Reconstructing past upwelling intensity and the seasonal dynamics of primary productivity along the Peruvian coastline from mollusk shell stable isotopes

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[1] We present here a potential new method to evaluate past variations of the mean intensity of Peruvian coastal upwelling and of the seasonal timing of phytoplankton blooms. This method uses a combination of the monthly carbon and oxygen isotopic signals preserved in fossil mollusk shells, and a series of corrections
to extract the variations of the dissolved inorganic carbon (DIC) δ\(^{13}\)C. Based on the analysis of five shell samples (85 shells in total) from the southern Peruvian coast, we suggest that the mean coastal upwelling intensity can be determined from a linear relationship between average values of corrected shell δ\(^{13}\)C and δ\(^{18}\)O. This new potential proxy would bring additional independent information valuable to interpret paleoproductivity changes reconstructed from marine sediment of the nearby continental shelf. Results obtained on fossil samples from the middle Holocene show an increase in upwelling intensity during this period associated to a spatial reorganization of upwelling centers along the South Peruvian coast. At the seasonal scale, corrected shell δ\(^{13}\)C enrichment indicates a phytoplankton bloom. Seasonal timing of phytoplankton blooms can be estimated by the lag with the annual temperature cycle reproduced by shell δ\(^{18}\)O monthly variations. The results obtained with two modern shell samples indicate phytoplankton blooms occurring during summer and fall, consistently with in situ productivity observations. Our method relies on revisited assumptions about the influence of temperature and metabolism in mollusk shell δ\(^{13}\)C. We further discussed the validity of these assumptions and the potential implications for the interpretation of similar data sets.

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1. Introduction

[2] Marine phytoplankton performs approximately 50% of the net global carbon fixation through photosynthesis, and thus acts as a critical link between the organic and inorganic carbon reservoirs [Behrenfeld et al., 2006; Alvain et al., 2008]. This biological carbon fixation is strongly influenced by climate change in the low latitude oceans, with warmer waters increasing stratification and reducing productivity [Cox et al., 2000; Bopp et al., 2001; Behrenfeld et al., 2006; Steinacher et al., 2010]. The majority of marine primary productivity in the tropics is concentrated in upwelling zones where it is promoted through a supply of nutrients. Upwelling intensity is a major but complex parameter within the global carbon cycle. Deep waters saturated in CO\(_2\) are upwelled and act as a carbon source upon exchange with the atmosphere, while the high primary productivity increases the oceanic biological carbon pump. The response of primary productivity to the rate of upwelling may also be limited by alternate parameters such as terrestrial iron input [Martin et al., 1994; Hutchins et al., 2002; Dezileau et al., 2004] or light availability [Cole and Cloern, 1984]. A comparison of 30 model simulations against in situ data from the tropical Pacific by Friedrichs et al. [2009] revealed that the majority of models significantly underestimate current primary productivity. Estimates of the response of upwelling intensity and marine productivity to greenhouse warming remain highly uncertain.

[3] Reconstructions of past changes in upwelling intensity and marine productivity are required to fully understand their controls and to constrain model simulations. Many studies using marine sediment cores have been devoted to this issue. Despite their high interest, these studies often face two limitations: (1) paleoupwelling intensity are often inferred from paleoproductivity indicators based on the assumption that upwelling systematically promotes productivity, which is not the case in high nutrient low chlorophyll (HNLC) zones such as the Peruvian upwelling and (2) the mean annual carbon export budget simulated in biogeochemical models is an integration of seasonal scale processes that cannot be studied in sediment cores as a result of their low temporal resolution. Seasonal variability in the coastal Peruvian upwelling is recorded in mollusk shell Δ\(^{14}\)C signals [Jones et al., 2009]. For ancient periods, variations of mean paleoupwelling intensity can be indicated by variations of marine reservoir age estimated by the radiocarbon analysis of contemporaneous marine shells and plant remains [Fontugne et al., 2004; Ortlieb et al., 2011]. However, this method has significant uncertainties.
Monthly averages of chlorophyll concentrations were constructed from satellite data, in situ sampling and model simulations. Coastal Peru is characterized by year-round southeasterly trade winds that generate strong Ekman transport and coastal upwelling. Because the continental slope is so close to the shore in Peru, the surface conditions over the Peruvian shelf are closely related to the coastal upwelling. Deep waters are upwelled along the Peruvian coast in localized upwelling centers and then advected offshore. Therefore, a steep sea-surface temperature (SST) gradient is observed between cool coastal waters and relatively warmer waters offshore. Deep waters are upwelled throughout the year along the Peruvian coastline, with a maximum experienced during the austral winter (June to September).

The vertical advection of deep water provides an annual supply of nutrients to the surface, supporting a highly productive phytoplankton bloom. Average chlorophyll concentrations decrease seaward from ~10 mg/m³ on the coast to ~1 mg/m³ ~300 km offshore. Estimates of the paleoenvironmental conditions in this region are largely based on proxies derived from phytoplankton preserved within sediment cores from the continental shelf, approximately 30 to 140 km offshore, within the close influence of the coastal upwelling. Whereas low frequency temporal variability (≥10¹ yr) of average productivity is expected to be similar on the coastline and over the shelf, coastal and shelf phytoplankton blooms are characterized by different assemblages with different seasonal timings and strength. The environmental conditions of the coastline recorded by mollusk shells may be significantly different, at the seasonal scale, from the conditions over the shelf recorded by sediment cores.

Satellite data, in situ sampling and model simulations indicate that blooms along the Peruvian coastline currently occur during austral summer (Figure 1), in opposition to the seasonal phasing of upwelling intensity. Unlike the physically analogous Chilean region of the Humboldt Current, phytoplankton growth in the coastal Peruvian upwelling is not limited by the nutrient supply from the deep sea, but potentially by light (low stratus cloud cover is persistent from June to November) or the supply of bio-available iron such as observed in the HNLC equatorial Pacific.

1.1. Coastal Peru

Coastal Peru is characterized by year-round southeasterly trade winds that generate strong Ekman transport and coastal upwelling. The continental slope is so close to the shore in Peru, the surface conditions over the Peruvian shelf are closely related to the coastal upwelling. Deep waters are upwelled along the Peruvian coast in localized upwelling centers and then advected offshore. Therefore, a steep sea-surface temperature (SST) gradient is observed between cool coastal waters and relatively warmer waters offshore. Deep waters are upwelled throughout the year along the Peruvian coastline, with a maximum experienced during the austral winter (June to September).

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1.2. Environmental Information Potentially Reconstructed From Mollusk Stable Isotopes

High resolution microsampling of M. donacium shells (see section 3.1) allows the evaluation of monthly variations in both δ¹⁸O and δ¹³C incorporated in shell aragonite (CaCO₃). The oxygen isotopic fractionation between aragonite and sea-
water is a temperature dependent reaction; therefore the δ18O signal from *M. donacium* provides a proxy record for temperature reconstructions provided the seawater δ18O can be estimated [Carré et al., 2005a].

[9] The carbon isotopic composition of mollusk shells may have multiple influences: (1) the isotopic composition of the dissolved inorganic carbon (DIC), δ13C_DIC, (2) the proportion of metabolic carbon in carbonate ions involved in the aragonite precipitation (metabolic effect) (see discussion in section 4.2), (3) kinetic disequilibrium effect (see McConnaughey and Gillikin [2008] for a detailed review) and (4) a temperature-related fractionation for which the mechanisms remain poorly constrained (see discussion in section 4.1.2). In section 4, we discuss a potential method for correcting shell δ13C so shell profiles only reflect δ13C_DIC variations, which contain the desired environmental information.

[10] Photosynthesis reactions preferentially make use of isotopically lighter 12CO2. This has two implications: (1) at the ocean scale, as phytoplankton die this 13C enriched organic matter sinks to the seafloor and is mineralized at depth. Deep waters upwelled along the Peruvian coast are therefore characterized by 13C depleted DIC. (2) On a local scale, a phytoplankton bloom induces a 13C enrichment of the surface water DIC during the growth phase and a depletion of 13C during the following organic matter degradation phase. Thus, if the isotopic carbon ratios in mollusk shells are representative of marine DIC, they may provide insights into the variability of upwelling activity and primary production at monthly to millennial timescales [Killingley and Berger, 1979; Jones and Allmon, 1995]. Furthermore, δ13C_DIC of surface waters is also influenced by air-sea CO2 exchange which depends on the difference of CO2 partial pressure (pCO2) between the atmosphere and the ocean [Lynch-Stieglitz et al., 1995]. The relative contribution of these environmental controls over the δ13C_DIC depends on local oceanographic features and will be discussed. The isotopic influence of one possible complicating factor, the influence of terrestrial freshwater runoff, is not significant in Peru because of the extreme aridity (Figure 2) and the weak discharge of coastal rivers (Worldclim 1.4 data set; available at http://www.worldclim.org/current), as confirmed in situ by monthly salinity measurements [Carré et al., 2005a].

2. Material and Study Sites

[11] The bivalve *Mesodesma donacium* inhabits the subtidal to intertidal zone of sandy beaches along the

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**Figure 2.** The two sampling sites of Rio Ica and QLB in Southern Peru where both modern and fossil *M. donacium* shells were collected. Greyscale patterns over the continent indicate annual precipitation (Worldclim 1.4 data set). Color patterns in the ocean indicate mean annual sea surface temperature (NASA’s MODIS data set). Cooler SSTs along the coast are related to the presence of upwelling, which appears stronger at 15°S near the Ica site than at 18°S near the QLB site.
Peruvian and Chilean coastline, and provides typical individual records of approximately one to two years [Carré et al., 2005a]. Fossil mollusk shells were collected from two archeological sites along the Peruvian coastline: Rio Ica (14°52′S, 75°33′W) [Engel, 1957] and Quebrada de los Burros (QLB) (18°10′S, 70°38′W) [Lavallée et al., 1999; Carré et al., 2009] (Figure 2). Modern shell samples were collected from the respective nearby beaches in small mounds formed by fishermen activity during the second half of the 20th century. The sample size ranged from 13 to 20 shells (Table 1). Preservation of these historical shells was particularly high (as indicated by the remains of preserved organic material) due to the extremely arid Peruvian coastline which receives precipitation of less than 20 mm yr\(^{-1}\) (Worldclim 1.4 data set). Sample horizons of the archeological sites were dated by radiocarbon AMS measurements on charcoal fragments recovered among shell material (Table 1). A total of 85 shells were analyzed.

### 3. Methods

#### 3.1. Shell Preparation and Microsampling

Mollusk shells were embedded in polyester resin and radially sectioned using a diamond wire saw. Sections 1 mm thick were mounted onto glass slides and polished before sampling of the outer shell layer, along the direction of growth, with a Micromill™ automated microsampler. Each microsample constituted about 0.1 mg of powdered calcium carbonate, and represented about one month of shell growth based on shell inner growth lines (see Carré et al. [2005a, 2009] for details about sclerochronology). With this technique, occasional areas of recrystallized carbonate located on the shell surface can be identified by their color and avoided in the microsampling. Despite the high spatial control of the micro sampler, an uncertainty remained over the identification of tidal growth lines and thus in the temporal resolution. The time span represented by a single microsample ranged between 0.5 to 2 months. Based on the \(\delta^{18}O\) profiles and the number of microsamples in a peak-to-peak 1 year cycle, the average time resolution of shell isotopic signals was re-estimated to be \(\sim 1.1\) months.

#### 3.2. Isotopic Analyses

Approximately 0.05 mg of aragonite powder was sub-sampled from every microsample and analyzed for carbon (\(\delta^{13}C\)) and oxygen (\(\delta^{18}O\)) stable isotope composition with a Kiel III carbonate device coupled to a Finnigan Delta Plus isotope ratio mass spectrometer. The carbonate device drops excess 100% phosphoric acid onto calcium carbonate samples held at 70°C. Measurement reproducibility was 0.04‰ for \(\delta^{13}C\) and 0.07‰ for \(\delta^{18}O\) based on routine analyses quality control calcite standards. Isotopic values were placed on the VPDB scale by measurement against internal laboratory calcite standards that were measured against the international standards NBS19 and LSVEC [Verkouteren, 1999] for \(\delta^{13}C\) and NBS19 and NBS18 for \(\delta^{18}O\).

### 4. Results and Discussion

#### 4.1. Influences on Shell \(\delta^{13}C\)

Besides the seawater \(\delta^{13}C_{\text{DIC}}\), mollusk shell aragonite \(\delta^{13}C\) may also be influenced by kinetic fractionation, temperature, and the contribution of metabolic (also referred to as respired) carbon. We discuss below these influences in the conditions of our study.

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**Table 1.** Radiocarbon AMS Dates Measured on Charcoal Samples Associated to the Sampled *M. donacium* Shells

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample Name</th>
<th>Number of Shells</th>
<th>(^{14}C) Date (B.P.)</th>
<th>Laboratory Reference</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°S</td>
<td>Ica(_{\text{mod}})</td>
<td>15</td>
<td>N/A</td>
<td>Modern</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ica(_{\text{inca}})</td>
<td>20</td>
<td>510 ± 40</td>
<td>OS-65628</td>
<td>Inca</td>
</tr>
<tr>
<td></td>
<td>Ica(_{\text{mH}})</td>
<td>20</td>
<td>5840 ± 35</td>
<td>OS-60543</td>
<td>Middle Holocene</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5900 ± 40</td>
<td>OS-60564</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5940 ± 45</td>
<td>OS-60556</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6070 ± 30</td>
<td>OS-60544</td>
<td></td>
</tr>
<tr>
<td>18°S</td>
<td>QLB(_{\text{mod}})</td>
<td>17</td>
<td>N/A</td>
<td>Modern</td>
<td></td>
</tr>
<tr>
<td></td>
<td>QLB(_{\text{mH}})</td>
<td>13</td>
<td>6490 ± 60</td>
<td>GfA-97287</td>
<td>Middle Holocene</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6510 ± 60</td>
<td>GfA-97288</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6630 ± 70</td>
<td>GfA-97289</td>
<td></td>
</tr>
</tbody>
</table>

*a* Three time periods were represented by the shells collected; the modern day, Inca period and middle Holocene.

*b* Dates published by Lavallée et al. [1999].
4.1.1. Kinetic Effect

A kinetic effect can be diagnosed by highly depleted values and a strong positive correlation between shell $\delta^{13}C$ and $\delta^{18}O$ [McConnaughey et al., 1997]. Since this was not observed in $M$. donacium shells, we discounted the influence of a significant kinetic effect in our study.

4.1.2. Temperature Influence

From the analysis of seawater $\delta^{13}C_{\text{DIC}}$ and aragonite $\delta^{13}C$ in several mollusk species, Grossman and Ku [1986] calculated empirical equations of the temperature dependent carbon fractionation in biogenic aragonite for Hoeglundinae and mollusks between 2.6 and 22°C:

$$\varepsilon_{\text{Hoeg.--DIC}}(\delta) = 2.40 - 0.108 \cdot T(\circ C)(R = 0.89, N = 52)$$

(1)

$$\varepsilon_{\text{mollusk--DIC}}(\delta) = 2.66 - 0.131 \cdot T(\circ C)(R = 0.82, N = 26)$$

(2)

Later, Romanek et al. [1992] studied carbon fractionation of inorganic aragonite and calcite and found no temperature dependence for the aragonite-HCO$_3^-$ fractionation, suggesting that “aragonite-secreting taxa are influenced by temperature-dependent biological disequilibrium effects ("vital effects").” After this temperature dependence observed by Grossman and Ku [1986] was qualified “vital effect,” most researchers studying carbon stable isotopes in mollusk shells used the fractionation factor calculated by Romanek et al. [1992] and considered that carbon isotopes in biogenic aragonite were not influenced by temperature [McConnaughey et al., 1997; Lorrain et al., 2004; McConnaughey and Gillikin, 2008; Gillikin et al., 2006a; Lartaud et al., 2010].

In contrast to these researchers, we have returned to the Grossman and Ku [1986] equation (2) for three reasons: (1) the empirical data set indicates a highly statistically significant, yet currently mechanically undefined relationship between temperature and $\varepsilon_{\text{mollusk--DIC}}^{13}C$; (2) as far as we know, no published data set using biogenic aragonite has invalidated this model; and (3) since we are studying biogenic aragonite, Grossman and Ku [1986] model is more appropriate than Romanek et al. [1992] model on inorganic aragonite. To support this latter reason, it seems important to remind that the mineralization processes for biogenic and inorganic aragonite are very different chemically and thermodynamically. First, aragonite does not spontaneously precipitate in the ocean and only exists because of shell organic matrix [Watabe and Wilbur, 1960; Suzuki et al., 2009]. The crystal growth in shells is fully biologically controlled (timing, place, rate, and directions) through complex interactions with a large range of multifunctional proteins that constitute the shell organic matrix [Watabe and Wilbur, 1960; Wheeler et al., 1981; Addadi and Weiner, 1992; Marin and Luquet, 2004; Marin et al., 2007; Suzuki et al., 2009]. The processes of organic aragonite precipitation involves the catalytic action of enzymes [Bevelander and Benzer, 1948; Freeman and Wilbur, 1948; Marxen et al., 2003, Marin and Luquet, 2004] which have a temperature dependent efficiency [Somero, 1969; Ikemoto, 1975; Hall, 1985; Pick and Karlish, 1982; Wolfenden et al., 1999]. Enzymatic reactions also induce a temperature dependent isotopic fractionation [Northrop, 1981; Schowen and Schowen, 1981; Liu and Warshel, 2007]. A temperature-dependent $\delta^{13}C$ fractionation between HCO$_3^-$ and the other inorganic carbon species may also be involved. Studying the mechanisms behind a $\delta^{13}C$ temperature effect in biogenic aragonite is beyond the scope of this paper, but it is clear that the question requires further research. The correlation between temperature and $\varepsilon_{\text{mollusk--DIC}}^{13}C$ may only be indirect and not causal but it still reveals the existence of a chemical and/or biological effect that can be estimated through temperature. The fact that Grossman and Ku [1986] calculated a similar equation for the foraminifera Hoeglundinae and twelve species of mollusks suggests that this effect may indeed be characteristic of a large range of aragonite-secreting organisms.

In light of these observations and until further results suggest otherwise, correcting our mollusk shell $\delta^{13}C$ data for an expected and quantified temperature effect using $\delta^{18}O$ based temperature reconstructions [Carré et al., 2005a] was selected as the most suitable course of action.

4.1.3. Correcting Shell $\delta^{13}C$ for the Temperature Effect

We analyzed the oxygen isotopic composition of seawater samples from the southern coast of Peru collected between 2002 and 2007 (Table 2). In the Río Ica area, average isotopic values were $\delta^{18}O_{\text{seawater}} = 0.26\%_{\text{o}} V-\text{SMOW} (\sigma = 0.11, N = 8)$, whereas in the QLB area it was estimated at $\delta^{18}O_{\text{seawater}} = 0.21\%_{\text{o}} V-\text{SMOW} (\sigma = 0.15, N = 20)$. The water $\delta^{18}O$ on this coast displays little variation and no seasonality because it is not significantly affected by freshwater input. This was confirmed in modern
conditions by seawater δ18O measurements (Table 2) and monthly salinity time series [Carré et al., 2005a]. Despite some variations of humidity, the coastal climate remained arid or semi-arid in southern Peru [Eitel et al., 2005; Kuentz et al., 2012] and precipitation was reduced in the Andes during the middle Holocene [Baker et al., 2001; Rein et al., 2005]. It can thus be considered constant in average throughout the year, and shell δ18O variations can be interpreted as reflecting changes in SST. The middle Holocene shell δ18O values were also corrected for changes in the mean ocean water δ18O caused by variations in ice volume. This was conducted using the sea level curve of Lambeck and Chappell [2001] with an estimate of a 1.05‰ decrease in oceanic δ18O between the Last Glacial Maximum and the present-day [Duplessy et al., 2002]. A correction of 0.049‰ and 0.079‰ was applied to mid-Holocene shells of Rio Ica and QLB respectively. Paleotemperature values were calculated using the Carré et al. [2005a] transfer equation. Temperature-related carbon fractionation was calculated using equation (2) and isotopic temperature estimates, and then subtracted from shell δ13C values (Figure 3). We therefore generated signal of corrected δ13C values (δ13Ccorr) which are primarily influenced by the variations of δ13Ccorr and the contribution of metabolic carbon. The standard error of δ13Ccorr was estimated at 0.17‰ (1σ) and combines analytical errors on both shell δ13C and δ18O and the monthly variability of water δ18O. The 85 individual corrected δ13C profiles are represented in Figure 4 and span from ~10 months to ~24 months for the larger shells.

4.2. The Influence of Metabolic Carbon

The relative proportion of carbon of metabolic versus environmental origin is an uncertain parameter that may strongly vary with species and environment [Tanaka et al., 1986; Klein et al., 1996; McConnaughey et al., 1997; Gillikin et al., 2006a, 2007; McConnaughey and Gillikin, 2008]. In early studies, authors proposed that shell δ13C variations mainly reflected δ13CDIC and could therefore be used as paleoenvironmental tracers [Mook and Vogel, 1968; Mook, 1971; Killingley and Berger, 1979; Arthur et al., 1983; Krantz et al., 1987, 1988; Arthur et al., 1983; McConnaughey et al., 1997; McConnaughey and Gillikin, 2008].

Table 2. Seawater δ18O Data

<table>
<thead>
<tr>
<th>Coastal Site</th>
<th>Lat.</th>
<th>Long.</th>
<th>Date (dd-mm-yy)</th>
<th>δ18O‰ (V-SMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lagunillas</td>
<td>13°55'S</td>
<td>76°19'W</td>
<td>09-08-03</td>
<td>0.28</td>
</tr>
<tr>
<td>Rio Ica beach</td>
<td>14°52'S</td>
<td>75°34'W</td>
<td>11-02-07</td>
<td>0.39</td>
</tr>
<tr>
<td>Puerto Caballos</td>
<td>14°56'S</td>
<td>75°29'W</td>
<td>15-12-07</td>
<td>0.32</td>
</tr>
<tr>
<td>Puerto Lomas</td>
<td>15°33'W</td>
<td>75°50'W</td>
<td>13-08-02</td>
<td>0.03</td>
</tr>
<tr>
<td>Tanaka</td>
<td>15°43'S</td>
<td>74°28'W</td>
<td>25-01-03</td>
<td>0.19</td>
</tr>
<tr>
<td>Ilo</td>
<td>17°38'S</td>
<td>71°21'W</td>
<td>22-08-02</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Figure 3. δ13C (open diamonds) and δ18O (open squares) measured with a monthly resolution along the growth axis of a modern shell (brmd24) collected live in June 2003 on the Llostay beach (close to the QLB site). δ18O values were converted to temperature using Carré et al.'s [2005a] equation and a water δ18O value of 0.18‰(V-SMOW). δ13Ccorr values (closed diamonds) were calculated from shell δ13C corrected from the temperature fractionation effect and the Suess effect. Positive corrections appear in red and negative corrections in blue.
Figure 4. $\delta^{13}C$ profiles for all shells corrected for the temperature effect and for the Suess effect (modern shells only). Isotopic values were positioned on a monthly time axis after re-evaluating the mean microsampling resolution for every shell.
intraseasonal shell $\delta^{13}C$ variations were mainly due to metabolic effect modulated by food availability. This model, however, cannot be generalized since it did not fit the other $P. maximus$ records published in the same article, where shell $\delta^{13}C$ variations followed a classic $\delta^{13}C_{DIC}$ seasonal cycle, with low values during winter for the freshwater input and high values in spring during the peak of phytoplankton productivity. In summary, there remains little evidence for significant seasonal variations of metabolic carbon contribution in mollusk shells. The contribution of metabolic carbon in mollusk shells can be estimated using the following equation from McConnaughey et al. [1997]:

$$M \cdot \delta^{13}C_{\text{met}} + (1 - M) \cdot \delta^{13}C_{\text{Env}} = \delta^{13}C_{\text{shell}} - \varepsilon_{\text{arag-HCO}_3}$$

(3)

Where $M$ is the fraction of metabolic carbon, $\delta^{13}C_{\text{met}}$, $\delta^{13}C_{\text{Env}}$, and $\delta^{13}C_{\text{shell}}$ the isotopic value of the metabolic $\text{HCO}_3$, environmental $\text{HCO}_3$ and shell aragonite respectively. $\varepsilon_{\text{arag-HCO}_3}$ is the enrichment factor between shell aragonite and $\text{HCO}_3$ in the extrapalleal fluid. When using this equation, most authors assume that $\varepsilon_{\text{arag-HCO}_3}$ is constant and equal to the enrichment factor calculated for inorganic aragonite (2.7 ± 0.6‰). Further research is needed to demonstrate the validity of this assumption. Because of the biological influence in the mineralization process, the average enrichment factor may be different for shell aragonite, and may also vary during the mollusk life with environmental or biological factors. Following the discussion of section 4.1.2, considering a temperature dependence of the enrichment factor may be a first improvement in the estimation of $M$.

[21] We used an approximate value of $-20\%$ for the metabolic carbon. The $\delta^{13}C_{\text{DIC}}$ value of sea surface water on the southern Peruvian coast was estimated at $-0.18 \%$ ($\sigma = 0.47\%$) based on 17 measurements between $14^\circ S$ and $18^\circ S$ in the 2001–2004 period (Table 3). The average $\delta^{13}C_{\text{shell}}$ value was $0.17\%$ for the Ica modern shells and $0.58\%$ for the Llostay modern shells. Using an enrichment factor calculated from the Grossman and Ku [1986] relationship for biogenic aragonite and an average temperature value of $17^\circ C$, the estimates of the metabolic contribution were $2\%$ for Ica and $0.2\%$ for Llostay.

[22] We concluded that $\delta^{13}C$ variations in $M. donacium$ shells are not significantly affected by inner variations of the metabolic effect because of three observations: (1) the estimates of the metabolic carbon percentages in $M. donacium$ were low, (2) no systematic ontogenic decreasing trend was observed.
in the individual carbon isotopic signals, (3) no δ¹³C depleted values were associated to Mn and Ba peaks in *M. donacium* modern shells (shells brmd21 and brmd24 in the work of Carré et al. [2005a, 2006]). As a result we suggest that δ¹³C*corr* profiles in Figure 3 mainly reflect variations of seawater δ¹³C*DIC*.

### 4.3. Correcting for the Suess Effect

[23] Since the industrial revolution, the combustion of fossil fuels has provided an additional source of ¹³C enriched carbon into the atmosphere, decreasing the δ¹³C global value of the atmospheric CO₂. This anthropogenic influence is referred to as the Suess effect. This additional ¹³C diffuses into the ocean and has reduced the surface ocean ¹³C since the industrial revolution [Keeling, 1979; Quay et al., 1992; Bacastow et al., 1996]. To allow comparisons between the modern day and preindustrial periods, this anthropogenic effect should be removed from modern shell δ¹³C values. The amplitude of the Suess effect varies with local oceanographic characteristics. Based on estimations of anthropogenic carbon concentration in the South East Pacific [Goyet et al., 2009], we calculated a Suess effect correction of 0.5‰ for the Peruvian coast. This value is lower than the Suess effect measured in the Caribbean (0.9‰) and in New Caledonia (0.7‰) by Böhm et al. [1996], which is consistent with a larger contribution of deep water in Peru. We tested whether the seasonal variation of the coastal upwelling strength could induce seasonal variations of the Suess effect that would dampen the shell δ¹³C amplitude. Since no significant difference was found between δ¹³C annual amplitude of modern and fossil shells, we assumed this potential effect was not significant. An example of a modern shell δ¹³C signal corrected for the Suess effect and the temperature effect is shown in Figure 3.

### 4.4. Stable Isotopes and the Intensity of Coastal Upwelling

[24] Considering the assumptions discussed in sections 4.1 and 4.2, shell δ¹³*C*corr* reflect δ¹³*C*DIC*. The full data set plotted together (Figure 5) shows a strong linear correlation between mean δ¹³*C*corr* and mean δ¹⁸O values, with a slope value of −0.80. Mean values of both δ¹³*C*DIC* and δ¹⁸O carbonates are expected to provide an indication of the background signal generated by the presence of deep water. Deep water brought to the surface by coastal upwelling is characterized by lower temperatures (corresponding to higher δ¹⁸O carbonates values) associated with lower δ¹³*C*DIC* readings.

[25] To test the hypothesis that the linear relationship between mean δ¹³*C*corr* and δ¹⁸O carbonates which appears in our data set is related to the upwelling mean intensity, we compared it to the relationship between δ¹³*C*DIC* and δ¹⁸O carbonates expected along a depth profile within the 100m surface layer using the following equation:

\[
\frac{\partial (\delta^{13}C_{DIC})}{\partial (\delta^{18}O_{carb})} = \left[ \frac{\partial (\delta^{13}C_{DIC})}{\partial (D)} \right] \cdot \left[ \frac{\partial (D)}{\partial (\delta^{18}O_{carb})} \right]_{M. donacium} M. donacium
\]

where *D* is the water depth (m), and *T* is the water temperature (°C). δ¹³*C*DIC* depth profiles measured by Quay et al. [2003] provide an average estimate of 6.10⁻³ ‰m⁻¹ for \( \partial (\delta^{13}C_{DIC})/\partial (D) \) in the 100m surface layer. The temperature-depth dependence \( \partial(T)/\partial(D) \sim -0.03°Cm⁻¹ \) in the surface layer of the coastal Peru based on in situ measurements of IMARPE. \( \partial(T)/\partial(\delta^{18}O_{carb}) \) in aragonite was estimated at −3.66°C‰ for *M. donacium* by Carré et al. [2005a]. A value of −0.73 is obtained from equation (4), very close to the slope value of −0.80 obtained from our data set (Figure 5). This result supports our hypothesis that the linear relationship between δ¹³*C*corr* and δ¹⁸O carbonates mean values obtained from mollusk shells defines a gradient of influence of deep water, equivalent to a gradient of upwelling intensity. Our interpretation is also supported by temperature instrumental data indicating a stronger upwelling today at 15°S (sample ICA*mod*) than at 18°S (sample QLB*mod*) (Figures 1 and 5).
The linear relationship between average values of shell $\delta^{18}O$ and $\delta^{13}C_{corr}$ defines a coastal upwelling intensity axis (Figure 6). So far, and because of the complex influences of mollusk $\delta^{13}C$ signal, the local variations of paleoupwelling intensity were inferred from shell $\delta^{18}O$ [Carré et al., 2005b, 2012] based on the negative relationship between sea surface temperature and upwelling rate. Although this approach is generally accurate, additional influences on shell $\delta^{18}O$, such as evaporation or fresh water input, may lead to incorrect interpretations. The combination of shell $\delta^{18}O$ and $\delta^{13}C_{corr}$ and the position of average values relatively to the upwelling axis allow us to detect environmental influences. A position close to the upwelling $\delta^{18}O - \delta^{13}C_{corr}$ relationship suggest that upwelling rate is the major control of the average water geochemistry, whereas evaporative conditions (for instance in a close embayment) are indicated by a deviation toward $\delta^{18}O$ enrichment, and fresh water influence is indicated by a combined depletion of $\delta^{18}O$ and $\delta^{13}C_{corr}$ (Figure 6). The upwelling $\delta^{18}O - \delta^{13}C_{corr}$ relationship proposed here relies on a $\delta^{13}C_{DIC}$-depth relationship, a temperature-depth relationship and a specific paleotemperature relationship (equation (3)); it is thus only valid for southern Peru and M. donacium shells although the method could be similarly applied with other species in other regions.

The $\delta^{18}O$ and $\delta^{13}C$ signals confirm that coastal upwelling conditions were significantly stronger during the middle Holocene (Figure 5), which had been already suggested by independent paleoenvironmental results [Bétancourt et al., 2000; Holmgren et al., 2001; Placzek et al., 2001; Rech et al., 2003; Fontugne et al., 2004; Koutavas and Sachs, 2008; Ortlieb et al., 2011]. Furthermore, during the middle Holocene, the strongest coastal upwelling was experienced at 18$^\circ$S (Figure 5), whereas under modern conditions, upwelling intensity at 18$^\circ$S is currently weaker than at 15$^\circ$S. This result suggests a spatial reorganization of the intensity of coastal upwelling centers, possibly as a response to a different wind field.

### 4.5. Seasonal Signals of Stable Isotopes

For modern samples, the average annual amplitudes of shell $\delta^{13}C_{corr}$ range from 0.72‰ (ICA mod) to 0.85‰ (QLB mod). In fossil samples, average annual $\delta^{13}C_{corr}$ amplitude is 0.80‰ for Ica Inca, 0.83‰ for Ica mH, and 0.99‰ for QLB mH. The difference between these values is not statistically significant. For the whole Peruvian South coast, we obtain an average annual $\delta^{13}C_{corr}$ amplitude of 0.83‰. Trends in $\delta^{18}O$ follow the seasonal patterns of temperature, with low $\delta^{18}O$ values representing the warmer temperatures of austral summer (Figures 3 and 8). Although $\delta^{13}C_{corr}$ monthly signals exhibit a less pronounced seasonal pattern than $\delta^{18}O$, seasonal $\delta^{13}C_{corr}$ variations are generally in phase with, or lag slightly behind, temperature. Enriched $\delta^{13}C_{corr}$ values are generally recorded in summer and depleted values are recorded during winter. If trends in shell $\delta^{13}C_{corr}$ represent $\delta^{13}C_{DIC}$ variations (section 4.3), then mollusk shells are recording seasonal fluctuations of $\delta^{13}C_{DIC}$ in coastal waters. At the seasonal scale, $\delta^{13}C_{DIC}$ is controlled by a combination of...
(1) primary productivity, (2) upwelling seasonality, and (3) sea-atmosphere CO\textsubscript{2} exchange.

[29] Carbon isotope fractionation occurs during sea-atmosphere CO\textsubscript{2} exchange. $^{13}$CO\textsubscript{2} is favored in the outgassing reaction that induces an enrichment of $^{13}$C\textsubscript{DIC} within surface waters. This effect increases with the CO\textsubscript{2} flux, which depends on the pCO\textsubscript{2} difference between the atmosphere and the surface water. Carbon isotopic equilibration takes approximately 10 years therefore $^{13}$C\textsubscript{DIC} is never in isotopic equilibrium with the atmosphere along the Peruvian coast where the surface water is constantly replaced by deep water through upwelling. At the seasonal scale, carbon fractionation in sea-atmosphere exchange is mainly due to kinetic effects [Lynch-Stieglitz et al., 1995]. The net CO\textsubscript{2} flux of the Peruvian coast is toward the atmosphere due to the very high pCO\textsubscript{2} values that characterize upwelled waters. The CO\textsubscript{2} flux, and therefore the fractionation effect, is strongest during the winter when ΔpCO\textsubscript{2} may reach 1000 ppm and weakest during the summer when ΔpCO\textsubscript{2} is closer to 0 ppm. Therefore, the effect of air–sea CO\textsubscript{2} exchange on the $^{13}$C\textsubscript{DIC} is enrichment during the winter and depletion during the summer. Since this is opposite to most trends recorded in mollusk shells, we conclude that air–sea CO\textsubscript{2} exchange have a minor control on seasonal $^{13}$C\textsubscript{DIC} variations.

[30] In contrast to air–sea exchange, seasonal variability in the intensity of coastal upwelling would produce $^{13}$C\textsubscript{DIC} in phase with the temperature annual cycle. This effect can be estimated from the seasonal variations of the thermocline depth and the trend in $^{13}$C\textsubscript{DIC}–depth relationship. In situ measurements reveal that the amplitude of the thermocline seasonal vertical movement in non–El Niño years is ∼30m. Considering a 6.10$^{-3}$ %\textsubscript{o} m$^{-1}$ depletion for $^{13}$C\textsubscript{DIC} with depth [Quay et al., 2003], the effect of upwelling seasonality is estimated to be about 0.2%, which cannot explain the 0.83% of variations observed in shell samples.

[31] The primary control for $^{13}$C\textsubscript{DIC} seasonal variations would therefore be the remaining variable: primary productivity. Productivity peaks induce $^{13}$C enrichment of the DIC in the surface layer, which would generally occur during summer as indicated by in situ and satellite chlorophyll a measurements [Echevin et al., 2008]. The phasing of the productivity effect is thus in agreement with $^{13}$C\textsubscript{DIC} variations measured in mollusk shells. To further test this hypothesis, we used the relationship between $^{13}$C\textsubscript{DIC} and PO\textsubscript{4} in the ocean published by Broecker and Maier-Reimer [1992], which allows for an estimate on the productivity effect on $^{13}$C\textsubscript{DIC} without air–sea exchange:

\[
^{13}\text{C}_{\text{DIC}} = 2.7 - 1.1 \times \text{PO}_{4}
\] (5)

The seasonal variation in PO\textsubscript{4} at 15°S on the Peruvian coast is ∼0.8 μg L$^{-1}$ (measured by IMARPE in oceanographic cruises between 1964 and 2008, excluding El Niño years), which corresponds to a $^{13}$C\textsubscript{DIC} seasonal variation of ∼0.9‰ based on equation (5). This value is very close to the amplitude of $^{13}$C\textsubscript{DIC} recorded in mollusk shells, which supports our hypothesis that the dominant control on seasonal variations of $^{13}$C\textsubscript{DIC} recorded by shell $^{13}$C\textsubscript{corr} is primary productivity.

[32] In order to quantitatively estimate the seasonal timing of phytoplankton blooms and its variability with sites and periods, lag periods between $^{13}$C\textsubscript{corr} and $^{18}$O were evaluated using cross-correlation. Correlations between $^{13}$C\textsubscript{corr} and $^{18}$O trends of individual shells were evaluated between lag periods of ±6 data points. The lag corresponding to the highest positive correlation between isotopic signals, multiplied by the microsampling resolution, was interpreted as the monthly time difference between the productivity bloom ($^{13}$C\textsubscript{corr} maximum) and the February temperature maximum/August temperature minimum for positive and negative correlations respectively (Figure 7). Compared to a simple peak–to-peak distance between $^{13}$C\textsubscript{corr} and $^{18}$O, this technique takes into account the full shape of the signal and is thus more reliable for estimating a time lag. The seasonal timing of blooms determined from each shell were then classified into austral spring (October–December), summer (January–March), autumn (April–June) or winter (July–September).

[33] The seasonal timings of phytoplankton blooms evaluated by this new technique were plotted as frequency distributions for the middle Holocene, the Inca period and modern day (Figure 8). Modern shell samples from both locations reveal that phytoplankton blooms were most common during austral summer, in agreement with chlorophyll a data (Figure 1) [Thomas et al., 1994; Echevin et al., 2008], which supports the reliability of the technique for paleoenvironmental analysis.

4.6. Past Seasonal Dynamics of Phytoplankton Bloom

[34] Based on our assumptions and method, the lag between $^{13}$C\textsubscript{corr} and $^{18}$O seasonal signals in individual shells provides an indication of the season of the main phytoplankton bloom (Figure 7). In our
case study, we show that modern and fossil samples show similar coastal phytoplankton dynamics at 15°S: bloom development appears to coincide mainly with summer, which corresponds to the warmer SSTs and autumn, which correspond to the onset of upwelling strengthening (Figure 8). This would imply that light is the first limiting factor for phytoplankton growth and upwelled nutrients are a second limiting factor. At 18°S (QLB site), the modern and middle Holocene samples also show a predominance of summer blooms. However, an increase in spring blooms and an absence of fall blooms are also observed. This result suggests that light was the only limiting factor at that time and that upwelled nutrients were not at all limiting, which is consistent with stronger upwelling mean conditions.

The influences of gas air-sea exchanges, upwelling seasonality, and biological effects, were likely secondary in our case study, but they still exist and might in some circumstances be predominant in the δ13Ccorr signal, inducing thus some noise in the final result. The precision of this technique for evaluating the seasonal timing of phytoplankton blooms is also limited by the variability of the temperature profile and the uncertainties in the δ18O signal. Finally, the method is based on an isotopic model that could be improved by comparing mollusk shell profiles with in situ weekly measurements of marine δ13C\text{DIC}, productivity, and wind stress over an annual cycle. Such calibration work may allow for more detailed reconstructions. Nevertheless, mollusk stable isotopes could potentially provide new valuable insights into long-term variability of coastal seasonal biogeochemical processes.

5. Conclusions

In this study we proposed a new method to evaluate past variations (1) of the mean intensity of
the Peruvian coastal upwelling and (2) of the seasonal timing of phytoplankton blooms. This method uses a combination of the monthly carbon and oxygen isotopic signal preserved in fossil shells of *M. donacium*. Our method involves a re-evaluation of the paradigm that considers that the $\delta^{13}C$ enrichment factor between shell aragonite and HCO$_3^-$ is constant and equal to the enrichment factor of inorganic aragonite. We considered that it is more likely to vary with temperature following Grossman and Ku’s [1986] empirical model, although the mechanism remains unknown. After being corrected for temperature and Suess effects, shell $\delta^{13}C_{\text{corr}}$ variations are believed to primarily reflect $\delta^{13}C_{\text{DIC}}$ variations. At the centennial to millennial scale, $\delta^{13}C_{\text{DIC}}$ mean values are primarily affected by the mean intensity of the upwelling, while primary productivity is the main factor controlling seasonal $\delta^{13}C_{\text{DIC}}$ variations.

[37] Five shell samples from the southern Peruvian coast were analyzed and show a strong linear correlation between average values of shell $\delta^{13}C_{\text{corr}}$ and $\delta^{18}O$, similar to the expected relationship along a gradient of influence of deep water, which represents a gradient of upwelling intensity. We then proposed a proxy model to estimate the past intensity of the coastal upwelling in Peru. This method could bring additional independent information valuable to interpret paleoproductivity changes reconstructed from marine sediment of the nearby continental shelf. Results obtained on fossil samples from the middle Holocene suggest an increase of the upwelling during this period, consistent with existing independent paleoenvironmental reconstructions. Additionally, fossil shells show a spatial reorganization of upwelling centers along the South Peruvian coast. At the seasonal scale, shell $\delta^{13}C_{\text{corr}}$ enrichment was interpreted as the indication of a phytoplankton bloom. Bloom seasonal timings may thus be estimated by the lag between shell $\delta^{13}C_{\text{corr}}$ and the annual temperature cycle reproduced by shell $\delta^{18}O$ monthly variations. The results obtained with two modern shell samples indicate phytoplankton blooms occurring during summer and fall, consistently with in situ productivity observations. The timing of productivity blooms was similar in fossil samples suggesting little change in limiting factors of phytoplankton growth. One strength of this study lies in the large amount of data which averages out a significant part of random uncertainty and provides statistical robustness to the results. Although this work is only valid for southern Peru and the mollusk species *M. donacium*, this approach could be developed in other similar areas like the Benguela current system where the upwelling maintains arid conditions on the coast, and where numerous fossil shell middens are preserved.

[38] However, while our interpretation in this case study is arguably the most parsimonious hypothesis with regards to actual knowledge of carbon isotopes in mollusk shells, it is clear that further investigation is needed to understand the factors that influence the carbon isotopic fractionation in biogenic aragonite. We estimated here that the enrichment factor $\varepsilon_{\text{arag-HCO}_3^-}$ is more likely to be not constant in biogenic aragonite, which should lead to a re-evaluation of the contribution of the metabolic carbon in the shell formation.

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