text{ g m}^{-2} \text{ yr}^{-1}$ ). Accumulation rates were more variable for the 11°S transect.

6 Cumulative POC burial rates across the margin in Fig. 5b were calculated by integrating the  
7 measured POC accumulation at each station over the distance between stations in Fig. 5a.  
8 POC burial increased sharply on the middle shelf to ca. 100 m at both latitudes, at which point  
9 the rates diverged to give higher burial at 12°S down to the lower edge of the OMZ. Burial at  
10 11°S amounted to  $254 \text{ kmol C m}^{-1} \text{ yr}^{-1}$  (per meter of coastline). A lower value of  $181 \text{ kmol C}$   
11  $\text{m}^{-1} \text{ yr}^{-1}$  was calculated for 12°S, possibly due to the steeper slope down to ca. 1000 m. Mean  
12 POC burial on the margin, calculated by dividing the total cumulative burial by the transect  
13 length, was  $6.8$  (11°S) and  $6.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$  (12°S). This compares to a range of  $1.2$  to  $2.9$   
14  $\text{mmol C m}^{-2} \text{ d}^{-1}$  for the average continental margin (Table 3).

15

#### 16 **4.5 DIC fluxes**

17 Measured DIC fluxes were high on the middle shelf ( $65.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) and decreased quasi-  
18 exponentially with depth (Table 2). DIC fluxes were low in the OMZ at 12°S ( $2.2 - 4.7 \text{ mmol}$   
19  $\text{m}^{-2} \text{ d}^{-1}$ ) and similar to the deep sites ( $1.2 - 2.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ ). Measured DIC in the benthic  
20 chambers was assumed to originate entirely from POC mineralization. There was no clear  
21 increase or decrease in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration in the benthic chambers that would  
22 indicate an important role for carbonate precipitation/dissolution (data not shown). This is  
23 also inferred from porewater gradients of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Fig. S3).  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  fluxes  
24 show that the potential contribution of carbonate precipitation was  $< 5 \%$  of the DIC flux  
25 across all stations. This is well within the error of the DIC flux (Table 2), such that carbonate  
26 precipitation can be ignored for all practical purposes.

27 Modelled DIC concentrations inside the benthic chambers at 12°S showed good agreement  
28 with those calculated from measured TA and  $\text{pCO}_2$  concentrations (Fig. S2). Measured and  
29 modelled fluxes agreed to within  $\pm 50 \%$ , but most stations were simulated to within  $\pm 20 \%$   
30 or better (Fig. 6a). It should be remembered that the model is not only constrained by the DIC  
31 fluxes but also by porewater distributions and benthic DIN and  $\text{O}_2$  fluxes (Bohlen et al.,  
32 2011). Thus, whilst the modelled DIC fluxes could be improved, they form only one aspect of

1 the overall goodness-of-fit to the observed database. In general, the agreement between the  
2 modelled and measured DIC fluxes affords confidence in the modelled DIC fluxes at 11°S  
3 where in situ pCO<sub>2</sub> measurements were not made (Table 2). The simulated DIC fluxes at 11°S  
4 showed the same trends as 12°S, although the flux on the middle shelf (8.2 mmol m<sup>-2</sup> d<sup>-1</sup>) was  
5 a factor of 8 smaller (Table 2).

#### 6 **4.6 Organic carbon burial efficiency (CBE)**

7 At each station, CBE (%) was calculated as POC accumulation rate ÷ (POC accumulation rate  
8 + DIC flux) × 100 % (Table 2). Measured and modelled CBE at 12°S showed very good  
9 agreement (Fig. 6b). Low CBEs of 19 ± 6 % to 28 ± 12 % were derived for St. 1 to 4 on the  
10 shelf. This contrasts with the elevated POC accumulation rates, but is in agreement with the  
11 high DIC fluxes (Fig. 6a). Low CBE of 19 ± 6 % were also observed at the 409 m site where  
12 winnowing is suspected to occur. Relatively high CBEs were calculated at St. 5 to 7 in mid-  
13 water depth range of ca. 200 to 300 m (55 ± 23 % to 74 ± 37 %) and at the deep oxygenated  
14 sites (46 ± 48 % to 64 ± 19 %). At 11°S, model-derived CBE showed broadly similar trends,  
15 although the CBE at the shelf station was higher (47 %). The highest CBE of 81 % was  
16 calculated for the 695m station (11°S) in oxygen deficient waters (O<sub>2</sub> < 20 μM) below the  
17 OMZ. A detailed discussion of the uncertainties in the CBE estimates is provided in  
18 Appendix A.

#### 19 **4.7 Primary production and organic carbon rain rate**

20 Primary production (PP) estimates from the ROMS-BioEBUS model for 11 and 12°S are  
21 shown in Fig. 7. The data represent the annual mean ± s.d. for the locations close to where  
22 BIGO landers were deployed. Diatoms dominated the PP at both latitudes PP, with rates  
23 decreasing offshore from ca. 110 mmol m<sup>-2</sup> d<sup>-1</sup> at the shallowest site to ca. 80 mmol m<sup>-2</sup> d<sup>-1</sup> at  
24 the deepest site. The model revealed a much larger intraannual variability ranging from ca. 70  
25 to 170 mmol m<sup>-2</sup> d<sup>-1</sup> with highest values in austral summer (see Fig. S4).

26 Organic carbon rain rates to the seafloor (RRPOC) were calculated as the sum of the benthic  
27 carbon oxidation rate (i.e. DIC flux) and POC accumulation (Table 2). For the 11°S and 12°S  
28 transects, the modelled and measured DIC fluxes were used, respectively. RRPOC showed a  
29 rapid decrease on the shelf stations at 12°S with a more attenuated decrease with depth (Fig.  
30 7a). Station 8 (409 m) at 12°S is again an exception due to the low POC accumulation there.



1 At 11°S the trends were not so obvious due to fewer sampling stations (Fig. 7b). The fraction  
2 of PP reaching the sediment was highest at the shallowest station at 12°S (65%), decreasing to  
3 <12 % at the OMZ and deep stations (Fig. 7c).

## 4 **5 Discussion**

### 5 **5.1 Spatial patterns of organic carbon preservation**

6 Fine-grained continental margin sediments in the modern ocean (<1000 m) account for 70 -  
7 85 % of global POC burial (Hedges and Keil, 1995; Burdige, 2007). The mean POC burial  
8 flux on the margin (1.2 to 2.9 mmol C m<sup>-2</sup> d<sup>-1</sup>) is equivalent to around 3 % of primary  
9 production (Table 3). Although the POC burial flux on the Peruvian margin is far higher, it  
10 accounts for a similar fraction of primary production, thus implying a lack of preferential  
11 carbon burial compared to the average continental margin. However, the CBE reveals  
12 interesting spatial trends in carbon preservation that are not discernible by comparison of  
13 mean burial fluxes.

14 Previously-published CBEs for a range of marine environments show a positive dependency  
15 on sedimentation accumulation rate (Fig. 8). This arises because sediment accumulation is  
16 intrinsically linked to carbon burial flux, which itself is strongly tied to rain rate (Müller and  
17 Suess, 1979). In addition, sediments underlying oxygen-deficient waters (O<sub>2</sub> < 20 µM) appear  
18 to have a higher CBE than those deposited under oxygenated bottom waters. Data from Peru  
19 seaward of the shelf agree with this idea (red stars, Fig. 8). However, the CBE above and  
20 below the OMZ is inconsistent with the existing database. Firstly, CBEs for the anoxic shelf  
21 (blue stars) plot within the range for normal oxic conditions instead of >50 % expected for the  
22 oxygen-depleted conditions encountered. The 195 m site located on the shelf break is an  
23 exception, although the CBE does have high uncertainty (74 ± 37 %). In agreement, Reimers  
24 and Suess (1983a) also estimated a rather low CBE of 16 to 38 % on the outer shelf break at  
25 11°S (186 m depth). Secondly, sediments underlying oxygenated bottom waters (O<sub>2</sub> > 20 µM)  
26 below the OMZ have a higher-than-expected CBE (green stars) and plot alongside those from  
27 oxygen-deficient and euxinic waters. These discrepancies are the focus of the following  
28 discussion.

#### 29 **5.1.1. Low CBE on the shelf**

1 Our low calculated shelf CBEs imply that POC is preferentially degraded there relative to  
2 deeper sites. Trends in sediment grain size and POC content support this basic idea. The fine-  
3 grained sediment fraction (clay plus silt) at 11°S is >80 % on the shelf and decreases to ca. 60  
4 % below the OMZ due to increasing fractions of coarser particles (Mosch et al., 2012). Given  
5 that POC content correlates inversely with grain size (Mayer, 1994; Bergamaschi et al.,  
6 1997), higher contents would be predicted on the shelf relative to the OMZ. In reality, POC is  
7 < 5 % in shallower waters and >15 % in the OMZ (Fig. 4). We can therefore assume that the  
8 ratio of organic carbon to particle surface area (OC/SA) is likely to be lower on the shelf  
9 compared to the OMZ. Low OC/SA ratios indicate organic matter in a more advanced state of  
10 diagenetic alteration, possibly by sorptive preservation or physical protection within  
11 mesopores (Keil et al., 1994, Mayer, 1994; Hedges et al., 1999). We can be confident that the  
12 OC/SA ratio is largely unaffected by differences in the structural composition and reactivity  
13 of POC, since organic matter on the margin is almost entirely marine-derived (Arthur et al.,  
14 1998; Reimers and Suess, 1983b). The evidence suggests that benthic mineralization is more  
15 complete on the shelf compared to the OMZ.

16 Results from biochemical studies dovetail with this idea. Spatial differences in the quality of  
17 organic matter on the shelf and slope have been described (Levin et al., 2002; Niggemann and  
18 Schubert, 2006; Lomstein et al., 2009). These workers found the highest amino acid content  
19 of sedimentary organic matter (i.e. 'fresher' material) on the outer shelf and within the OMZ  
20 (ca. 130 – 360 m). Relatively low values were reported for the middle shelf, indicating more  
21 degraded material. Sediments from the Arabian Sea OMZ are also enriched in high-quality  
22 hydrolysable amino acids (Koho et al., 2013). Similarly, more extensive diagenetic alteration  
23 of organic matter on the Peru shelf relative to the OMZ has been inferred from the amino acid  
24 degradation index (Lomstein et al., 2009). Enhanced carbon preservation in the OMZ has  
25 been noted previously, and detected as the formation of insoluble humin termed 'proto-  
26 kerogen' (Reimers and Suess (1983a,b). Considering these results collectively, the low POC  
27 content and CBE on the shelf seem to be rooted in the quality of buried material.

28 Prolonged exposure of sediments to O<sub>2</sub> strongly modulates amino acid and aldose  
29 distributions in sediments, thereby decreasing the quality and quantity of buried material  
30 (Hedges et al., 1999). Furthermore, OC/SA ratios and CBE are inversely correlated with the  
31 oxygen exposure time (OET) of organic matter (Hartnett et al., 1998; Hedges et al., 1999).  
32 Whilst the significance of bottom water O<sub>2</sub> on carbon preservation remains controversial

1 (Demaison and Moore, 1980; Pedersen and Calvert, 1990; Canfield, 1994; Hedges and Keil,  
2 1995; Hulthe et al., 1998; Burdige, 2007), the presence of O<sub>2</sub> could explain the low OC/SA  
3 ratios and CBEs on the Peruvian shelf in a similar way as described for the Arabian Sea OMZ  
4 (Keil and Cowie, 1999). Although shelf bottom waters were anoxic at the time of sampling,  
5 periodic intrusions of oxygenated water occasionally lead to a deepening of the upper edge of  
6 the OMZ to 200 m or more (e.g. Levin et al., 2002). The frequency and duration of these  
7 episodes can be several months, driven by seasonal and sub-seasonal anomalies in  
8 oceanographic conditions such as positive ENSO periods and the passage of coastal trapped  
9 waves (Gutiérrez et al., 2008). During these events, bottom water O<sub>2</sub> concentrations can vary  
10 by several tens of μM within days or weeks (Gutiérrez et al., 2008), leading to an increase in  
11 the OET of organic matter.

12 Oxygenation is followed by an increase in macrozoobenthos species richness, density,  
13 bioturbation potential, and the construction of sediment burrows and galleries that could  
14 further increase the OET of organic matter (Tarazona et al., 1988; Gutiérrez et al., 2008). This  
15 has been observed offshore Chile, where prolonged ventilation leads to a switch in the  
16 polychaete assemblage from tube-dwelling, interface feeders to burrowing, deposit feeders  
17 (Gutiérrez et al., 2008; Sellanes et al., 2007). This sequence of events likely explains the non-  
18 zero bioturbation coefficients on the shelf (Table S2). It also fits with the previous  
19 biochemical data since sediments with episodic exposure to O<sub>2</sub> tend to display  
20 biogeochemical characteristics of permanently oxic settings (Aller, 1994). Redox oscillations  
21 caused by the arrival of burrowing animals may further enhance mineralization of refractive  
22 organic compounds via priming or co-oxidation pathways, leading to a further reduction in  
23 CBE (Aller, 1998; Canfield, 1994; Hulthe et al., 1998). On the basis of the information  
24 currently available, therefore, we argue that occasional bathing of shelf sediments with  
25 oxygenated bottom waters is a determining, if not dominating, factor driving the low CBE  
26 observed there.

### 27 **5.1.2. High CBE below the OMZ**

28 Oceanographic conditions below the OMZ are relatively quiescent and more conducive to  
29 steady state diagenesis (Scholz et al., 2011). The OET of organic matter in sediments at the  
30 deepest sites was calculated by dividing the O<sub>2</sub> penetration depths by the <sup>210</sup>Pb<sub>xs</sub>-derived  
31 sediment accumulation rates. Penetration depths calculated using the relation of Cai and  
32 Sayles (1996) were 4 mm at 11°S (St. 6) and 7 mm at 12°S (St. 10). The corresponding OETs

1 are 8 and 12 years (respectively). An empirical relationship between CBE and OET derived  
2 for a range of marine settings predicts a CBE of around 20 % for these OETs although there is  
3 considerable uncertainty associated with this trend (Hartnett et al., 1998). This is similar to  
4 the normal oxic settings in Fig. 8 and much lower than the determined value of >60 %. Hence,  
5 factors other than the OET of carbon in the sediment must influence the CBE at the deep sites.

6 Our CBE calculations at the deep sites may be influenced by lateral particle transport and  
7 sediment mobilization by current-induced resuspension. The increase in sediment mass and  
8 aluminium accumulation below the OMZ suggests that terrestrial lithogenic material is  
9 preferentially deposited there. The shelf area between 6 and 10°S is a major area of sediment  
10 reworking and winnowing by the poleward-flowing Peru Undercurrent with average near-  
11 bottom velocities of 8-9 cm s<sup>-1</sup> (Suess et al., 1987; Chaigneau et al., 2013). Fine-grained  
12 biogenic debris from this area may undergo multiple deposition/resuspension cycles as it is  
13 redistributed down the slope in the benthic boundary layer in a southerly direction (Krissek et  
14 al., 1980; Suess et al., 1987; Kim and Burnett, 1988; Arthur et al., 1998). Furthermore,  
15 sediment winnowing at 11 and 12°S occurs in discrete depth intervals in the depth range  
16 between 400 and 800 m due to the presence of near-critical topographic slopes (e.g. Mosch et  
17 al., 2012). At near critical slopes, internal waves can resuspend sediment through the  
18 generation of bores from internal tides which is then transported upslope or downslope  
19 (Hosegood and van Haren, 2004; Martini et al., 2013). This is identifiable from the low mass  
20 accumulation rates at St. 8 at 12°S (Table 2) and the characteristic presence of foraminiferal  
21 sands and phosphorites that form under these conditions (Glenn and Arthur, 1988; Reimers  
22 and Suess, 1983b; Arthur et al., 1998; Mosch et al., 2012). Non-linear internal wave trains  
23 have also been observed on the shelf at 11°S and 12°S causing short pulses of elevated near-  
24 bottom velocities (Sommer et al., 2014). It is thus not unreasonable to argue that sediment  
25 winnowing higher up on the slope contributes to the sediment that accumulates below the  
26 OMZ. In that case, the OET of organic matter would be enhanced during transit in the benthic  
27 boundary layer. Consequently, POC deposited at the deeper sites investigated in this study is  
28 likely to be in a more advanced state of degradation than particles that settle vertically,  
29 thereby leading to CBE that are apparently elevated. Arthur et al. (1998) argued along similar  
30 lines to explain the presence of highly degraded organic matter at sites close to ours.  
31 Unusually high CBEs in the southern California Basins suggest that particle transport  
32 mechanisms may play wider role in carbon preservation patterns in slope sediments (Berelson  
33 et al., 1996).

## 1 5.2 Carbon mineralization in the water column

2 A comparison of the rain rate and PP estimates from the ROMS-BioEBUS model shows that  
3 only a minor fraction of PP reaches the seafloor beyond the middle shelf (Fig. 7c). The true  
4 fraction may be even lower since modelled PP is 2 to 3 times below the range of 250 to 400  
5  $\text{mmol m}^{-2} \text{d}^{-1}$  reported previously (Walsh, 1981; Quiñones et al. 2010 and references therein).  
6 Robust PP estimates close to the coastline are impeded by the relatively coarse spatial  
7 resolution ( $1/9^\circ$ ) in the model which cannot accurately resolve nearshore processes. The  
8 model also represents climatological conditions (i.e. interannual steady state), whereas PP  
9 during neutral or cold (La Niña) ENSO phases (this study) may deviate from the mean value  
10 (Ryan et al., 2006). Nonetheless, based on the data in Fig. 7c, it appears that the Peruvian  
11 margin broadly behaves as an open ocean setting when compared to existing empirical  
12 relationships relating PP to rain rate (e.g. Betzer et al., 1984).

13 The rate at which organic matter is respired during transit through the water column is usually  
14 calculated using sediment trap data (Martin et al., 1987). The unrespired fraction of export  
15 production has been widely described using the following function:

$$16 \quad F(z) / EP = (z/100)^{-b} \quad (7)$$

17 where EP is the export production, typically defined at 100 m,  $F(z)$  is the sinking flux at  
18 depth,  $z$  (m), below 100 m, and  $b$  is the dimensionless attenuation coefficient (Martin et al.,  
19 1987). Low  $b$  indicates slow degradation in the water column and a high fraction of export  
20 production reaching the sediment and vice-versa. A mean  $b$  of 0.86 for oxic open-ocean  
21 waters was derived by Martin et al. (1987), which is similar to  $0.82 \pm 0.16$  quoted by Berelson  
22 (2001) for a range of marine settings. Primeau (2006) proposed a lower  $b$  of  $0.70 \pm 0.08$  based  
23 on a reanalysis of Berelson's data. A recent study in the North Atlantic using free-drifting  
24 sediment traps also reported a  $b$  of 0.70 (Giering et al., 2014).

25 We estimated  $b$  by fitting the calculated rain rates at  $11^\circ\text{S}$  and  $12^\circ\text{S}$  to the following function  
26 analogous to Eq. (7):

$$27 \quad \text{RRPOC}(z) / \text{EP}(z) = (z/101)^{-b} \quad (8)$$

28 The EP at each station was determined by multiplying the PP estimate from the pelagic model  
29 by the ratio of particle export to primary production ( $pe$  ratio, Dunne et al., 2005). The  $pe$   
30 ratio was assumed to be constant across the margin and was calculated as  $\text{PP} / \text{RRPOC}$  using  
31 data from St. 2 ( $12^\circ\text{S}$ ). This station was taken as the reference point since the water depth

1 (101 m) is approximately 100 m. The derived  $pe$  ratio was 0.26; consistent with observations  
2 that most PP in the Humboldt system is mineralized in the surface mixed layer under non-El-  
3 Niño conditions (Quiñones et al. 2010 and references therein). The two shallowest stations  
4 with water depth  $< 101$  m were excluded from the analysis in addition to St. 8 since, as  
5 mentioned, we suspect that sediment resuspension by bottom currents is important there. To  
6 offset the potential bias in our RRPOC estimates due to seasonal variability in primary  
7 production, the PP was averaged over the period corresponding to the cruise and one month  
8 previous (see Appendix).

9 The best fit to Eq. (8) shown in Fig. 9 was obtained with  $b = 0.54 \pm 0.14$  (NonlinearModelFit  
10 function in MATHEMATICA). The  $b$  value considering data from  $12^{\circ}\text{S}$  only is  $0.85 \pm 0.25$  (the  
11 result for  $11^{\circ}\text{S}$  is not statistically significant at the 95 % level). Our derived  $b$  coefficients thus  
12 tend toward the higher open-ocean composite estimates of Martin (1987) and Primeau (2006).  
13 Yet, previous studies indicate that respiration of organic matter is significantly reduced in  
14 oxygen-deficient water columns (Martin et al., 1987; Devol and Hartnett, 2001; Van Mooy et  
15 al., 2002). For example, a  $b$  of 0.32 was determined for the Peruvian OMZ at  $15^{\circ}\text{S}$  using  
16 sediment trap data (Martin et al., 1987). Devol and Hartnett (2001) calculated a value of 0.36  
17 for the Mexican margin using benthic carbon oxidation rates and burial fluxes. This agrees  
18 with 0.40 derived using moored sediment trap data from the same location (Van Mooy et al.,  
19 2002). These workers supported their fieldwork with laboratory experiments showing that  
20 natural particulate material collected at the base of the euphotic zone was degraded less  
21 efficiently under anoxic versus oxic conditions. A notable exception to these studies is the  $b$   
22 value of 0.79 derived for the Arabian Sea OMZ using sediment traps (Berelson, 2001).  
23 Nonetheless, based on these findings, a much lower  $b$  coefficient for our composite data set  
24 may have been expected.

25 We propose that the high  $b$  determined in this study is attributed to the multiple  
26 resuspension/deposition of slope sediments by internal waves discussed above. Resuspension  
27 enhances the particle residence time in the water column and shifts the site of labile POC  
28 mineralization away from the sediments. This will reduce the benthic DIC flux and thus lower  
29 the calculated RRPOC. This explanation is consistent with unusually high CBE below the  
30 OMZ. The low rain rate calculated for St. 8 at  $12^{\circ}\text{S}$  further exemplifies the importance of  
31 sediment reworking on the calculated rain rates (Fig. 8). By implication, particle transport  
32 through the water column on the Mexican margin and at the deep offshore station at Peru

1 (15°S) is more controlled by vertical settling, resulting in shorter residence times and  
2 enhanced carbon preservation. The good agreement between the *b* coefficients determined  
3 independently by traps and benthic data from Mexico supports this idea (Devol and Hartnett,  
4 2001; Van Mooy et al., 2002). In contrast, the latitudinal differences in *b* at Peru (this study;  
5 Martin et al., 1987) could simply reflect bias from comparing benthic- and pelagic-derived  
6 rain rates from a complex margin system displaying high temporal variability in productivity  
7 (Walsh et al., 1981).

## 8 **5 Conclusions**

9 Fieldwork undertaken on the fascinating Peruvian margin has improved our understanding of  
10 POC cycling in anoxic margin sediments and expanded the existing CBE database. Our key  
11 findings are: (1) Low CBE in shelf sediments is driven by the episodic intrusion of  
12 oxygenated waters. This is consistent with the existing CBE database if the shelf can be  
13 geochemically classified as a ‘normal’ setting despite fluctuating bottom water O<sub>2</sub> levels.  
14 Previous biochemical analyses suggest that this is the case. (2) High CBE in oxygenated  
15 waters (O<sub>2</sub> >20 μM) below the OMZ is caused the deposition of reworked, degraded material  
16 originating from sites higher up on the slope. They are, therefore, not representative of  
17 oxygenated sediments. (3) Low oxygen concentrations in the OMZ below 200 m are  
18 associated with the preservation of POC in sediments, although the redistribution and  
19 accumulation of reworked sediments at these depths needs to be more clearly examined. (4)  
20 POC rain rates are not overly enhanced by low oxygen concentrations compared to other  
21 oxygen-deficient environments.

22 Our conclusions regarding this last point require further validation with particle fluxes  
23 measurements from sediment traps. Trap data may reveal lower rates of POC mineralization  
24 in the water column, as observed in other low-oxygen settings. If this turns out to be the case,  
25 it would imply either that POC fluxes are either subject to high temporal variability or that a  
26 fraction of labile material resuspended from the sea bed is degraded in the benthic boundary  
27 layer and exported down the slope. The increase in sedimentation rates and high CBE below  
28 the OMZ supports the latter alternative. These investigations would benefit from an improved  
29 understanding of particle disaggregation by zooplankton and subsequent stimulation of the  
30 microbial loop (Giering et al., 2014).

1 A major outstanding barrier for deriving annual carbon and nutrient budgets on the Peruvian  
2 margin is the uncertainty associated with non-steady state conditions. Inter- and intraannual  
3 oceanographic anomalies dictate the depth and intensity of oxygen-deficiency, nutrient levels  
4 and *Thioploca* spp. biomass (Gutiérrez et al., 2008). Consequently, the contribution of the  
5 sediments to primary production on short (e.g. days, weeks) and long (e.g. months, years)  
6 time scales is completely unknown. This is a topic that could be tackled by incorporating  
7 benthic processes into the pelagic model ROMS-BioEBUS. Model predictions would be  
8 strengthened with benthic flux data collected during the low productivity season (austral  
9 winter).

## 10 **Acknowledgements**

11 We thank the captains and crew of RV Meteor cruises M77 and M92 for their assistance  
12 during the fieldwork. Biogeochemical analyses were performed with the invaluable assistance  
13 of B. Domeyer, M. Dibbern, R. Ebbinghaus, R. Suhrberg, S. Trinkler and V. Thoenissen.  
14 Preparation and deployment of large instruments was smoothly achieved with the wizardry of  
15 S. Kriwanek, A. Petersen, M. Türk and S. Cherednichenko. We would also like to thank R.  
16 Schulz from the Laboratory for Radioisotopes (LARI) at the University of Göttingen for the  
17 <sup>210</sup>Pb analyses. This work is a contribution of the Sonderforschungsbereich 754 "Climate –  
18 Biogeochemistry Interactions in the Tropical Ocean" ([www.sfb754.de](http://www.sfb754.de)) which is supported by  
19 the Deutsche Forschungsgemeinschaft.

## 20 **Appendix A: Uncertainties in CBE calculations**

21 The burial efficiency of carbon is the basic quantitative metric which allows comparisons of  
22 carbon preservation at different locations. Quantification of the CBE requires at least two of  
23 the following three pieces of information, (i) the rain rate of organic carbon to the sediment,  
24 (ii) the rate of carbon burial at the sediment depth where POC content remains constant, and  
25 (iii) the depth-integrated rate of organic carbon oxidation (Burdige, 2007). That is, at steady-  
26 state, (i) = (ii) + (iii). They are typically quantified using (in the same order) (i) sediment trap  
27 particle fluxes, (ii) sedimentation rates (using radioactive isotopes) combined with carbon  
28 content measurements, and (iii) stoichiometric mass balances, diagenetic models or benthic  
29 fluxes. Each of these approaches integrates the carbon flux over very different time scales;



1 from days to weeks for traps to hundreds or thousands of years for burial (Burdige, 2007).  
2 This temporal decoupling creates uncertainty which may affect CBE estimates.

3 Our calculated CBE rely on the use of benthic data only (i.e. (ii) and (iii) above) as opposed to  
4 sediment trap fluxes. It is well known that sediment trap data have multiple sources of  
5 uncertainty (Buesseler et al., 2007). Traps only capture the settling flux on time scales of  
6 deployment, typically days to weeks, which may be insufficient to capture temporal  
7 variability (Haake et al., 1992). Traps may also underestimate the particle flux in water depths  
8 < 1500 m due to high lateral current velocities (Yu et al., 2001), potentially leading to an  
9 overestimate of fluxes further offshore. This effect is exacerbated over the shelf and upper  
10 slope where particles are transported in the benthic boundary layer (Jahnke et al., 1990).  
11 These dynamics may be particularly pertinent for the Peru margin where sediments are  
12 frequently resuspended by bottom currents and transported down the slope (Reimers and  
13 Suess, 1983c). Nonetheless, sedimentation rate and carbon oxidation rate calculations are not  
14 free from their own uncertainties, as discussed in the subsequent paragraphs.

15 Benthic chambers are arguably the best tools to estimate the exchange of solutes between the  
16 sediments and the water column (Tengberg et al., 2005). Yet, as for traps, DIC flux may  
17 display short-term (sub-annual) variability via changes in productivity and thus not truly  
18 reflect the long-term mean degradation rate. Mean PP estimates using the pelagic model do  
19 reveal substantial intraannual variability on the Peru margin (Fig. S4). Both campaigns at  
20 11°S and 12°S took place toward the end of austral summer, that is, the high productivity  
21 season, which suggests a bias in our DIC fluxes towards higher values (Echevin et al., 2008).  
22 However, because benthic carbon mineralization rates do not respond quantitatively and  
23 synchronously to changes in rain rate, it is not possible to accurately ascertain if this timing  
24 adversely affects our assumption that the measured DIC flux accurately represents the mean  
25 flux. The time scale of the bulk organic carbon mineralization is determined by the reactivity  
26 of the individual biomolecules which vary over many orders of magnitude (Middelburg,  
27 1989). Experiments with fresh phytoplankton have shown that approximately 50 % of organic  
28 carbon degrades rapidly within 1 month of deposition on the seafloor with the other 50 %  
29 requiring many months or years to degrade (Westrich and Berner, 1984). This implies that  
30 variability in the measured benthic DIC fluxes will largely reflect the previous month of  
31 deposition of the labile POC fraction. In that regard, the benthic DIC flux provides a more  
32 attenuated estimate of changes in rain rate than sediment trap data. Based on the modelled

1 primary production rates during the sampling months, which were around 25 % higher than  
2 the annual mean (Fig. S4), we tentatively estimate that the measured DIC fluxes at 12°S are  
3 roughly 25 % higher than the long-term average. The analytical error on the DIC flux  
4 calculation from TA and pCO<sub>2</sub> measurements is negligible by comparison. Correcting the  
5 DIC flux for seasonal variability would increase our CBE estimates by around 4 to 5 % on the  
6 shelf and 5 to 7 % in deeper waters. Strictly, though, the mean DIC flux for the last ca. 100  
7 years would be required to be consistent with the burial data.

8 Artifacts in flux estimates due to enclosure of bottom water by benthic chambers have been  
9 discussed extensively in the literature (e.g., Hammond et al., 1996; Tengberg et al., 2005).  
10 Uncertainty in chamber volume, leakage and improper alteration of the hydrodynamic regime  
11 inside the chambers all influence our confidence in any particular concentration measurement  
12 or flux estimate. We can be reasonably confident that leakage through the bottom of the  
13 chambers in contact with the sediments did not occur at the sampling stations. Silicate  
14 (assumed conservative tracer) and O<sub>2</sub> (optode) concentration gradients inside the chambers  
15 were linear and showed no evidence of infiltration of chamber water by the outside bottom  
16 water (Sommer et al., unpub. data). Furthermore, the surface sediments were cohesive and  
17 porous along the whole margin (Table 1), allowing penetration of the benthic chambers to 8 to  
18 10 cm below the sediment surface and rendering leakage unlikely. Yet, we cannot rule out the  
19 possibility that the measured DIC fluxes deviated from the true fluxes due to changes in water  
20 flow across the sediment-water interface. This artefact is mostly prominent in sandy  
21 sediments where current-driven advection through the surface layers contributes significantly  
22 to solute exchange between sediments and seawater (Jahnke et al., 2000). The cohesive and  
23 fine-grained sediments (sandy mud to slightly sandy mud) at Peru typically have low  
24 permeability where molecular diffusion dictates the benthic flux (Huettel et al., 1996). Thus,  
25 error in the DIC flux due to chamber artifacts as well as seasonal variability is likely to be  
26 much smaller than the difference in DIC flux measured in the two chambers during each  
27 lander deployment, that is, due to seafloor heterogeneity (Table 2).

28 Our POC accumulation rates have a relative error determined by the uncertainty in  $\omega_{acc}$  and  
29 POC content. The uncertainty in POC content was assumed to be  $\pm 20$  %, mainly due to data  
30 scatter. Whilst this is realistic for most of sites investigated here, productivity and sediment  
31 POC content have increased on the Peruvian margin in the last 200 years coincident with  
32 expansion of the OMZ driven by a northward displacement of the Intertropical Convergence

1 Zone (Gutiérrez et al., 2009). This is clearly seen in the upper 10 cm of the outer shelf and  
2 OMZ sediments (Fig. 4) and undermines our ability to accurately define the depth where the  
3 POC content shows little change with sediment depth. The regime shift is not recorded at the  
4 middle shelf sites because the high sedimentation rates restrict the observable archive to the  
5 last 100 years. Similarly, the deep stations below the OMZ are presumably beyond the sphere  
6 of influence of short-term climactic variations. These sites show the expected decrease in  
7 POC for sediments undergoing steady-state mineralization with very little mixing by  
8 bioturbation. For the stations affected by the regime shift (St. 4 to 7), we calculated the CBE  
9 based on the average POC content in this recent layer (upper ~10 cm) where our  $^{210}\text{Pb}_{\text{xs}}$   
10 measurements were made. A 50 % decrease in POC content at these stations would lower the  
11 CBE by 20 to 40 %. Note that higher POC mineralization rates associated with the increase in  
12 POC content over recent centennial time scales should be accurately reflected in the DIC flux.  
13 Diffusive path lengths calculations (Lasaga and Holland, 1976) show that DIC concentrations  
14 in the upper 10 cm will adjust to new depositional conditions at the sediment surface within a  
15 few years only.

16 Sediment accumulation rates ( $\omega_{acc}$ ) were constrained using  $^{210}\text{Pb}_{\text{xs}}$  data (half-life of 22 yr)  
17 using a model that utilizes a widely used empirical description of bioturbation intensity with  
18 sediment depth (Christensen, 1982). We estimated that  $\omega_{acc}$  are accurate to within  $\pm 20$  % for  
19 the derived bioturbation coefficients (Table S2). Continuously supplied tracers such as the  
20  $^{210}\text{Pb}_{\text{xs}}$  radioisotope have a characteristic time scale equal to about 5 half-lives, that is, ca. 110  
21 yr. Therefore, our accumulation rates correspond to recent sediments deposited since the  
22 Little Ice Age and are of the same order as those published previously for the same area  
23 (Reimers and Suess, 1983c; Kim and Burnett, 1988; Levin et al., 2002; Gutiérrez et al., 2009).  
24 They are not applicable to the older underlying sediment, where mass accumulation rates are  
25 lower and have undergone hiatuses in the past (Reimers and Suess, 1983b; Gutiérrez et al.,  
26 2009; Schönfeld et al., 2014). However, sedimentation and bioturbation rates inferred from  
27 radioisotopes with vastly different half-lives often differ by an order-of-magnitude or more  
28 (e.g. Smith et al., 1993). Bioturbation coefficients of ca.  $100 \text{ cm}^2 \text{ yr}^{-1}$  were derived from  $^{234}\text{Th}$   
29 (half-life 24 d) distributions below the OMZ on the Peru margin (Levin et al., 2002), which is  
30 four orders-of-magnitude higher than we determined using  $^{210}\text{Pb}_{\text{xs}}$ . Given the low  
31 sedimentation and bioturbation rates at the deeper stations, the  $^{210}\text{Pb}_{\text{xs}}$  distributions may thus

1 indicate higher rates of sediment mixing and lower sedimentation rates than derived with the  
2 model.

3 We used the anthropogenic enrichment peak of the nuclide  $^{241}\text{Am}$  as an independent time  
4 marker to validate the lead chronology (Fig. 2).  $^{241}\text{Am}$  originates from nuclear tests in the  
5 southern hemisphere beginning in the early 1950s. At four stations,  $\omega_{acc}$  was estimated by  
6 dividing the depth of the  $^{241}\text{Am}$  peak by 60 years without correcting for compaction, resulting  
7 in rates of  $0.15 \text{ cm yr}^{-1}$  at St. 5, and  $0.05 \text{ cm yr}^{-1}$  at St. 4, 7, and 9. No  $^{241}\text{Am}$  was detectable at  
8 the other stations. These rates agree with the  $^{210}\text{Pb}_{xs}$  values to within 10 to 50 % (Table 2).  
9 Although  $\omega_{acc}$  estimated this way are only approximate, they confirm the order-of-magnitude  
10 values determined by the  $^{210}\text{Pb}_{xs}$  model. Furthermore, it is obvious that the  $^{234}\text{Th}$ -derived  
11 bioturbation coefficient of  $100 \text{ cm}^2 \text{ yr}^{-1}$  does not capture the activity of the  $^{210}\text{Pb}_{xs}$  data (red  
12 curve, Fig. 2). The high  $^{234}\text{Th}$ -derived coefficient is very likely a model artifact caused by the  
13 use of short-lived radioisotopes to infer mixing rates in weakly mixed sediments (Lecroart et  
14 al., 2010).

15 Clearly, there are multiple potential sources of uncertainty in CBE estimates based on DIC  
16 fluxes and POC burial fluxes. Yet, whilst concerns remain regarding both short- and long-  
17 term variability in fluxes, we believe our derived CBEs are robust on decadal time scales. The  
18 mean relative error in CBE across all stations is around 40 % (at  $12^\circ\text{S}$ ); a fair representation  
19 of the combined uncertainties.

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7

1 Table 1: Stations and instruments deployed on the Peruvian margin. Water depths were  
 2 recorded from the ship's winch. Bottom water temperature and dissolved oxygen are CTD  
 3 measurements. Surface (0.5 cm, 11°S; 0.25 cm, 12°S) porosity values are also given.

Station	Instrument <sup>a</sup>	Date	Latitude (S)	Longitude (W)	Depth (m)	Temp. (°C)	Porosity (-)	O <sub>2</sub> <sup>b</sup> (°C)
11°S								
1	BIGO 5	15.11.2008	11°00.02'	77°47.72'	85	12.7		bdl
	MUC 52	12.11.2008	10°59.99'	77°47.40'	78		0.93	
2	BIGO-T6 <sup>c</sup>	29.11.2008	10°59.80'	78°05.91'	259	12.2	0.95	bdl
3	BIGO 1	05.11.2008	11°00.00'	78°09.92'	315	11.6		bdl
	MUC 19	03.11.2008	11°00.01'	78°09.97'	319		0.95	
4	BIGO 3	20.11.2008	11°00.02'	78°15.27'	397	9.6		bdl
	MUC 33	06.11.2008	11°00.00'	78°14.19'	376		0.93	
5	BIGO 2	05.11.2008	11°00.01'	78°25.55'	695	6.7		6.2
	MUC 25	04.11.2008	11°00.03'	78°25.60'	697		0.84	
6	BIGO 6 <sup>c</sup>	29.11.2008	10°59.82'	78°31.05'	978	4.7		40.3
	MUC 53	13.11.2008	10°59.81'	78°31.27'	1005		0.78	
12°S								
1	BIGO I-II	15.01.2013	12°13.506'	77°10.793'	74	14.0		bdl
	MUC 13	11.01.2013	12°13.496'	77°10.514'	71		0.96	
	MUC 39	25.01.2013	12°13.531'	77°10.061'	72		0.96	
2	BIGO I-V	27.01.2013	12°14.898'	77°12.705'	101	13.8		bdl
	MUC 16	12.01.2013	12°14.897'	77°12.707'	103		0.97	
3	BIGO II-IV	20.01.2013	12°16.689'	77°14.995'	128	13.7		bdl
	MUC 46	27.01.2013	12°16.697'	77°15.001'	129		0.98	
4	BIGO I-I	11.01.2013	12°18.711'	77°17.803'	142	13.4		bdl
	MUC 10	09.01.2013	12°18.708'	77°17.794'	145		0.96	
5	BIGO I-IV	23.01.2013	12°21.502'	77°21.712'	195	13.0		bdl
	MUC 45	27.01.2013	12°21.491'	77°21.702'	195		0.96	
6	BIGO II-II	12.01.2013	12°23.301'	77°24.284'	244	12.0		bdl
	MUC 5	07.01.2013	12°23.329'	77°24.185'	253		0.96	
	MUC 34	23.01.2013	12°23.300'	77°24.228'	244		0.96	
7	BIGO II-I	08.01.2013	12°24.905'	77°26.295'	306	12.5		bdl
	MUC 9	08.01.2013	12°24.894'	77°26.301'	304		0.95	
	MUC 36	24.01.2013	12°25.590'	77°25.200'	297		0.95	
8	BIGO II-V	24.01.2013	12°27.207'	77°29.517'	409	10.6		bdl
	MUC 23	15.01.2013	12°27.198'	77°29.497'	407		0.90	
	MUC 24	15.01.2013	12°27.195'	77°29.483'	407		-	
9	BIGO II-III	16.01.2013	12°31.366'	77°34.997'	756	5.5		19
	MUC 17	13.01.2013	12°31.374'	77°35.183'	770		0.84	
10	BIGO I-III	19.01.2013	12°34.911'	77°40.365'	989	4.4		53
	MUC 28	19.01.2013	12°35.377'	77°40.975'	1024		0.74	

4 <sup>a</sup> The first Roman numeral of the BIGO code for 12°S denotes the lander used and the second  
 5 to the deployment number of that lander. For 11°S, the Arabic number refers to the  
 6 deployment number. The lander at St. 2 is denoted BIGO-T (see text).

7 <sup>b</sup> bdl = below detection limit (5 µM).

8 <sup>c</sup> These deployments occurred during leg 2 of cruise M77. All others from 11°S took place  
 9 during leg 1.

10



Table 2. Measured and modelled carbon fluxes and burial efficiencies.

	Middle shelf		Outer shelf			OMZ			Below OMZ	
12°S transect	St. 1	St. 2	St. 3	St. 4	St. 5	St. 6	St. 7	St. 8	St. 9	St. 10
<i>Measured data</i>										
Water depth, m	74	101	128	142	195	244	306	409	756	989
Sediment accumulation rate ( $\omega_{acc}$ ), cm yr <sup>-1</sup> <sup>a</sup>	0.45	0.32	0.20	0.04	0.10	0.07	0.05	0.011	0.035	0.06
Mass accumulation rate (MAR), g m <sup>-2</sup> yr <sup>-1</sup> <sup>b</sup>	1800	768	600	128	320	182	150	44	259	540
POC content at 10 cm (POC <sub>10</sub> ), % <sup>c</sup>	3.3	3.8	7.2	8.6	12.8	14.2	15.5	5.2	4.0	1.8
POC accumulation rate at 10 cm (POC <sub>AR10</sub> ), g C m <sup>-2</sup> yr <sup>-1</sup> <sup>d</sup>	60	29	34	11	41	26	23	2	10	10
Benthic DIC flux ( $J_{DIC}$ ), mmol m <sup>-2</sup> d <sup>-1</sup> <sup>e</sup>	65.9±21	27.9±4.2	20.4±7	8.0±0.4	3.2±1	4.7±1	2.7±0.1	2.2±0.3	2.8±3	1.2±0.1
POC rain rate (RRPOC), mmol m <sup>-2</sup> d <sup>-1</sup> <sup>f</sup>	79.5±33	34.2±11	28.2±12	10.5±3	12.5±6	10.6±4	8.0±2	2.7±1	5.2±5	3.4±1
Carbon burial efficiency at 10 cm (CBE), % <sup>g</sup>	17±7	19±6	28±12	24±7	74±37	55±23	66±19	19±6	46±48	64±19
<i>Modelled data</i>										
POC accumulation rate at 10 cm, g C m <sup>-2</sup> yr <sup>-1</sup> <sup>h</sup>	59	29	34	9	38	27	26	2	11	12
Benthic DIC flux, mmol m <sup>-2</sup> d <sup>-1</sup>	61.8	27.9	18.0	8.4	5.2	4.9	4.0	2.2	3.3	1.7
POC rain rate, mmol m <sup>-2</sup> d <sup>-1</sup> <sup>j</sup>	75.3	34.5	25.9	10.6	13.9	11.1	10.0	2.6	5.8	4.4
Carbon burial efficiency at 10 cm, % <sup>k</sup>	18	19	30	20	62	56	60	15	43	61
Primary production from ROMS, mmol m <sup>-2</sup> d <sup>-1</sup>	122	115	110	107	101	96	92	87	77	73
<i>11°S transect</i>										
	St. 1					St. 2	St. 3	St. 4	St. 5	St. 6
<i>Measured data</i>										
Water depth, m	85					259	315	397	695	978
Sediment accumulation rate ( $\omega_{acc}$ ), cm yr <sup>-1</sup> <sup>m</sup>	0.3					0.06	0.05	0.05	0.08	0.052
Mass accumulation rate (MAR), g m <sup>-2</sup> yr <sup>-1</sup> <sup>b</sup>	1200					132	150	370	464	343
POC content at 10 cm (POC <sub>10</sub> ), % <sup>n</sup>	2.4					14.2	15.3	12.6	6.8	3.8
POC accumulation rate at 10 cm (POC <sub>AR10</sub> ), g C m <sup>-2</sup> yr <sup>-1</sup> <sup>d</sup>	29					19	23	46	32	13
<i>Modelled data</i>										
POC accumulation rate at 10 cm, g C m <sup>-2</sup> yr <sup>-1</sup> <sup>h</sup>	31					16	17	44	32	16
Benthic DIC flux, mmol m <sup>-2</sup> d <sup>-1</sup> <sup>p</sup>	8.2					7.7	5.9	4.0	1.7	2.1
POC rain rate, mmol m <sup>-2</sup> d <sup>-1</sup> <sup>j</sup>	15.3					11.4	9.8	14.0	9.0	5.9
Carbon burial efficiency at 10 cm, % <sup>k</sup>	47					32	40	71	81	64
Primary production from ROMS, mmol m <sup>-2</sup> d <sup>-1</sup>	112					94	91	88	80	76

- <sup>a</sup> Determined from  $^{210}\text{Pb}_{\text{xs}}$  (see Table S2 in the Supplement). Sedimentation rates at St. 2 (101 m) and St. 6 (250 m) were not measured and instead estimated from the neighbouring stations.  $\omega_{acc}$  has a 20 % uncertainty.
- <sup>b</sup> Calculated as  $\omega_{acc} \times (1 - \phi(L)) \times \rho \times 10000$  ( $\rho$  = dry solid density,  $2 \text{ g cm}^{-3}$ ).
- <sup>c</sup> For St. 8 at  $12^\circ\text{S}$  (409 m) the content at 3 cm was used since the underlying sediment is old, non-accumulating clay. For the OMZ stations the mean POC content in the upper 10 cm was used. This was approximated as follows:  $\text{POC}_{10} (\%) = \frac{1}{10} \int_0^{10} \text{POC}(x) dx$  where  $\text{POC}(x)$  is in %.
- <sup>d</sup> Calculated as  $\text{MAR} \times \text{POC}_{10} / 100$ .
- <sup>e</sup> Mean fluxes calculated from the in situ TA and  $\text{pCO}_2$  measurements in two benthic chambers. No  $\text{pCO}_2$  measurements were made at  $11^\circ\text{S}$ . Errors represent 50 % of the difference of the two fluxes.
- <sup>f</sup> Calculated as  $\text{POC}_{\text{AR}10} (\text{in mmol m}^{-2} \text{ d}^{-1}) + J_{\text{DIC}}$
- <sup>g</sup> Calculated as  $\text{POC}_{\text{AR}10} (\text{in mmol m}^{-2} \text{ d}^{-1}) / \text{RRPOC} \times 100 \%$ . Errors were calculated using standard error propagation rules assuming a 20 % uncertainty in  $\omega_{acc}$  and  $\text{POC}_{10}$ .
- <sup>h</sup> Calculated analogously to footnote d using modelled data.
- <sup>j</sup> Calculated analogously to footnote f using modelled data.
- <sup>k</sup> Calculated analogously to footnote g using modelled data.
- <sup>m</sup> Determined from  $^{210}\text{Pb}_{\text{xs}}$  modelling (See Bohlen et al., 2011).
- <sup>n</sup> For the OMZ stations, the mean POC content in the upper 10 cm was used (see footnote c).
- <sup>p</sup> Calculated as the depth-integrated POC degradation rate (Bohlen et al., 2011).

Table 3. Mean rates of organic carbon accumulation and primary production on the Peruvian margin from this study compared to global averages by Burdige (2007) and Sarmiento and Gruber (2006). Units:  $\text{mmol m}^{-2} \text{d}^{-1}$ .

	11°S	12°S	Burdige (2007) <sup>a</sup>	Sarmiento and Gruber (2006) <sup>b</sup>
POC accumulation				
Shelf (0 – 200 m)	13.8	9.9	4.0	-
Upper slope (200 – 1000 m)	7.2	2.8	1.0	-
Total margin (0 – 1000 m)	6.8	6.1	2.9 (1.2)	1.4
Primary production (0 – 1000 m)	250 – 400 <sup>c</sup>		-	71

<sup>a</sup> From Table 4 and 5 in Burdige (2007) based on a large number of independent studies. The number in parenthesis considers low POC burial rates in sandy sediments.

<sup>b</sup> From Table 6.5.1 in that study.

<sup>c</sup> Range based on previous reports (Walsh, 1981; Quiñones et al. 2010 and references therein).

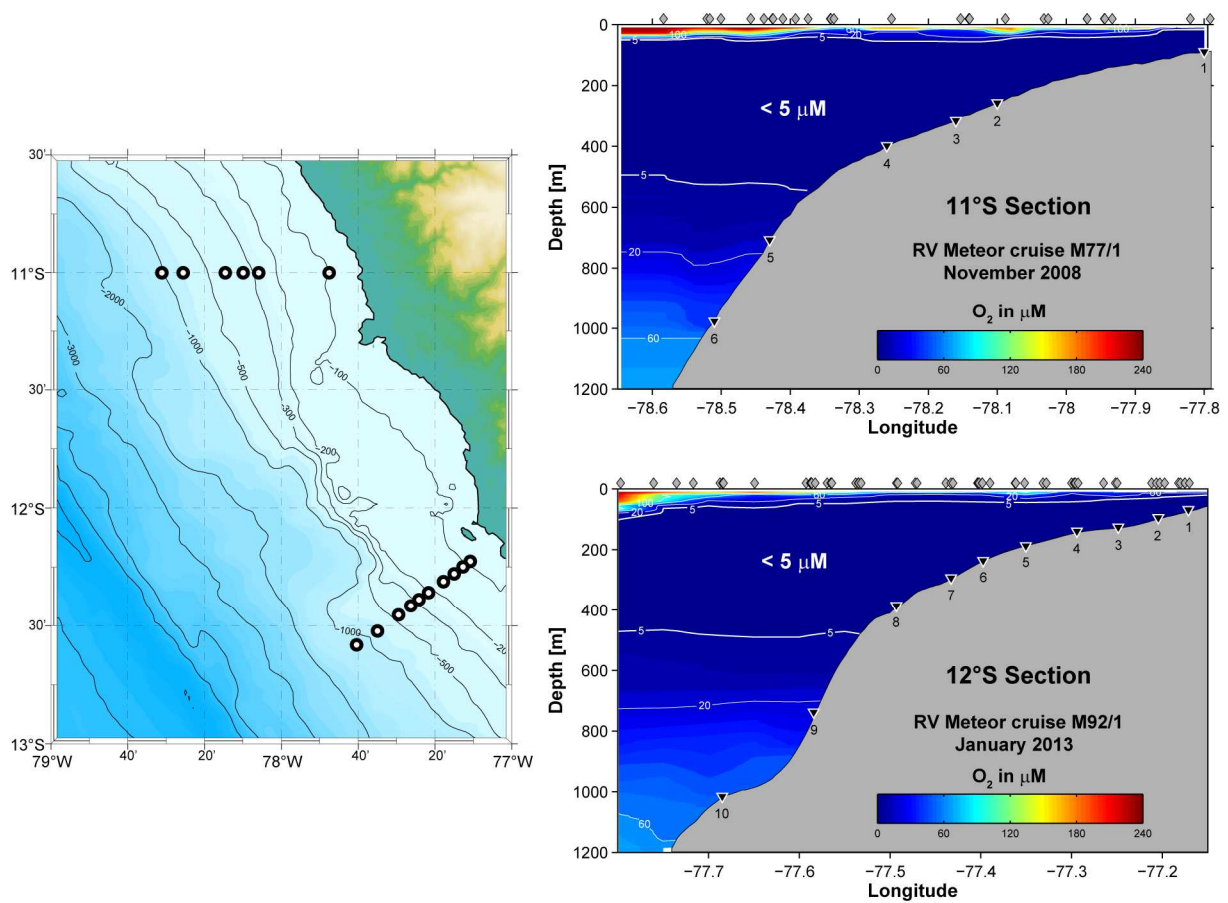


Figure 1. Slope bathymetry (contours in m) and benthic sampling stations on the Peruvian margin at 11°S and 12°S (left). The two panels on the right show cross-sections of dissolved oxygen concentrations ( $\mu\text{M}$ ) measured using the CTD sensor calibrated against Winkler titrations (detection limit 5  $\mu\text{M}$ ). The station locations are indicated by the black triangles and the CTD stations used to make the plots are indicated by the grey diamonds.

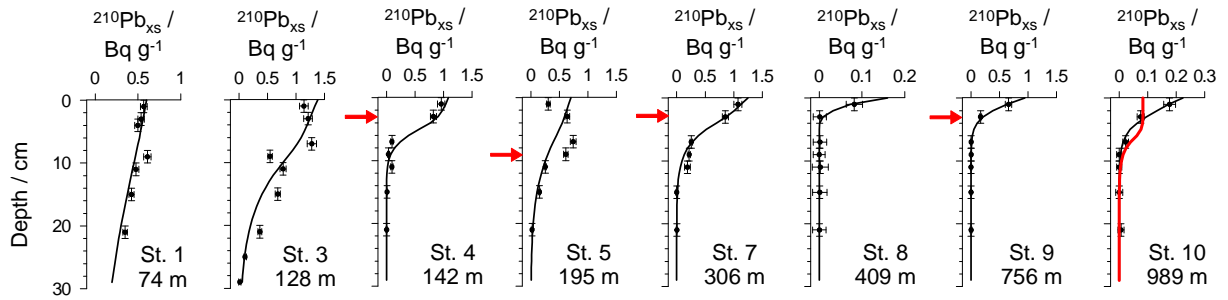


Figure 2. Measured (symbols) and modelled (curves)  $^{210}\text{Pb}_{\text{xs}}$  at  $12^\circ\text{S}$  (see Bohlen et al. (2011) for  $^{210}\text{Pb}_{\text{xs}}$  at  $11^\circ\text{S}$ ). Vertical error bars span the depth interval from where the sample was taken, whereas horizontal error bars correspond to the analytical uncertainty. Derived upper boundary fluxes and bioturbation coefficients are listed in Table S2. The red arrows indicate the profile steps reflecting the detection of  $^{241}\text{Am}$  and indicating the depth-position of the peak with activities as follows: St. 4 =  $3.7 \pm 1.0 \text{ Bq kg}^{-1}$ , St. 5 =  $5.8 \pm 0.99 \text{ Bq kg}^{-1}$ , St. 7 =  $6.6 \pm 0.95 \text{ Bq kg}^{-1}$ , St. 9 =  $2.2 \pm 0.68 \text{ Bq kg}^{-1}$ . The accuracy of the peak depth is defined by the sampling resolution. The red curve at St. 10 shows the results of a model simulation using the  $^{234}\text{Th}$ -derived bioturbation coefficient of  $100 \text{ cm}^2 \text{ yr}^{-1}$  (see Appendix A).

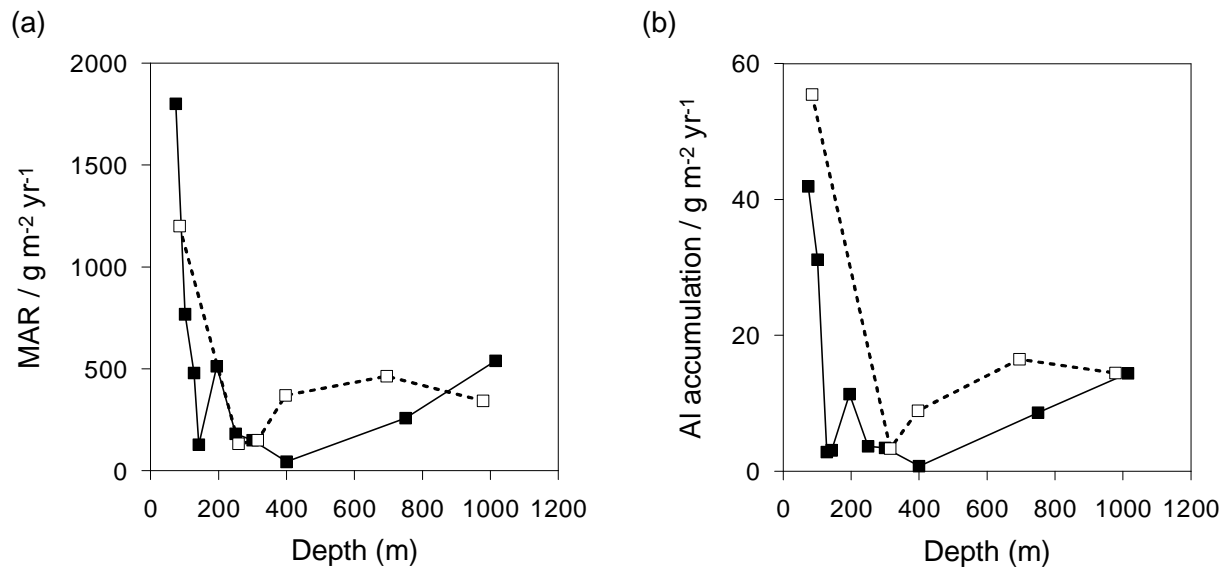


Figure 3. (a) Bulk sediment mass accumulation rates and (b) aluminium accumulation rates at 11°S (open symbols) and 12°S (closed symbols).

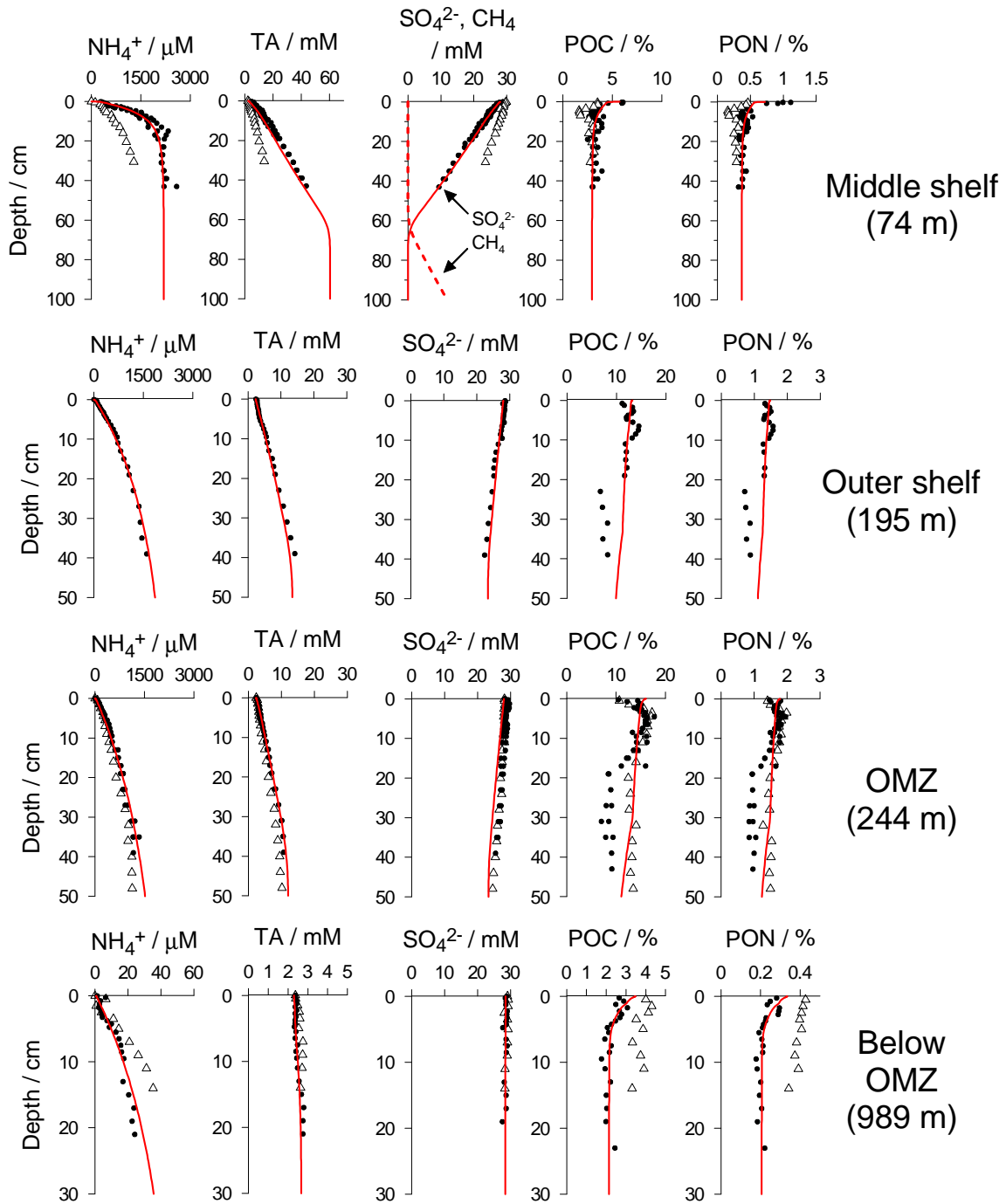


Figure 4. Dissolved and solid phase biogeochemical data for sediment cores from 12°S (filled symbols) with model simulation results (red curves). Four sites are chosen to exemplify the general trends on the middle shelf (St. 1, 74 m), outer shelf (St. 5, 195 m), OMZ (St. 6, 244 m) and below the OMZ (St. 10, 989 m). The full set of data and model results is given by Dale et al. (unpub. data). Also shown (open symbols) are data from three sites along 11°S (St. 1 (85 m), 3 (315 m) and 6 (978 m); Bohlen et al., 2011). For clarity, the simulation curves from 11°S have been omitted and are presented in Bohlen et al. (2011). POC and PON distributions were not shown in that study and are shown for the first time here.

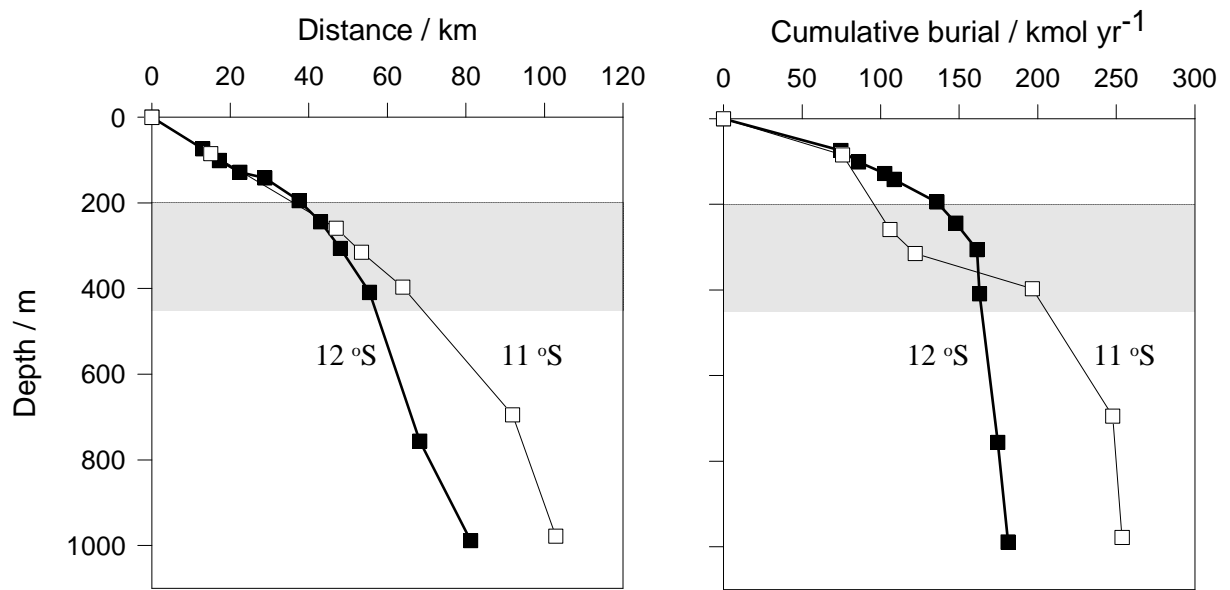


Figure 5. (a) Distance from the coastline versus water depth, and (b) cumulative organic carbon burial at 10 cm depth, ( $POC_{10}$ , measured data, Table 2) along the two transects. The grey shade highlights the OMZ stations (ca. 200 to 450 m).



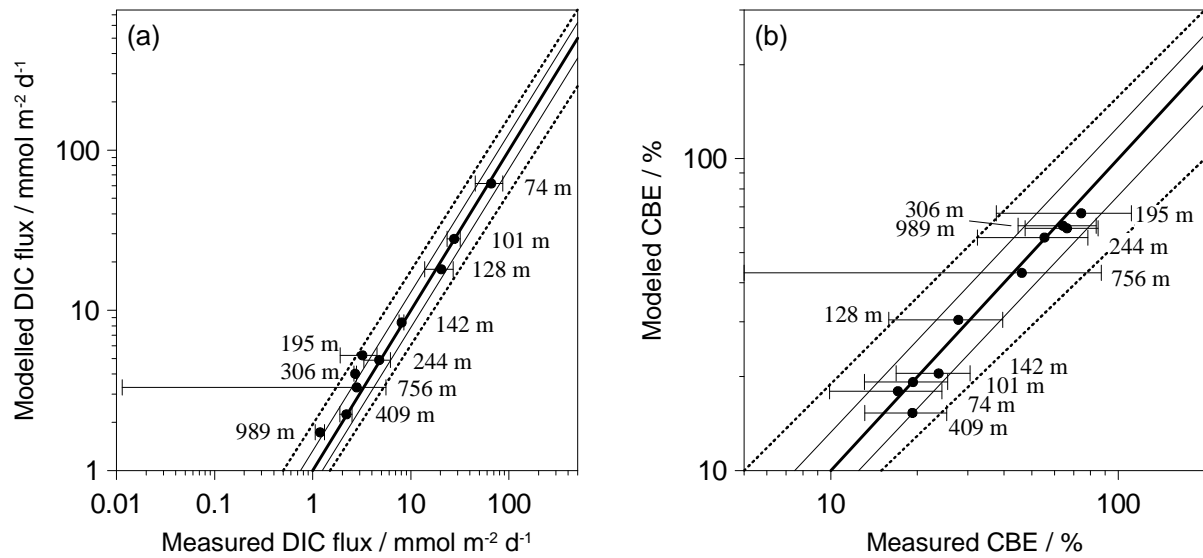


Figure 6. Measured versus modelled (a) DIC fluxes and (b) carbon burial efficiencies (CBE) at 12°S. The error bars are the uncertainties in Table 2. The thick solid line is the 1:1 curve. The thin solid lines and dashed lines denote  $\pm 25\%$  and  $\pm 50\%$  limits on the 1:1 correlation, respectively. The uncertainty in the measured DIC fluxes is equal to 50% of the difference of the two fluxes measured during each lander deployment, that is, due to seafloor heterogeneity (Table 2). This leads to a mean relative error in DIC flux of 20 to 30% at 12°S. The uncertainty in the CBE is calculated by propagation of errors in DIC flux and POC burial (Table 2).

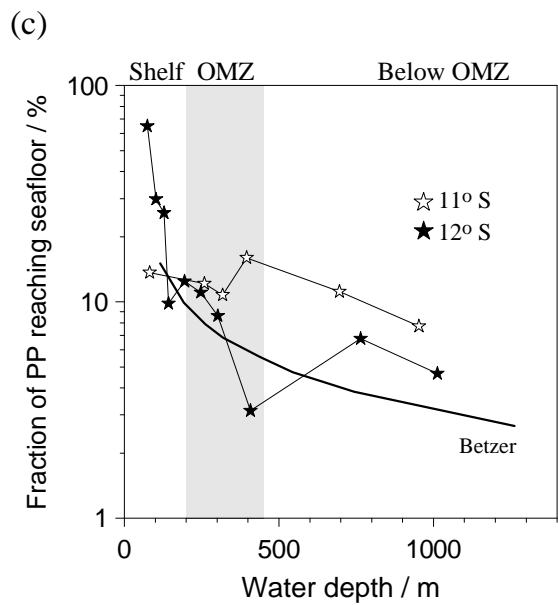
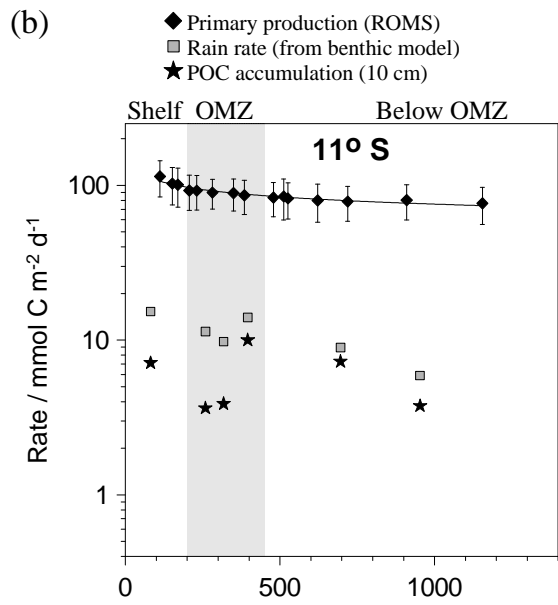
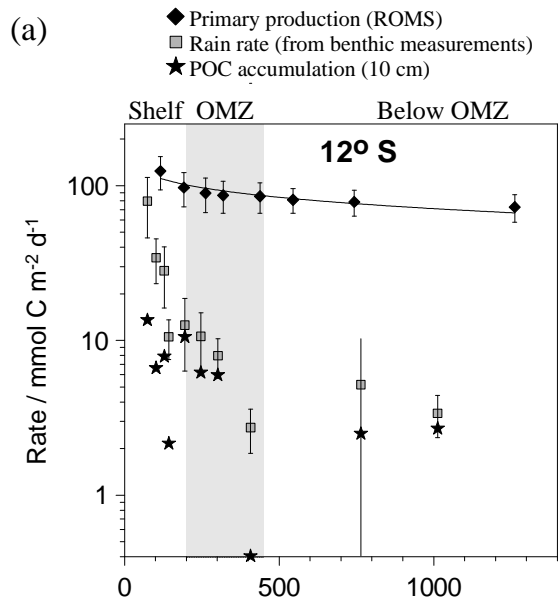


Figure 7. (a) Mean annual primary production ( $\pm$  s.d) for the 12°S transect calculated by the ROMS-BioEBUS model (diamonds). Rain rates to the seafloor (squares) and POC accumulation rates at 10 cm (stars) were estimated using the benthic measurements (Table 2). The solid line is a power law regression through the PP data. (b) As (a) for 11°S, except that rain rate is the modelled data. (c) Fraction of PP that reaches the seafloor calculated by dividing the rain rate by the PP calculated from the regression curve. The solid line is the predicted rain rate fraction at 12°S according to the empirical function of Betzer et al. (1984). The predicted fraction for 11°S differs by a few percent only (omitted for clarity). The grey shade highlights the OMZ stations (ca. 200 to 450 m).

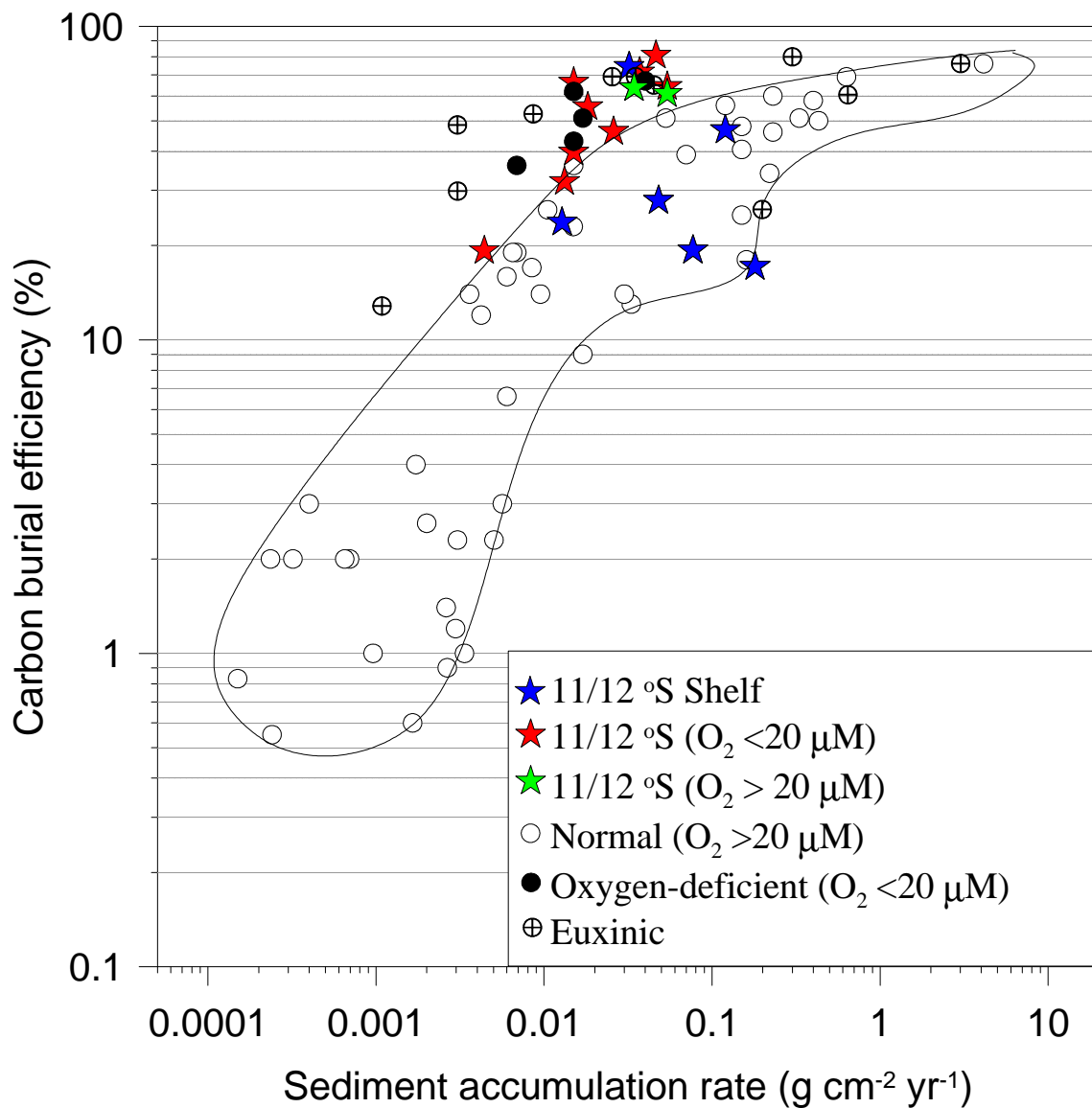


Figure 8. Carbon burial efficiency versus bulk sediment accumulation rate in contemporary ocean sediments. Open and filled circles represent sites from studies with bottom water  $\text{O}_2 > 20 \mu\text{M}$  and  $< 20 \mu\text{M}$ , respectively; the former enclosed by the solid line (Canfield, 1993, 1994; Burdige, 2007; Hartnett and Devol, 2003; Reimers et al., 1992). Euxinic settings are also indicated. Stars are data from this study for 11°S (modelled data) and 12°S (measured data). Blue stars indicate sites on the shelf, which mostly have lower-than-expected CBE compared to the existing database. Green stars correspond to the deep oxygenated sites ( $\text{O}_2 > 20 \mu\text{M}$ ) with higher-than-expected CBE.

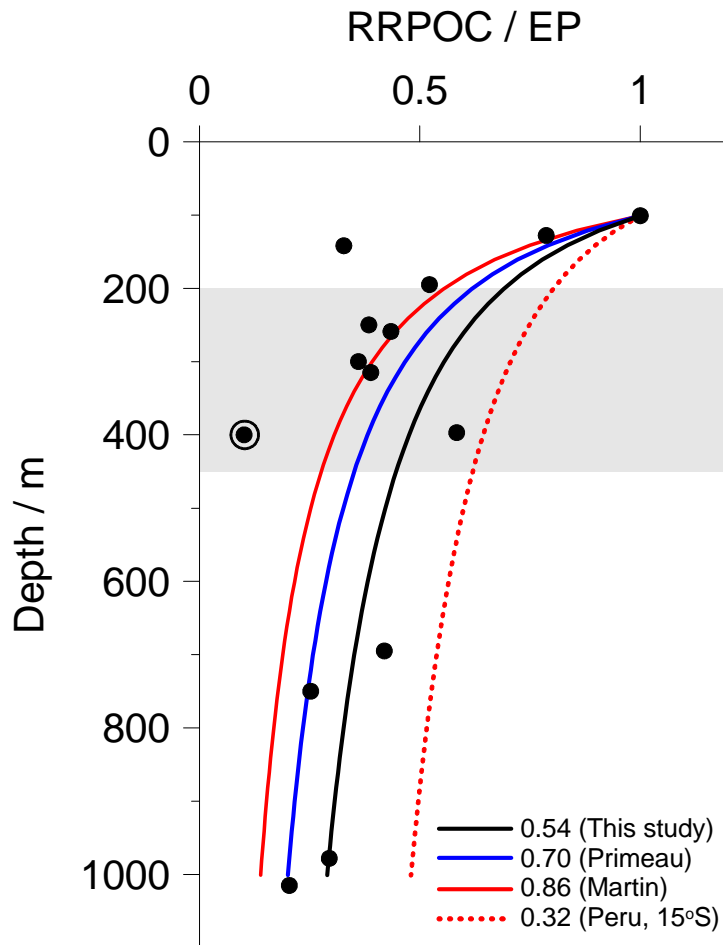


Figure 9. Fraction of export production reaching the sea floor at 11 and 12°S (circles) referenced to the datum at 101 m, where  $RRPOC = DIC \text{ flux} + POC \text{ burial}$ . The black line is the best-fit curve (Eq. 8) with an attenuation coefficient of  $b = 0.54$ . The datum from St. 8 (circled) is not included in the regression (see text). The blue and red lines show the open-ocean attenuation coefficients derived by Primeau (2006) and Martin et al. (1987), whereas the dashed red line corresponds to sediment trap data offshore of Peru at 15°S ( $b = 0.32$ , Martin et al., 1987), all normalized to unity. The grey shade highlights the OMZ stations (ca. 200 to 450 m).