

# A comparative study of the northwest Africa and eastern equatorial Pacific upwelling zones as sources of CO<sub>2</sub> during glacial periods based on boron isotope paleo-pH estimation

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**Abstract.** Paleo-pH reconstructions based on boron isotopic composition of foraminifera have been used to estimate glacial-interglacial changes in surface ocean  $p\text{CO}_2$  of the northwest African upwelling zone. On comparison with a similar study for the eastern equatorial Pacific upwelling zone, it can be concluded that the two major upwelling zones acted quite differently during the glacial periods as compared to today. While the pH of the surface ocean off northwest Africa was  $0.2 \pm 0.07$  units higher during the glacial period compared to that during Holocene, there was no significant glacial-interglacial change in the surface ocean pH in the eastern equatorial Pacific. Carbonate chemistry reconstructions based on the estimated pH changes suggest that the ocean-atmosphere  $p\text{CO}_2$  gradient off northwest Africa was lower by at least  $70 \pm 40$   $\mu\text{atm}$  during glacial periods compared to during the Holocene. In contrast, the ocean-atmosphere  $p\text{CO}_2$  gradient in the eastern equatorial Pacific was higher by at least  $80 \pm 40$   $\mu\text{atm}$  during glacial periods as compared to during the Holocene. Hence the eastern equatorial Pacific upwelling system was a significantly larger source of CO<sub>2</sub> to the atmosphere, while the one off northwest Africa was a significantly smaller source of CO<sub>2</sub> during the last glacial period. The  $p\text{CO}_2$  reconstructions further indicate that in spite of higher glacial productivity compared to during the Holocene, neither of the two areas became a sink of CO<sub>2</sub>.

## 1. Introduction

This paper is a follow up of a study by Sanyal *et al.* [1997] in which it was estimated, on the basis of the boron isotope paleo pH proxy, that the eastern equatorial Pacific Ocean was a larger source of CO<sub>2</sub> to the atmosphere during the glacial period compared to during the Holocene. In this study we do a similar boron isotope-based paleo pH estimation for the northwest African upwelling zone and compare the roles of upwelling regions in northwest Africa and eastern equatorial Pacific as sinks/sources of CO<sub>2</sub> over glacial-interglacial cycles. We choose to compare these two regions because they have been intensively studied in the past, using other proxies, in order to understand the influence of these highly productive upwelling regions on glacial atmospheric CO<sub>2</sub>.

Previous studies, based on variation in organic carbon accumulation over a glacial-interglacial timescale, estimated enhanced glacial productivity in the eastern equatorial Pacific and northwest Africa upwelling zones [Lyle *et al.*, 1988; Pedersen, 1983; Pederson *et al.*, 1991; Sarnthein *et al.*, 1987, 1988; Sarnthein and Winn, 1990]. Sarnthein *et al.* [1987, 1988] and Sarnthein and Winn [1990] suggested that the enhanced

productivity in both upwelling zones, in turn, contributed to the drawdown of glacial atmospheric  $p\text{CO}_2$ . However, Pederson *et al.* [1991], using carbon isotopic composition of organic matter, concluded that despite higher productivity the eastern equatorial Pacific was not a sink for CO<sub>2</sub> during the glacial period. This conclusion is also consistent with the paleo- $p\text{CO}_2$  reconstruction of Jasper *et al.* [1994] for the central equatorial Pacific based on photosynthetic fractionation of <sup>13</sup>C. On the other hand, no such  $p\text{CO}_2$  reconstruction over a glacial-interglacial timescale exists for the northwest Africa upwelling zone, though it should be noted that glacial-interglacial  $p\text{CO}_2$  reconstruction for eastern Angola Basin in southwest Africa, based on carbon isotopic composition of organic matter, suggests that this upwelling region was a smaller source of CO<sub>2</sub> during the glacial period [Muller *et al.*, 1994]. Recent advances in the boron isotope paleo-pH proxy provide an opportunity to quantify ocean-atmosphere  $p\text{CO}_2$  gradients in these two regions during the glacial periods and estimate the relative roles of these two upwelling zones as sources/sinks of CO<sub>2</sub> to the atmosphere.

## 2. Application of Boron Isotope Paleo-pH Proxy to Estimate Surface Ocean $p\text{CO}_2$

In order to assess accurately the influx/efflux of CO<sub>2</sub> it is appropriate to investigate directly changes of the surface ocean carbonate chemistry parameters (pH,  $p\text{CO}_2$ , carbonate ion concentration, total alkalinity, and total CO<sub>2</sub>). In this regard the boron isotopic composition ( $\delta^{11}\text{B}$ ) of planktonic foraminifera provides a proxy for estimating surface ocean pH of the past. These pH estimations, in turn, enable us to reconstruct the

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glacial surface ocean  $p\text{CO}_2$ . Subsequent comparison with the glacial atmospheric CO<sub>2</sub>, as recorded in ice cores, allows for estimation of changes in the ocean-atmosphere  $p\text{CO}_2$  gradient between the last glacial period and the Holocene. The advantage of this approach is that the pH across upwelling systems varies within a narrow range ( $\pm 0.05$ ), [Lee *et al.*, 1997; Copin-Montegut and Avril, 1995], and therefore, significant changes recorded at one location reflect changes in the entire upwelling region.

### 3. Samples and Methods

The cores selected for this study are V30-51k (19°52'N, 19°55'W; 3409 m) and V22-197 (14°10'N, 18°35'W; 3167m) off northwest Africa. For comparison with the eastern equatorial Pacific upwelling zone we have incorporated data of Sanyal *et al.* [1997] from core V19-28 (2°22'S, 84°39'W; 2670 m). These core positions are presently under the influence of upwelling systems as evidenced by supersaturation of the surface water with CO<sub>2</sub> at their respective locations [Broecker and Peng, 1982; Lee *et al.*, 1997; Copin-Montegut and Avril, 1995; Smethie *et al.*, 1985]. In this regard, it is noteworthy that a recent survey of carbonate chemistry parameters off northwest Africa by Lee *et al.* [1997] shows that CO<sub>2</sub> supersaturation due to the influence of upwelling extends from 10° to 35°N and occurs at least up to 20°W. The glacial and interglacial stages for the cores under consideration have been identified on the basis of a previously established oxygen isotope stratigraphy [Bloemendal *et al.*, 1988; Mix and Ruddiman, 1985; Ninkovich and Shackleton, 1975].

A single species of planktonic foraminifera, *Orbulina universa*, was handpicked from sediment samples (~200 individuals). The shells were crushed and soaked in 10% sodium hypochlorite solution for at least 24 hours. They were then washed thoroughly with quartz distilled water and dissolved in ~15-20  $\mu\text{L}$  2N HCl for complete dissolution. The samples were analyzed for boron isotopic composition by negative thermal ionization mass spectrometry (NTIMS) following the procedures described by Hemming and Hanson [1994] and Sanyal *et al.* [1997]. The analytical errors are reported as  $2\sigma_{\text{mean}}$  on the basis of repeated analyses (at least three) of a sample.

### 4. Paleo pH Estimations

The paleo-pH estimations have been made on the basis of an empirical  $\delta^{11}\text{B}$  versus pH curve for *O. universa*, which has been established on the basis of culture experiments [Sanyal *et al.*, 1996]. This species has several characteristics that make it better suited as a recorder of year-round surface mixed layer properties compared to other species in the upwelling zone. Plankton tow studies have shown that *O. universa* inhabit the surface mixed layer with a subsurface abundance maximum between 20 and 40 m [Hemleben and Bijma, 1994]. Moreover, in upwelling zones it has been shown to have the maximum abundance in surface waters [Ortiz *et al.*, 1995]. However, the abundance of *O. universa*, like most other species in upwelling regions, varies with the intensity of upwelling [Sautter and Thunell, 1991; B. Donner, personal communication, 1999]. In view of the absence of any species that has a uniform abundance throughout the year it is important to have a species that despite seasonal variation in abundance, is not exclusively an upwelling fauna but is present

almost all year round and hence integrates events throughout the year. In this regard, *O. universa* is better suited compared to most other species in the upwelling regions. That *O. universa* is not exclusively an upwelling fauna is evident from studies that found that the abundance of *O. universa* drops off in coastal upwelling regions while that of the upwelling species, *Globigerina bulloides*, increases [Ortiz and Mix, 1992]. Since it is not an exclusively upwelling fauna, it is found almost all year round in the upwelling regions [Ortiz and Mix, 1992; Sautter and Thunell, 1991]. Moreover, sediment trap studies have clearly shown that while the abundance of *O. universa* changes with upwelling intensity, it does not respond as strongly as other more abundant upwelling fauna, like *G. bulloides*, do [Sautter and Thunell, 1991; B. Donner, personal communication, 1999].

To test directly the validity of the boron isotopic composition of *O. universa* as a paleo pH proxy in the areas under consideration, the boron isotopic composition of Holocene *O. universa* from northwest Africa (V30-51K and V22-197) and the eastern equatorial Pacific Ocean [Sanyal *et al.*, 1997] were plotted against the pH of the modern surface ocean at the respective sample locations (Figure 1; see also Table 1). Figure 1 demonstrates that the boron isotopic composition of Holocene *O. universa* is consistent with the modern surface ocean pH at the respective core sites. It should also be noted that since there is little evidence of anthropogenic influence in the zones of upwelling [Lee *et al.*, 1997], the modern surface ocean pH in these zones must be similar to what they were during preindustrial times. We assume that the depth distribution of *O. universa* during the last glacial period was similar to that during the Holocene, and hence any change in the estimated pH is solely due to the changes in the carbonate chemistry in the depth habitat of *O. universa*.

The boron isotopic composition of glacial *O. universa* from northwest Africa is  $\sim 2.5 \pm 0.7\text{‰}$  higher than that of Holocene *O. universa* (Figure 2a and Table 1). On the basis of the empirical  $\delta^{11}\text{B}$  versus pH curve for this species it can be estimated that the

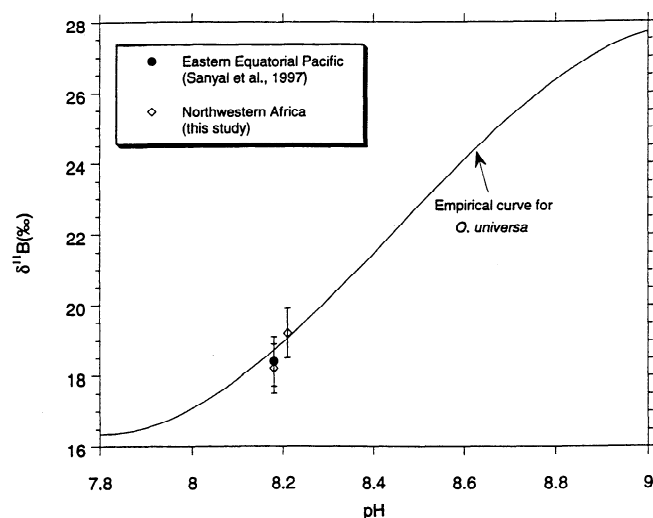


Figure 1. Plot of boron isotopic composition of Holocene *Orbulina universa* against the surface ocean pH at the site of the cores from which the samples were obtained. Also shown is the empirical  $\delta^{11}\text{B}$  versus pH curve for *O. universa* (based on culture experiments [Sanyal *et al.*, 1996]).

**Table 1.** Boron Isotopic Composition of *Orbulina universa*

Location	Time Period	$\delta^{11}\text{B}(\text{‰})$	pH(Estimated) <sup>a</sup>	pH (Modern)
<i>Northwest Africa</i>				
V30-51k <sup>b</sup>	stage 1	18.2±0.7	8.13±0.07	8.18
	stage 2	20.6±0.7	8.34±0.05	-
V22-197 <sup>c</sup>	stage 1	19.2±0.7	8.23±0.07	8.21
	stage 2	21.8±1.0	8.43±0.07	-
<i>Eastern Equatorial Pacific</i>				
V19-28 <sup>d</sup>	stage 1	18.4±0.7	8.15±0.07	8.18
	stage 2	17.6±0.7	8.05±0.07	-
V19-28	stage 5e	18.4±0.7	8.15±0.07	8.18
	stage 6	18.2±0.7	8.13±0.07	-

<sup>a</sup> Based on the empirical curve for *O. universa*. Errors are expressed as  $2\sigma_{\text{mean}}$  for repeated analyses of each sample.

<sup>b</sup> Location: 19°52'N, 19°55'W, 3409m.

<sup>c</sup> Location: 14°10'N, 18°35'W, 3167m.

<sup>d</sup> Location: 2°22'S, 84°39'W, 2670m.

pH in the northwest African surface ocean was  $0.2\pm 0.07$  pH units higher during the glacial period compared to that of the Holocene (Table 1). In contrast, as estimated in a previous study by Sanyal *et al.* [1997], there is no significant glacial-interglacial change in the boron isotopic composition of *O. universa* from the eastern equatorial Pacific, and hence no estimated glacial-interglacial change in surface ocean pH (Figure 2b and Table 1).

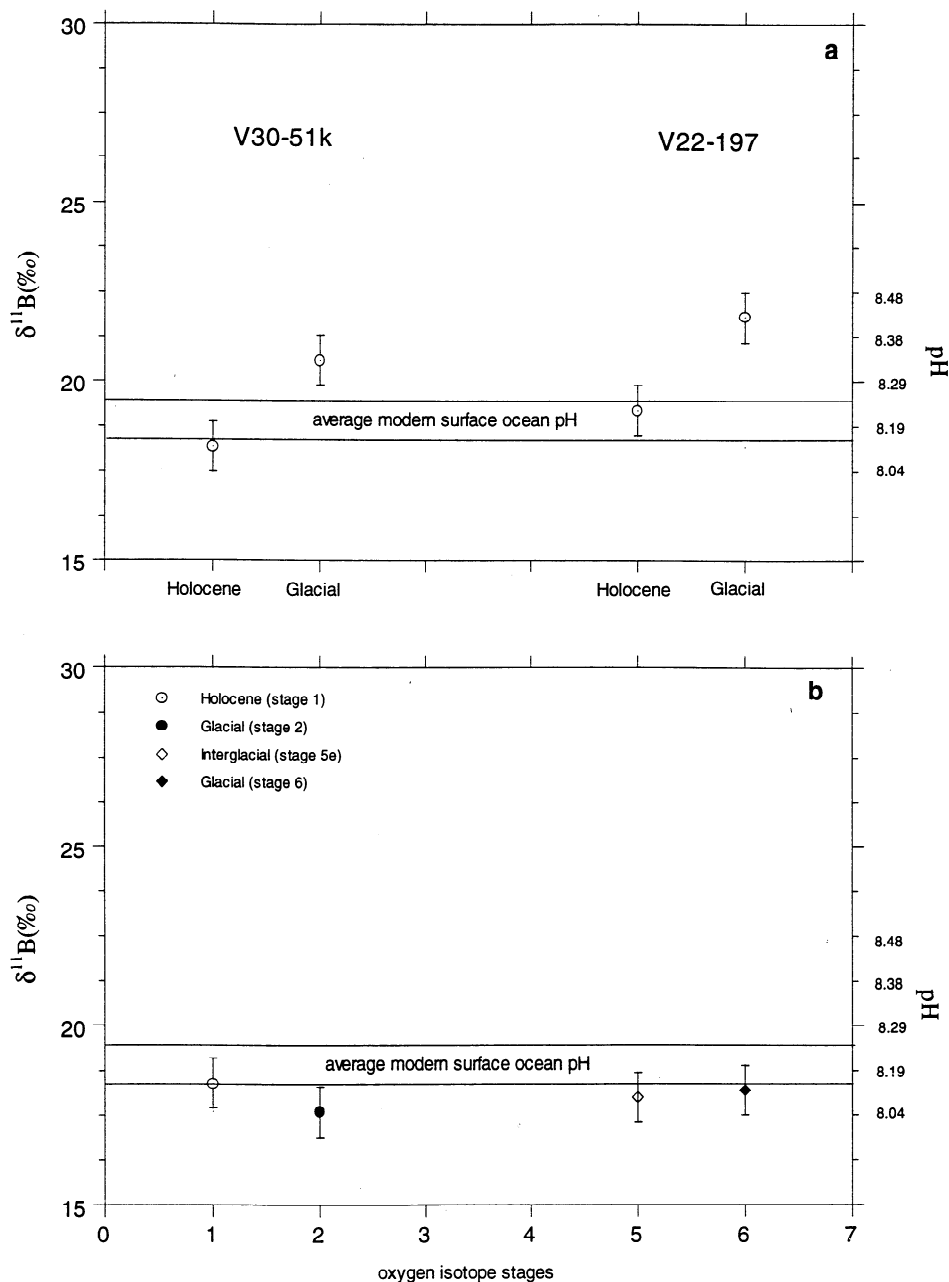
## 5. Reconstruction of Carbonate Chemistry of Glacial Surface Ocean in Northwest Africa

On the basis of the paleo-pH estimates the glacial-interglacial changes in the surface ocean  $p\text{CO}_2$  have been reconstructed in a stepwise fashion using the present-day surface ocean values of temperature ( $T$ ), total alkalinity (TAlk), total  $\text{CO}_2$  ( $\text{TCO}_2$ ),  $p\text{CO}_2$  and pH in northwest Africa as starting parameters (on the basis of the measurements by C. Copin-Montegut (personal communication, 1997) during *Eumeli 4* cruise (Table 2). A glacial-interglacial temperature change of  $3^\circ\text{C}$  is assumed on the basis of  $U_{37}^k$  sea surface temperature reconstructions of Zhao *et al.* [1995]. Various studies have estimated the  $p\text{CO}_2$  of the surface ocean, at different times of the year, in regions close to the core locations. The measured or estimated  $p\text{CO}_2$  in northwest Africa ranges from  $\sim 370$   $\mu\text{atm}$  to as high as  $440$   $\mu\text{atm}$  [Lee *et al.*, 1997; Copin-Montegut and Avril, 1995, also personal communication; Smethie *et al.*, 1985]. These differences have been attributed to seasonal variations in productivity, upwelling and temperature in the region [Copin-Montegut and Avril, 1995]. For the sake of simplicity we have assumed an average  $p\text{CO}_2$  of  $400\pm 30$   $\mu\text{atm}$  as our starting parameter. The Holocene ocean-atmosphere  $p\text{CO}_2$  gradient has been estimated by comparing the preindustrial atmospheric  $p\text{CO}_2$  of  $280$   $\mu\text{atm}$  (as recorded in ice cores) with the present-day surface ocean  $p\text{CO}_2$ . A correction for possible input of fossil fuel  $\text{CO}_2$  into the modern surface ocean is not necessary as there is little evidence of significant anthropogenic influence in this upwelling zone [Lee *et al.*, 1997]. The lack of anthropogenic influence in

upwelling zones is expected as these regions are supersaturated with respect to  $\text{CO}_2$  and hence not regions of active  $\text{CO}_2$  uptake.

In the first step of the calculations (Table 2 and Figure 3) the changes in  $\text{TCO}_2$  and TAlk were estimated to account for a 3% salinity increase during the last glacial period. In the next step the pH was set to the boron isotope-based estimated glacial value, and the other carbonate chemistry parameters were reconstructed via two end-member scenarios. In the first scenario it was hypothesized that changes in carbonate chemistry are brought about by changes in  $\text{TCO}_2$  in response to variations in nutrient content of the surface ocean (Figure 3, step 2). In the second scenario, on the other hand, it was assumed that changes in the carbonate chemistry are solely controlled by addition (due to dissolution in sediments) or removal (due to production) of calcium carbonate per unit water mass (Figure 3, step 3). While the first scenario would bring about a change mainly in  $\text{TCO}_2$ , the second would bring about a change in both TAlk and  $\text{TCO}_2$  in a ratio of 2:1. These two hypothetical end-member scenarios give an estimate of the maximum and minimum changes in the surface ocean  $p\text{CO}_2$  for a particular change in pH in the area under consideration. The actual change in surface ocean  $p\text{CO}_2$  was probably controlled by a combination of both scenarios and hence was between the two extreme  $p\text{CO}_2$  estimates.

The calculated (Table 2) surface ocean  $p\text{CO}_2$  for the northwest African upwelling zone ranges from  $230\pm 40$  (first scenario) to  $250\pm 40$   $\mu\text{atm}$  (second scenario). Hence the estimated drop in glacial surface ocean  $p\text{CO}_2$  ranges between  $170\pm 40$  (first scenario) and  $150\pm 40$   $\mu\text{atm}$  (second scenario). These reductions are significantly greater than the  $80$   $\mu\text{atm}$  decrease in atmospheric  $p\text{CO}_2$  recorded in ice cores. Hence, during glacial periods, there was a significant reduction of at least  $70\pm 40$   $\mu\text{atm}$  in the ocean-atmosphere  $p\text{CO}_2$  gradient in the northwest African upwelling zone, making this region a smaller source (but not a sink) of  $\text{CO}_2$  to the atmosphere. This conclusion is in agreement with the  $^{13}\text{C}_{\text{org}}$ -based paleo- $p\text{CO}_2$  estimates for the southwest Africa upwelling zone [Muller *et al.*, 1994].



**Figure 2.** (a) Boron isotopic composition of *O. universa* from Holocene and last glacial period obtained from cores V30-51k and V22-197 in the northwest African upwelling zone. (b) Boron isotopic composition of *O. universa* from stages 1, 2, 5c, and 6 obtained from core V19-28 in the eastern equatorial Pacific upwelling zone [Sanyal *et al.*, 1997]. The pH scale represents the calculated pH for corresponding boron isotopic composition based on empirical relationship between  $\delta^{11}\text{B}$  of *O. universa* and pH of seawater [Sanyal *et al.*, 1996].

In contrast, a similar reconstruction for the eastern equatorial Pacific [Sanyal *et al.*, 1997] shows that the ocean-atmosphere  $p\text{CO}_2$  gradient in the eastern equatorial Pacific was higher by at least  $80 \pm 40 \mu\text{atm}$  during the glacial periods. This in turn suggests that eastern equatorial Pacific was a larger source of  $\text{CO}_2$  to the atmosphere during glacial periods than it was during the Holocene. This conclusion is consistent with that of Pedersen *et al.* [1991], who estimated the surface ocean  $p\text{CO}_2$  in eastern equatorial Pacific on the basis of carbon isotopic composition of sedimentary organic matter.

## 6. Possible Scenarios for Glacial pH (and $p\text{CO}_2$ ) in Northwest African and Eastern Equatorial Pacific Upwelling Zones

Sanyal *et al.* [1997] explained the glacial pH and  $p\text{CO}_2$  in the eastern equatorial Pacific in terms of increase in whole ocean alkalinity in combination with lower nutrient utilization and/or higher carbonate productivity. The whole ocean glacial-interglacial alkalinity change, estimated to be  $\sim 300 \pm 20 \mu\text{eq kg}^{-1}$  on the basis of boron isotopic composition of benthic

**Table 2.** Calculated Carbonate Chemistry of Northwest African Surface Ocean During the Last Glacial Period

		<i>T</i> °C	<i>S</i>	TAlk μeq kg <sup>-1</sup>	TCO <sub>2</sub> μmol kg <sup>-1</sup>	pH	<i>p</i> CO <sub>2</sub> μatm	Δ <i>p</i> CO <sub>2</sub> ocean minus atmosphere <sup>a</sup>
		18.25	35.6	2370	<i>Holocene</i> 2109	8.18	400±30 <sup>b</sup>	120
Step 1	<i>S</i> increase (3%)	15.25	36.7	2441	<i>Glacial</i> 2172	8.21	370	-
Step 2								
Scenario 1	nutrient depletion	15.25	36.7	2441	2070	8.38±0.07	230±40 <sup>c</sup>	30
Scenario 2	carbonate addition	15.25	36.7	2705	2304	8.38±0.07	250±40 <sup>c</sup>	50

*T*, temperature; *S*, salinity; TAlk, total alkalinity; and TCO<sub>2</sub>, total CO<sub>2</sub>.

<sup>a</sup> Difference calculated with respect to preindustrial atmospheric *p*CO<sub>2</sub> of 280 μatm.

<sup>b</sup> See text.

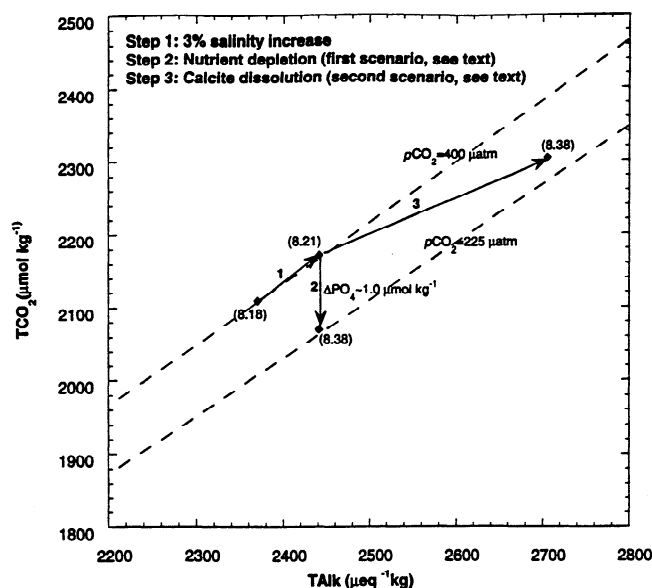
<sup>c</sup> Errors in *p*CO<sub>2</sub> based on uncertainty in boron isotope-based pH estimation of 0.07 pH units.

foraminifera [Sanyal *et al.*, 1995, 1997], was hypothesized to be due to enhanced respiration CO<sub>2</sub>-driven dissolution in porewater [Archer and Maier-Reimer, 1994].

Such a significant whole ocean alkalinity change would also be able to explain the entire *p*CO<sub>2</sub> and pH changes estimated for northwest Africa without calling for any significant accompanying change in nutrient utilization. This mechanism is similar to the second hypothetical end-member scenario described in the previous section (Figure 3, step 3). To corroborate this scenario, it would be important to estimate nutrient utilization in this region during the glacial period on the basis of nitrogen isotopes. However, in invoking this hypothesis both for northwest Africa and the eastern equatorial Pacific it is important to keep in mind that in a recent modeling study, Sigman *et al.* [1998] suggested that under certain scenarios it is

difficult to explain such a significant increase in whole ocean alkalinity via respiration CO<sub>2</sub>-driven calcite dissolution as proposed by Archer and Maier-Reimer [1994] without violating sedimentary evidences of glacial-interglacial changes in the depth of lysocline. Therefore we also explore alternative scenarios both for northwest Africa and eastern equatorial Pacific that do not invoke a whole ocean alkalinity change but are restricted to the local upwelling regimes.

An alternative scenario for northwest Africa would be to invoke changes in the CO<sub>2</sub> content of the surface ocean as the major mechanism to alter pH and *p*CO<sub>2</sub> of the surface ocean. This mechanism is similar to the first hypothetical end-member scenario described in previous section (Figure 3, step 2). In upwelling zones a reduction in surface ocean CO<sub>2</sub> content would be mainly related to nutrient depletion in the surface ocean since the CO<sub>2</sub> content in upwelling zones is mainly controlled by upwelling and productivity and not by atmospheric CO<sub>2</sub>. Such a nutrient depletion, in turn, could be brought about by a decrease in the nutrient content in the intermediate water that is the source of upwelled water [Boyle, 1988] or by enhanced nutrient utilization in the surface ocean. It is not possible, however, to bring about the entire estimated *p*CO<sub>2</sub> change solely by increasing nutrient utilization in the surface water since there is only a small amount of excess nutrients in the modern surface ocean in northwest Africa (0.3 μmol kg<sup>-1</sup> of PO<sub>4</sub>), and its total extraction would cause a decrease in *p*CO<sub>2</sub> of ~80 ppm (and a corresponding pH increase of ~0.1 pH units). On the other hand, if the entire *p*CO<sub>2</sub> change is attributed to nutrient depletion of intermediate source water, it will require a decrease of ~1 μmol kg<sup>-1</sup> in PO<sub>4</sub> concentration. This estimated change in nutrient concentration is higher than the 0.6 μmol kg<sup>-1</sup> depletion estimated by Boyle [1988] on the basis of Cd measurements (the change in TCO<sub>2</sub> due to nutrient depletion has been calculated assuming a P:C ratio in organic matter of 1:105). Hence it is difficult to attribute the entire change in *p*CO<sub>2</sub> and pH to a decrease in total CO<sub>2</sub> content of the northwest African surface ocean. It could be argued, however, that the estimated change in pH and *p*CO<sub>2</sub> was due to a combination of decrease in total CO<sub>2</sub> and increase in alkalinity. The alkalinity increase could be attributed to dissolution of calcite sediments brought about by nutrient-enriched deep water [Boyle, 1988] and/or to enhanced pore water dissolution [Archer and Maier-Reimer, 1994].



**Figure 3.** Diagrammatic representation of the estimated changes in the carbonate chemistry of the northwest African surface ocean between Holocene and the last glacial period. The numbers in parentheses represent pH values for respective water masses.

Hence, on the basis of geochemical evidences, it is not possible to put forward any single unequivocal scenario for explaining the reconstructed  $p\text{CO}_2$  changes in northwest Africa. It could be hypothesized, however, that a combination of the different factors mentioned above led to the glacial pH increase and accompanying decrease in surface ocean  $p\text{CO}_2$ .

For the eastern equatorial Pacific we also evaluate several alternative scenarios that could explain, without invoking a whole ocean alkalinity change, constancy of surface ocean pH over the glacial-interglacial time period and accompanying increase in ocean-atmosphere  $p\text{CO}_2$  gradient. It could be argued that the pH of the surface ocean would remain constant over glacial-interglacial timescales if there was no significant change in  $\text{TCO}_2$  and  $\text{TA}_{\text{alk}}$  in surface ocean. This would mean that there was no change in both alkalinity extraction per unit water mass and nutrient utilization in the surface ocean. Sedimentary records suggest that both calcite and organic carbon productivity actually increased during the glacial period [Lyle *et al.*, 1988]. On the other hand, evidence also indicates that upwelling increased significantly during the glacial period [Lyle *et al.*, 1992]. Hence it could be argued that even though calcite and organic carbon productivity increased, the excess demand for nutrient and alkalinity was matched by a higher input of nutrient and alkalinity into the surface ocean via enhanced upwelling during glacial period. This scenario is in conflict with the assertion, based on nitrogen isotope data [Farrell *et al.*, 1995], that nutrient utilization was lower during glacial period. Hence, under this scenario the changes in nitrogen isotope will have to be attributed to factors other than nutrient utilization.

Alternatively, if it is assumed that nutrient utilization in the surface ocean decreased during the glacial period, as suggested by the nitrogen isotope data [Farrell *et al.*, 1995], then there will be the need for a compensating effect, like increased alkalinity, to maintain the surface ocean pH at the interglacial level. This is because a decrease in nutrient utilization will lead to an increase in  $\text{TCO}_2$  of the surface ocean, which in turn will tend to decrease the pH of the surface ocean. The required increase in surface ocean alkalinity could be attributed to lesser alkalinity extraction (via calcite production) per unit mass of seawater. Since both the calcite productivity and upwelling increased during glacial periods [Lyle *et al.*, 1988, 1992], it could be hypothesized that an increase in alkalinity input due to enhanced upwelling exceeded the greater alkalinity demand due to higher calcite productivity. This would bring about a higher alkalinity in the surface ocean that could compensate for the effects of lower nutrient utilization to keep surface ocean pH constant.

To evaluate the validity of each of the above scenarios, it is essential to have quantitative estimates of the changes in rate of upwelling and productivity (both calcite and organic carbon) for the entire upwelling region in the eastern equatorial Pacific. Though quantitative estimates for upwelling in the central equatorial Pacific during glacial periods are available [Lyle *et al.*, 1992], the uncertainties are quite large and it cannot be assumed that the upwelling estimates for the central equatorial Pacific would be applicable to the eastern equatorial Pacific as well. Also Lyle *et al.* [1988] estimated productivity changes in the eastern equatorial Pacific during glacial periods on the basis of sedimentary records from core V19-28. However, recent studies have suggested that it is difficult to determine with certainty the exact productivity changes in an upwelling regime

on the basis of sedimentary records from a single or few cores [Betrand *et al.*, 1996]. Hence, to evaluate successfully the plausibility of each of the above scenarios, it is necessary to constrain better the changes in upwelling and productivity (both calcite and organic carbon) in the eastern equatorial Pacific over the glacial-interglacial time scale.

## 7. Conclusions

This study shows the potential of the boron isotopic composition of foraminiferal shells as a paleo-pH proxy to help evaluate the roles of different parts of the ocean as sources/sinks of CO<sub>2</sub> over glacial-interglacial timescales. On the basis of paleo-pH estimations it can be concluded that even though the ocean-atmosphere  $p\text{CO}_2$  gradients in the northwest African and eastern equatorial Pacific upwelling zones are similar during the Holocene, they changed in opposite directions during the last glacial period, affecting their relative roles as sources of CO<sub>2</sub> to the atmosphere. While the upwelling zone in the eastern equatorial Pacific became a significantly stronger source, the one in northwest Africa became a significantly smaller source of CO<sub>2</sub> to the glacial atmosphere.

The changes in surface ocean  $p\text{CO}_2$  in northwest Africa are consistent with the whole ocean alkalinity change estimated in previous studies on the basis of boron isotope paleo-pH reconstructions of the deep ocean [Sanyal *et al.*, 1995, 1997]. Alternatively, it could be explained by a combination of changes in both whole ocean alkalinity (associated with calcite dissolution) and surface ocean  $\text{TCO}_2$  concentration (associated with nutrient depletion) in the northwest African upwelling regime.

For the eastern equatorial Pacific the estimated  $p\text{CO}_2$  and pH in the glacial surface ocean have been previously explained by a whole ocean alkalinity increase coupled with lesser nutrient utilization in the surface ocean and/or excess calcite productivity. Alternatively, without invoking a whole ocean alkalinity increase, the constancy of pH in the surface ocean could be attributed to a combination of changes in both upwelling (leading to changes in nutrient and alkalinity supply to the surface ocean) and productivity (both calcite and organic carbon). To evaluate the validity of the different scenarios that do not incorporate whole ocean alkalinity change, it is essential to have an accurate quantitative estimate of the glacial-interglacial changes in rate of upwelling and productivity (both calcite and organic carbon) for the entire eastern equatorial Pacific upwelling region.

The  $p\text{CO}_2$  reconstructions further indicate that in spite of the higher glacial productivity compared to that during the Holocene [Sarnthein and Winn, 1990; Sarnthein *et al.*, 1988; Lyle *et al.*, 1988], neither of the two areas became a sink of CO<sub>2</sub> and hence did not play an active role in the drawdown of the atmospheric CO<sub>2</sub> during glacial periods. This points to the necessity of carrying out similar studies for other regions that could have had significant influence on the atmospheric  $p\text{CO}_2$ , like the Southern Ocean, in order to understand the possible causes of glacial-interglacial atmospheric CO<sub>2</sub> changes.

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