

Seasonal cycle of N:P:TA stoichiometry as a modulator of CO₂ buffering in eastern boundary upwelling systems

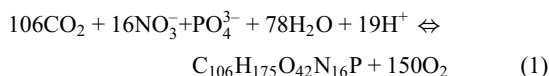
L. Gregor¹ and P. M. S. Monteiro²

Received 18 September 2013; accepted 3 October 2013.

[1] In this study we use the southern Benguela upwelling system to investigate the role of nutrient and carbon stoichiometry on carbonate dynamics in eastern boundary upwelling systems. Six months in 2010 were sampled along a cross-shelf transect. Data were classified into summer, autumn, and winter. Nitrate, phosphate, dissolved inorganic carbon, and total alkalinity ratios were used in a stoichiometric reconstruction model to determine the contribution of biogeochemical processes on a parcel of water as it upwelled. Deviations from the Redfield ratio were dominated by denitrification and sulfate reduction in the subsurface waters. The N:P ratio was lowest (7.2) during autumn once anoxic waters had formed. Total alkalinity (TA) generation by anaerobic remineralization decreased $p\text{CO}_2$ by 227 μatm . Ventilation during summer and winter resulted in elevated N:P ratios (12.3). We propose that anaerobic production of TA has an important regional effect in mitigating naturally high CO₂ and making upwelled waters less corrosive. **Citation:** Gregor, L., and P. M. S. Monteiro (2013), Seasonal cycle of N:P:TA stoichiometry as a modulator of CO₂ buffering in eastern boundary upwelling systems, *Geophys. Res. Lett.*, 40, doi:10.1002/2013GL058036.

1. Introduction

[2] Biogeochemical processes in continental margins differ greatly from the open ocean due to the strong linkage between surface and benthic systems [Monteiro, 2010]. Organic matter accumulates in the benthic boundary layer (BBL) and aerobic sediments where it is remineralized to inorganic constituents. Remineralization in an aerobic environment results in the breakdown of organic matter at close to stoichiometric ratios of nutrient uptake. In coastal systems, this typically takes place at stoichiometric ratios similar to the Redfield ratio [Boehme et al., 1998], which is defined in equation (1) [Redfield, 1958]:



Additional supporting information may be found in the online version of this article.

¹Department of Oceanography, University of Cape Town, Cape Town, South Africa.

²Council for Scientific and Industrial Research, Stellenbosch, South Africa.

Corresponding author: L. Gregor, Department of Oceanography, University of Cape Town, RW James Bldg., Ground Floor, Rm. 118, Residence Rd., Upper Campus, Cape Town, Western Cape, 7700 South Africa. (lukegre@gmail.com)

©2013. American Geophysical Union. All Rights Reserved.
0094-8276/13/10.1002/2013GL058036

The Redfield ratio (RR) is an estimate of the globally integrated nutrient ratios of organic matter over long time scales. However, note that this study deals with changes to the bulk nutrient ratios (ΔBNR) rather than the RR, but we assume that aerobic processes behave according to the RR.

[3] Anaerobic conditions favor alternate remineralization mechanisms, such as denitrification and ammonium oxidation by sulfate reduction, resulting in deviations from the RR. The two aforementioned mechanisms are also responsible for production of total alkalinity (TA) that in turn has a buffering effect on pH, calcium carbonate saturation state (Ω), and $p\text{CO}_2$ [Wolf-Gladrow et al., 2007]. Hu and Cai [2011] estimated that the net global production of TA in continental margins was 4–5 Tmol yr⁻¹—conservative compared to previous estimates (16–31 Tmol yr⁻¹) [Thomas et al., 2009]. Thomas et al. [2009] reported that buffering by anaerobic biogenic TA in the North Sea may account for up to 25% of CO₂ uptake.

[4] Evidence for anaerobic remineralization in eastern boundary upwelling systems is strong suggesting the potential for TA production. Denitrification in the Humboldt upwelling system (27–33°S) led to N:P ratios lower than the expected RR [Quiñones et al., 2010]. Similarly, Tyrrell and Lucas [2002] recorded nitrate losses and dissolved inorganic carbon (DIC) gains due to denitrification.

[5] In this study we used the deviations of ΔBNR from RR to calculate the contribution by various processes to DIC and TA in the southern Benguela. Unlike its northern counterpart, the southern Benguela is a seasonal upwelling system modulated by intraseasonal variation between the ridging South Atlantic anticyclone and westward moving midlatitude cyclones [Shillington et al., 2006]. Monteiro et al. [2006] found that seasonality was expressed in the region's biogeochemistry when decreased ventilation due to strengthening stratification at the end of summer resulted in hypoxia conducive to anaerobic remineralization in the sediments and occasionally the BBL.

2. Methods

[6] Data were collected on six occasions in the St. Helena Bay region off the west coast of South Africa during 2010 (Figure 1a). Temperature, salinity, and oxygen were measured at each of the 12 stations. Nitrate and phosphate were analyzed using standard procedures (see the supporting information). Additional samples were analyzed for DIC and TA as specified by Dickson and Goyet [1994]. Instrument precision for DIC and TA was determined by analysis of certified reference materials (4.5 and 2.2 $\mu\text{mol kg}^{-1}$, respectively). Both DIC and TA were normalized to a salinity of 34.8. $p\text{CO}_2$ was calculated from DIC and TA (see the supporting information for details). Air-sea CO₂ flux was

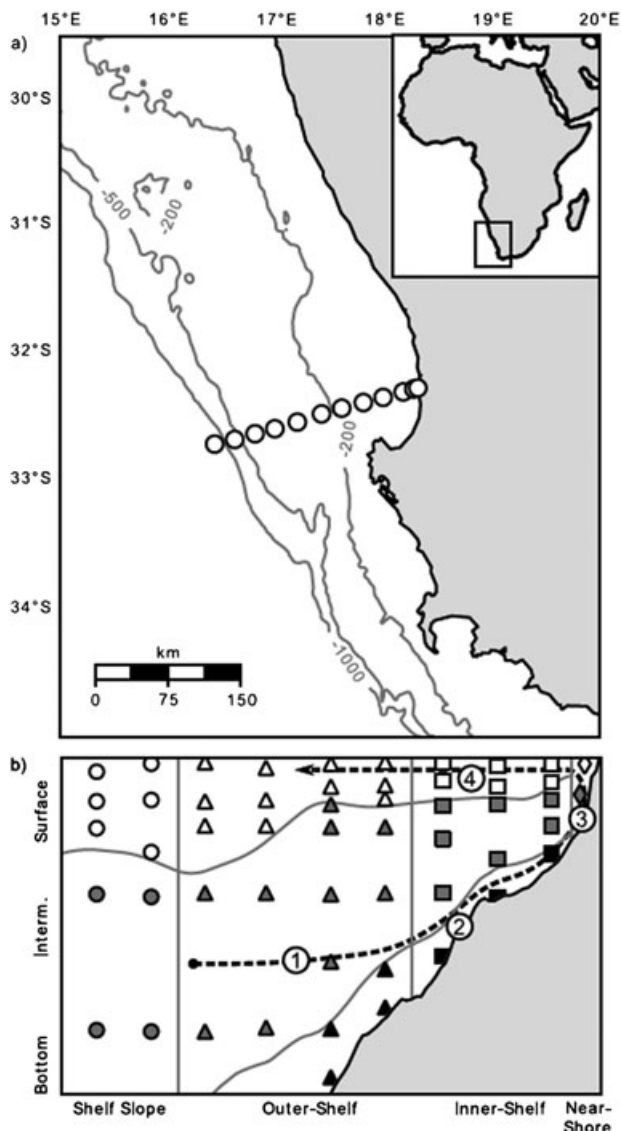


Figure 1. Map of the southern Benguela. (a) Sampling locations are shown by open circles. (b) The regions into which data were divided. Numbers 1–4 show the boxes chosen for the biogeochemical calculations and the dashed line shows the assumed transport. The markers show examples of sampling locations, with the shading representing the vertical zonation and the shapes the cross-shore location, and are consistent throughout all the figures. In the inverse model, region 1 represents South Atlantic Central Water.

calculated using cross-calibrated multiplatform winds [Atlas *et al.*, 2011] and the piston velocity parameterization by Wanninkhof *et al.* [2009]. Data points were classified into spatial groupings determined by thermocline depth, depth from the bottom, and longitude, with shelf slope, outer shelf, inner shelf, and nearshore regions horizontally and surface, intermediate, and bottom regions vertically (Figure 1b).

[7] An inverse model of stoichiometric influences to the marine carbonate system was constructed by using a simple box model approach. Four stages were used (Figure 1b): (1) source water, (2) inner shelf bottom, (3) nearshore surface, and (4) inner shelf surface. Magnitudes of DIC and TA fluxes for each contributing process were calculated

based on changes in nutrient, DIC, and TA stoichiometry (see the supporting information).

3. Results and Discussion

3.1. Physical Setting

[8] Seasonal upwelling in the southern Benguela is caused by the north-south migration of the South Atlantic anticyclone (SAAC) [Shillington *et al.*, 2006]. Upwelling occurs mainly during the SAAC's southern extent from September to May. A strong intraseasonal variability component is typically present throughout the summer due to the passage of midlatitude cyclones creating short-term variability in the pressure gradient which is also reflected in the modes of variability of phytoplankton production in response to upwelling [Hutchings *et al.*, 2009]. Stratification weakens during winter when intense mixing from westerly wind stress in combination with heat loss from the surface ocean to the atmosphere results in deeper mixed layers [Guastella, 1992].

[9] Seasonal stratification of the water column from summer heat flux also plays an important role in governing the biogeochemical variability of the southern Benguela [Monteiro *et al.*, 2006]. Retentive circulation in the St. Helena Bay region amplifies stratification throughout the summer upwelling period [Hutchings *et al.*, 2009]. Monteiro *et al.* [2006] found that remineralization coupled with decreased ventilation of bottom waters, due to stratification, toward the end of summer/autumn resulted in the formation of hypoxic and anoxic conditions [Pitcher and Matthews, 1996]. Our study included autumn as a separate season as evidence suggests that stratification during this season creates a significantly different biogeochemical environment [Pitcher and Nelson, 2006]. The seasonal cycle data were classified according to three categories: summer, autumn, and winter.

3.2. Initial Conditions: Source Water

[10] To understand the net CO₂ air-sea flux of an upwelled water parcel, the biogeochemical characteristics of the upwelling cycle need to be understood. Here we track a hypothetical water parcel from its upwelling source water with a biogeochemical signature of South Atlantic Central Water from the Cape Basin (salinity = 34.8, NO₃⁻ = 15 μmol kg⁻¹, PO₄³⁻ = 1.5 μmol kg⁻¹, DO = 200 μmol kg⁻¹, DIC = 2150 μmol kg⁻¹, and TA = 2350 μmol kg⁻¹) [Monteiro, 2010]. Simple meridionally integrated cross-shelf upwelling was assumed, depicted by the numbered stages in Figure 1b.

3.3. Remineralization

[11] The most dominant biogeochemical process in the subsurface waters (stages 1–2 in Figure 1b) was aerobic remineralization (RM), returning organic matter to inorganic components at stoichiometric ratios consistent with primary production (PP). These were assumed to be consistent with the ΔBNR for the entire study period, as was done for a similar study in coastal waters [Boehme *et al.*, 1998]. In absolute terms, the contribution to DIC by RM was largest during the upwelling season (37 μmol C kg⁻¹ d⁻¹) and smallest during winter (14 μmol C kg⁻¹ d⁻¹). ΔBNR of N:P (Figures 2a–2c) was lower than the RR (16:1) during summer and winter (both 12.3:1), suggesting nitrate loss or phosphate gain. This

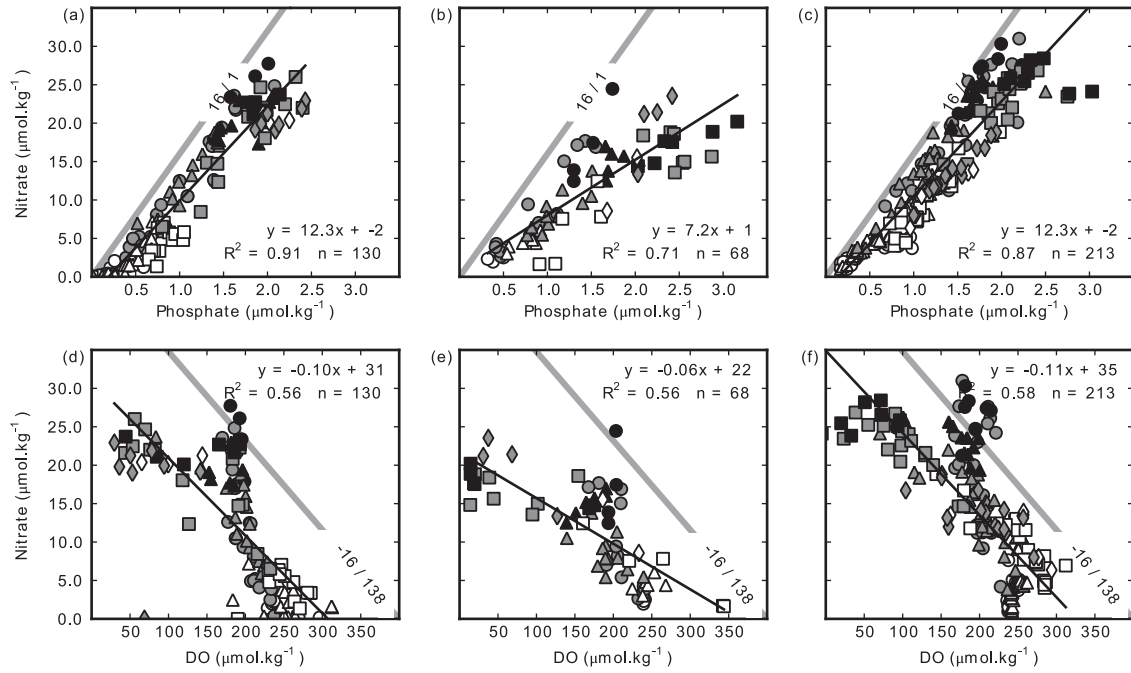


Figure 2. Nutrient plots of (a–c) nitrate versus phosphate and (d–f) nitrate versus dissolved oxygen (DO) where upwelling, stratified, and mixing seasons are shown, respectively. Best fits (black lines) were determined by least squares regression. Thick gray lines show the Redfield ratio. The shapes represent the cross-shelf zonation (shelf slope (circles), outer shelf (triangles), inner shelf (squares), and nearshore (diamonds)) and the shading of the shapes represents the vertical zonation (bottom (black), intermediate (gray), and surface (white)). Deviations from the Redfield ratio were greatest in autumn when anoxic conditions (low DO) allowed anaerobic remineralization to occur.

particularly is evident in autumn (Figure 2b) where the N:P is less than half the RR.

3.4. Denitrification

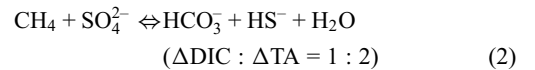
[12] Denitrification (DN) occurs in anoxic conditions where nitrate replaces oxygen as an electron acceptor [Wolf-Gladrow *et al.*, 2007]. Tyrrell and Lucas [2002] found that DN accounted for significant nitrate loss in shelf waters of the northern Benguela off the coast of Namibia. Their method to determine DN was also used in this study. The highest rate of DN (expressed as carbon rate) occurred during the upwelling period ($15 \mu\text{mol C kg}^{-1} \text{d}^{-1}$) and not during autumn ($12 \mu\text{mol C kg}^{-1} \text{d}^{-1}$). This was unexpected given the evidence in Figures 2a–2f and 3a–3c, where low dissolved oxygen (DO) concentrations in nearshore bottom waters, low N:P, and large changes in TA all suggest that DN should be strongest during autumn. This is explained by the methodology used to calculate the rates of DN (and other processes) where time-integrated DN was divided by the residence time of the surface water parcel. These residence times were determined by the rate of warming of surface water in the nearshore region ($0.52^\circ\text{C d}^{-1}$ [Guastella, 1992]). The residence times were 1.9, 4.3, and 6.3 days for summer, autumn, and winter, respectively.

[13] The Tyrrell and Lucas [2002] method used to calculate DN is sensitive to unaccounted contributions by phosphate flux from anaerobic sediments. Sulfur-reducing bacteria may induce stoichiometric N:P changes by storing phosphate during oxygen-replete conditions and releasing it during anoxic conditions leading to overestimation of DN [Brock and Schulz-Vogt, 2011]. Increased phosphate concentrations during autumn (90th percentile = $2.4 \mu\text{mol kg}^{-1}$)

relative to summer and winter (90th percentile = $2.1 \mu\text{mol kg}^{-1}$) support phosphate release. Similarly, low nitrate concentrations in autumn (90th percentiles = 18.8 and $22.8 \mu\text{mol kg}^{-1}$ for autumn and other seasons, respectively) suggest that DN also took place. The low N:P ratios during autumn were then a combination of denitrification and phosphate release, rather than a single contributing factor (see the supporting information for further evidence).

3.5. Sulfate Reduction

[14] The previous paragraph implies sulfate reduction (SR), which occurs during oxidation of methane under anaerobic conditions, shown below:



SR is energetically less favorable than DN, but the abundance of sulfate in upwelled waters allows these processes to occur simultaneously [Tyrrell and Lucas, 2002]. Because of the impact of equation (2) on proton balance, SR results in a stoichiometric increase of DIC:TA by 1:2, thus having significant impact on $p\text{CO}_2$, pH, and Ω in the BBL [Berner *et al.*, 1970; Wolf-Gladrow *et al.*, 2007]. The so-called “sulfur events” have been known to occur in the St. Helena Bay region during autumn [Bailey, 1991] and are thought to be linked to methane fluxes from the sediments, which accelerate the release of hydrogen sulfide (HS^-) into the BBL and occasionally to the surface [Pitcher and Matthews, 1996]. An important consideration for a net increase in TA concentration is the reoxidation pathway of HS^- , which determines whether TA gains are realized in the continental margin.

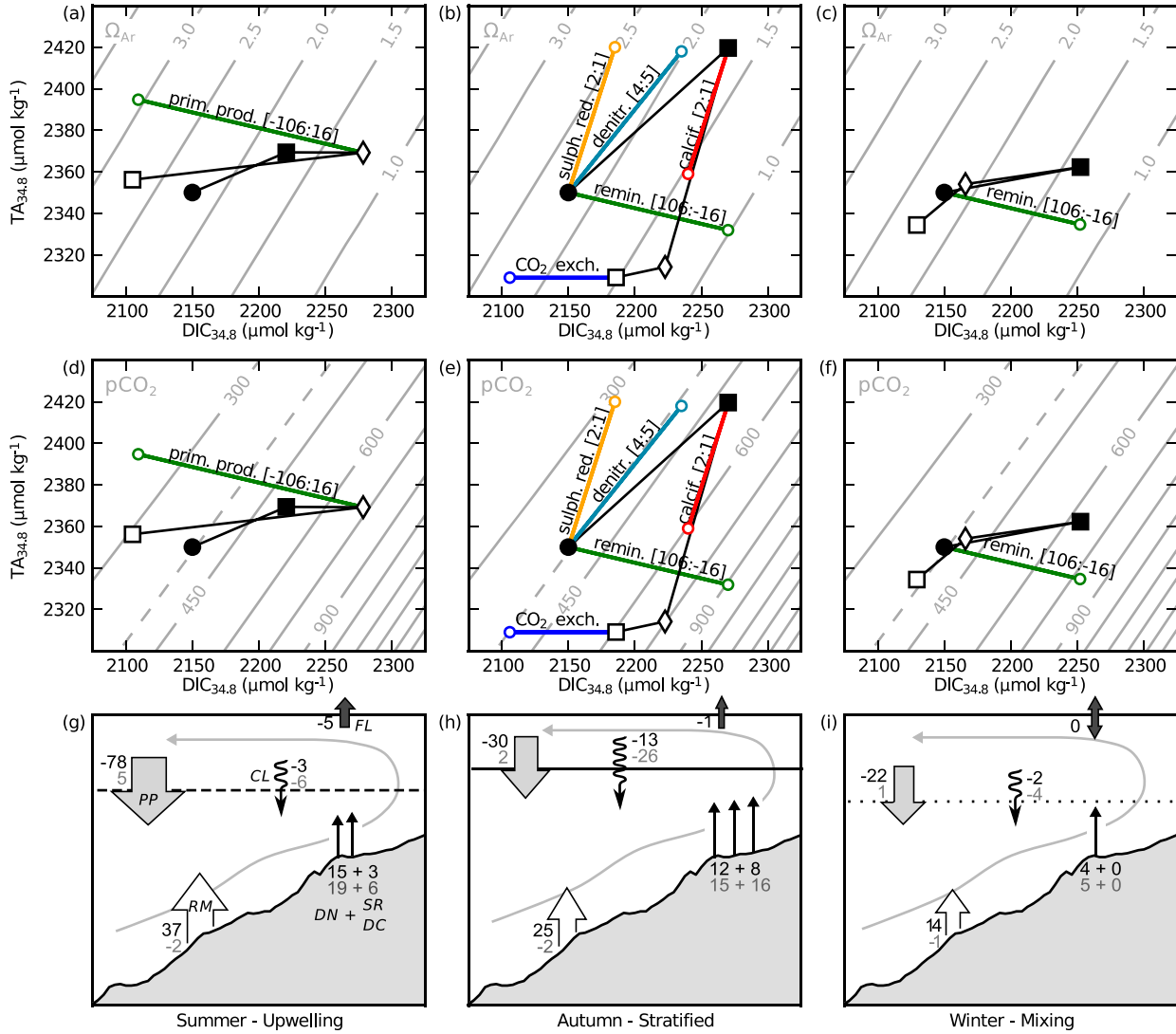


Figure 3. (a–f) Vector plots of average DIC and TA for regions 1–4 in Figure 1b. The colored lines show the expected trajectories of individual processes. Contour lines in Figures 3a–3c represent Ω_{Ar} and in Figures 3d–3f represent pCO_2 (0 m; 10°C; 34.8 salinity). As in Figure 2, shapes represent the cross-shelf zonation: shelf slope (circles), inner shelf (squares), and nearshore (diamond); and the shading represents the vertical zonation: bottom (black) and surface (white). (g–i) The schematic diagrams of biogeochemical contributions. Black numbers represent DIC and gray TA. The solid/dashed/dotted lines represent the thermocline and its intensity. Increases in DIC throughout all seasons were largely due to aerobic remineralization (RM). Large TA gains in autumn were due to benthic processes: denitrification (DN), sulfate reduction (SR), and calcite dissolution (CD). Strong primary production (PP) in summer reduced the surface DIC, while calcification (CL) in autumn resulted in decreased TA.

Three potential pathways of reoxidation are known: (1) reoxidation by benthic sulfur bacteria (*Thiomargarita* and *Beggiatoa*), which would result in no net TA gains [Brüchert *et al.*, 2009]; (2) formation and burial of pyrite via oxidation by iron [Hu and Cai, 2011]; and (3) methane bubbling, which transports HS⁻ into oxic subsurface or surface waters where elemental sulfur is formed [Brüchert *et al.*, 2009; Ohde and Mohrholz, 2011]. The latter two pathways result in a loss of HS⁻ without a proton release, thus a net increase in ΔTA . Evidence for pyrite formation in the southern Benguela is shown by Monteiro and Roychoudhury [2005], where high concentrations of river-borne trace metals associated with acid-volatile sulfide fraction in the sediments.

Large-scale “sulfur events” have also been reported in the southern Benguela, where elemental sulfur in surface water results in a milky appearance [Brüchert *et al.*, 2009; Ohde and Mohrholz, 2011].

3.6. Calcite Dissolution

[15] From our observations, we were not able to experimentally distinguish between SR and calcite dissolution (CD) as both processes result in the same ΔDIC and ΔTA . Unlike DN and SR, CD is an inorganic remineralization process and it is not dependent on anoxic conditions, but rather $\Omega_{Ca/Ar}$ (saturation state of calcite and aragonite). Though there is no evidence for $\Omega_{Ca/Ar} < 1$ (theoretical dissolution

point), it does not exclude the possibility of localized CD in the BBL and sediments. However, we hypothesize that Δ TA is dominated by HS⁻ loss, because the TA has a strong seasonality that is in phase with SR whereas CD would occur throughout the year from elevated aerobic/anaerobic respiration in the sediments.

3.7. TA Buffering

[16] All the discussed subsurface processes result in elevated DIC, yet this does not imply increased p CO₂ or Ω . Mean seasonal DIC:TA trajectories (Figures 3a–3f) indicate that SR and a smaller contribution from CD led to a reduction of p CO₂ due to TA increases, while RM led to increased p CO₂. The Δ DIC: Δ TA (5:4) stoichiometry of DN results in a nominal change in p CO₂ and Ω compared to remineralization. This emphasizes that anaerobic processes have a dominant feedback role and determine changes of p CO₂ in subsurface waters by offsetting increases of DIC from benthic respiration.

[17] Autumn DIC:TA vectors (Figures 3b and 3e) demonstrate the importance of this effect. A trajectory similar to that of DN (5:4) would have supported its role as a dominant regeneration pathway. However, the adherence of N:P to the RR does not support this and suggests that RM was the largest contributor to DIC. This implies that other processes with a steeper DIC:TA gradient, namely, SR and CD, had to be involved for the observed ratio to hold (Figures 2a–2c). The important outcome to note is that despite a large increase in DIC (120 μ mol kg⁻¹), p CO₂ increased and Ω decreased little from stages 1 to 2 (Figure 1b). This is due to buffering by increased [CO₃], which is a component of TA. Absence of TA production would have led to a p CO₂ increase of 290 μ atm and a reduction in Ω_{Ca} from 1.7 to 1.1. This may not be less than the theoretical saturation of $\Omega = 1$ but may have considerable ecosystem effects by disturbing the energy pathway between growth, reproduction, and calcification [Pörtner and Farrell, 2008].

[18] The similarities of the N:P and N:O stoichiometry (Figure 2) in summer and winter are not congruent to the DIC:TA vector plots (Figures 3a–3f). These differences arise in decoupling between stages 2 and 3 for the two seasons, where RM occurred predominantly between the two stages in summer. Weak upwelling in winter would have allowed offshore surface water, with low DIC, to advect and mix with the nearshore surface water.

3.8. Primary Production

[19] Water upwelled to the surface (stages 2 and 3) carries with it the net biogeochemical signature imposed in the subsurface most notably high Δ DIC and relatively unchanged Δ TA in summer and winter, and high Δ DIC and Δ TA in autumn. We will now discuss the processes affecting the surface stoichiometry trajectories.

[20] The stoichiometric reconstruction showed that primary production (PP) was dominant throughout all seasons with large DIC decreases. The rate of PP in the upwelling season (-78μ mol C kg⁻¹ d⁻¹) was more than double that of the stratified or mixing seasons (-30 and -22μ mol C kg⁻¹ d⁻¹, respectively). Probyn [1985] found that PP in the southern Benguela is dominated by diatoms whose preference for nitrate results in predominantly new production. Probyn [1985] found that new production in the

southern Benguela during summer accounted for 65% of PP in the shelf and nearshore regions.

3.9. Calcification

[21] Calcification (CL) during autumn resulted in a large decrease in TA during autumn (26μ mol kg⁻¹ d⁻¹) and caused p CO₂ to increase in surface waters, despite decreased DIC (Figure 3b). Evidence shows that CL occurred throughout 2010, though its contribution to the marine carbonate system peaked in autumn. Large coccolithophore (*Emiliania huxleyi*) blooms have been observed in the southern Benguela region, particularly in autumn [Weeks et al., 2011]. Giraudeau et al. [1993] proposed that high productivity throughout summer reduces DIC, thus increasing Ω_{Ca} . This increases the thermodynamic favorability toward coccolithophores, allowing blooms to occur.

3.10. Air-Sea CO₂ Fluxes

[22] Relative to other processes, CO₂ air-sea fluxes (Figures 3a–3c) were low, contributing nominally to Δ DIC. Outgassing was strongest during summer (5μ mol C kg⁻¹ d⁻¹ = $54 \text{ mmol m}^2 \text{ d}^{-1}$) due to high p CO₂ in newly upwelled nearshore water and strong winds. The inclusion of offshore stations in the model would have resulted in a sink (Figure 3a), as uptake of CO₂ was stronger farther offshore [Gregor and Monteiro, 2013]. Fluxes for autumn and winter were -1 and 0μ mol C kg⁻¹ d⁻¹ (11 and $6 \text{ mmol m}^2 \text{ d}^{-1}$), respectively. Lower average wind speeds resulted in lower CO₂ flux over these periods. Again, the inclusion of offshore stations during autumn would have resulted in a net source due to increased surface p CO₂ [Gregor and Monteiro, 2013].

3.11. The Importance of TA in Upwelling Systems

[23] Total alkalinity production on continental shelves has been shown to be insignificant on a global scale, contributing between 4 and 5 Tmol TA yr⁻¹ [Hu and Cai, 2011]. However, in this study, we suggest that shelf production of TA has an important local and regional role through mitigation of low Ω and high p CO₂ in naturally corrosive upwelling systems. Thomas et al. [2009] observed the same effect in the North Sea and noted that this may increase the capacity of the continental shelf pump to export CO₂. We propose the following hypothesis: nutrient trapping (POC/PON) and resulting anaerobic remineralization on the continental shelf of upwelling systems buffers p CO₂ and Ω by means of enhanced TA flux within the sediments and the BBL.

[24] Monteiro et al. [2011] suggested that eastern boundary upwelling systems with wide continental shelves, such as the southern and central Benguela systems, were conducive to retention of organic matter and the consequent formation of hypoxic benthic water. The corollary suggests that narrow, well-ventilated shelves with little or no anaerobic remineralization would not experience the same buffering effect despite greater off-shelf export of POC. The North American West Coast, a narrow shelf system, exemplifies this where Feely et al. [2008] presented evidence that the aragonite saturation horizon had shoaled in several nearshore regions. However, a simple comparison is perhaps not adequate as biogeochemical ocean-shelf boundary conditions also play an important role in defining the character of a system, especially in narrow shelf systems [Monteiro et al., 2011]. This is demonstrated in the Humboldt system where ocean biogeochemical boundary conditions are

defined by an extensive oxygen minimum zone, where denitrification occurs and plays a major role in the redox states of the shelf [Quiñones *et al.*, 2010].

4. Conclusion

[25] In this study we found that TA generation by DN and SR was responsible for reducing $p\text{CO}_2$ and increasing Ω_{Ar} by 227 μatm and 0.6, respectively, in autumn. $p\text{CO}_2$ observed in summer upwelling and winter mixing seasons was higher than that in autumn even though DIC was highest (Figure 3). This suggests that while less significant on a global scale, shelf production of TA may be an important mechanism to buffer potential outgassing of high DIC and the effects of natural corrosiveness of eastern boundary upwelling systems and other hypoxic systems. The contemporary and paleo-ecological consequences of this potentially important feedback between shelf sediment/BBL anoxia and $p\text{CO}_2/\text{pH}$ need to be explored further [Kemp, 1990]. The release of alkalinity flux from these environments may help explain why calcifiers such as molluscs are able to exist and accumulate in otherwise highly corrosive environments.

[26] **Acknowledgments.** The authors wish to thank the Departments of Environment (Ocean and Coasts Branch) and Agriculture and Fisheries for allowing the sampling of the St. Helena Bay Monitoring Line to be undertaken onboard their ships. A big thanks to Howard Waldron for his supervision and insightful comments on the manuscript. I am thankful to the National Research Fund (NRF) for a studentship and the Council for Scientific and Industrial Research (CSIR) Parliamentary Grant cofunded by ACCESS. This research was conducted as part of the Southern Ocean Carbon-Climate Observatory (SOCCO) program.

[27] The Editor thanks Helmuth Thomas and an anonymous reviewer for their assistance in evaluating this paper.

References

- Atlas, R., R. N. Hoffman, J. Ardizzone, S. M. Leidner, J. C. Jusem, D. K. Smith, and D. Gombos (2011), A cross-calibrated, multiplatform ocean surface wind velocity product for meteorological and oceanographic applications, *Bull. Am. Meteorol. Soc.*, 92(2), 157–174, doi:10.1175/2010BAMS2946.1.
- Bailey, G. W. (1991), Organic carbon flux and development of oxygen deficiency on the modern Benguela continental shelf south of 22°S: Spatial and temporal variability, *modern and ancient continental shelf anoxia*, *Geol. Soc. London Spec. Publ.*, 58, 171–183.
- Berner, R. A., M. R. Scott, and C. Thomlinson (1970), Carbonate alkalinity in the pore waters of anoxic marine sediments, *Limnol. Oceanogr.*, 15(4), 544–549.
- Boehme, S. E., C. L. Sabine, and C. E. Reimers (1998), CO₂ fluxes from a coastal transect: A time-series approach, *Mar. Chem.*, 63, 49–67.
- Brock, J., and H. N. Schulz-Vogt (2011), Sulfide induces phosphate release from polyphosphate in cultures of a marine *Beggiatoa* strain, *ISME J.*, 5(3), 497–506, doi:10.1038/ismej.2010.135.
- Brüchert, V., B. Currie, and K. R. Peard (2009), Hydrogen sulfide and methane emissions on the central Namibian shelf, *Prog. Oceanogr.*, 83(1), 169–179.
- Dickson, A., and C. Goyet (1994), *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Seawater*, 2nd ed., 187 pp., Volume 74 of ORNL CDIAO: Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Feeley, R. A., C. L. Sabine, J. M. Hernandez-Ayon, D. Ianson, and B. Hales (2008), Evidence for upwelling of corrosive “acidified” water onto the continental shelf, *Science*, 320(5882), 1490–1492, doi:10.1126/science.1155676.
- Giraudeau, J., P. M. Monteiro, and K. Nikodemus (1993), Distribution and malformation of living coccolithophores in the northern Benguela upwelling system off Namibia, *Mar. Micropaleontol.*, 22(1-2), 93–110, doi:10.1016/0377-8398(93)90005-I.
- Gregor, L., and P. M. Monteiro (2013), Is the southern Benguela a significant regional sink of CO₂, *S. Afr. J. Sci.*, 109(5/6), 1–5.
- Guastella, L. (1992), Sea surface heat exchange at St. Helena Bay and implications for the southern Benguela upwelling system, *S. Afr. J. Mar. Sci.*, 12(1), 61–70.
- Hu, X., and W.-J. Cai (2011), An assessment of ocean margin anaerobic processes on oceanic alkalinity budget, *Global Biogeochem. Cycles*, 25, GB3003, doi:10.1029/2010GB003859.
- Hutchings, L., *et al.* (2009), The Benguela current: An ecosystem of four components, *Prog. Oceanogr.*, 83(1-4), 15–32, doi:10.1016/j.pocean.2009.07.046.
- Kemp, S. (1990), Alkalinity: The link between anaerobic basins and shallow water carbonates?, *Naturwissenschaften*, 77(9), 426–427.
- Monteiro, P. M. (2010), Eastern boundary current systems, in *Carbon and Nutrient Fluxes in Continental Margins: A Global Synthesis*, 1st ed., edited by K.-K. Liu *et al.*, chap. 2.4, pp. 64–77, Springer, Berlin, Heidelberg.
- Monteiro, P. M., and A. N. Roychoudhury (2005), Spatial characteristics of sediment trace metals in an eastern boundary upwelling retention area (St. Helena Bay, South Africa): A hydrodynamical biological pump hypothesis, *Estuarine Coastal Shelf Sci.*, 65(1-2), 123–134, doi:10.1016/j.ecss.2005.05.013.
- Monteiro, P. M., B. de Witte, M. I. Scranton, A. Paulmier, and A. K. van der Plas (2011), The role of open ocean boundary forcing on seasonal to decadal-scale variability and long-term change of natural shelf hypoxia, *Environ. Res. Lett.*, 6(2), 025002, doi:10.1088/1748-9326/6/2/025002.
- Monteiro, P. M. S., A. van der Plas, V. Mohrholz, E. Mabilhe, A. Pascall, and W. Joubert (2006), Variability of natural hypoxia and methane in a coastal upwelling system: Oceanic physics or shelf biology? *Geophys. Res. Lett.*, 33, L16614, doi:10.1029/2006GL026234.
- Ohde, T., and V. Mohrholz (2011), Interannual variability of sulfur plumes off the Namibian coast, *Int. J. Remote Sens.*, 32(24), 9327–9342, doi:10.1080/014311612011.554455.
- Pitcher, G., and W. Matthews (1996), Noxious *Gymnodinium* species in south african waters, *Harmful Algae News*, 15, 1–3.
- Pitcher, G., and G. Nelson (2006), Characteristics of the surface boundary layer important to the development of red tide on the southern Namaqua shelf of the Benguela upwelling system Greville, *Limnology*, 51(6), 2660–2674.
- Pörtner, H. O., and A. P. Farrell (2008), Physiology and climate change, *Science*, 322(5902), 690–692, doi:10.1126/science.1163156.
- Probyn, T. (1985), Nitrogen uptake by size-fractionated phytoplankton populations in the southern Benguela upwelling system, *Mar. Ecol. Prog. Ser.*, 22, 249–258, doi:10.3354/meps022249.
- Quiñones, R., M. A. Gutiérrez, G. Daneri, D. Gutiérrez-Aguilar, H. E. Gonzalez, and F. P. Chavez (2010), Eastern boundary current systems, in *Carbon and Nutrient Fluxes in Continental Margins: A Global Synthesis*, 1st ed., edited by K.-K. Liu *et al.*, chap. 2.3, pp. 44–64, Springer, Berlin, Heidelberg, doi:10.1007/978-3-540-92735-2.
- Redfield, A. C. (1958), The biological control of chemical factors in the environment, *Am. Sci.*, 46(3), 205–221.
- Shillington, F., C. Reason, C. Duncombe-Rae, P. Florenchie, and P. Penven (2006), Large scale physical variability of the Benguela current large marine ecosystem (BCLME), *Large Mar.*, 14, 15–30.
- Thomas, H., L.-S. Schiettecatte, K. Suykens, Y. Koné, E. Shadwick, F. Prowe, Y. Bozec, H. J. de Baar, and A. Borges (2009), Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments, *Biogeosciences*, 6(2), 267–274.
- Tyrrell, T., and M. Lucas (2002), Geochemical evidence of denitrification in the Benguela upwelling system, *Cont. Shelf Res.*, 22, 2497–2511.
- Wanninkhof, R., W. E. Asher, D. T. Ho, C. Sweeney, and W. R. McGillis (2009), Advances in quantifying air-sea gas exchange and environmental forcing, *Annu. Rev. Mar. Sci.*, 1(1), 213–244, doi:10.1146/annurev.marine.010908.163742.
- Weeks, S., G. Pitcher, and S. Bernard (2011), Satellite monitoring of the evolution of a coccolithophorid bloom in the southern Benguela upwelling system, *Oceanography*, 17(1), 83–89.
- Wolf-Gladrow, D. A., R. E. Zeebe, C. Klaas, A. Körtzinger, and A. G. Dickson (2007), Total alkalinity: The explicit conservative expression and its application to biogeochemical processes, *Mar. Chem.*, 106(1-2), 287–300, doi:10.1016/j.marchem.2007.01.006.