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Modern sea surface productivity and temperature estimations

off Chile as detected by coccolith accumulation rates

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Abstract

14 Recent coccoliths from 74 surface sediment samples recovered from the southeastern Pacific off Chile were examined quantitatively to investigate modern regional gradients 15 16 of sea surface productivity and temperature. All findings are based on coccolith 17 accumulations rates. Therefore an approach was designed to estimate recent sedimentation rates based on ²¹⁰Pb and bulk chemistry analyses of the same set of surface 18 19 samples. Highest total coccolith accumulation rates were found off north-central Chile, 20 where seasonal upwelling takes place. Based on a multiple linear regression between 21 calculated coccolith accumulation rates and World Ocean Atlas derived sea surface 22 temperatures, a calibration model to reconstruct annual average temperatures of the 23 uppermost 75 m of the water column is provided. The model was cross-validated and the 24 SST estimates were compared with SST observed and SST estimates based on diatoms 25 and planktic foraminifera, showing a good correlation.

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1. Introduction

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Coccolithophores, one of the main open ocean primary producers, have a broad fossil record, which makes them an outstanding biostratigraphical group and gives them potential for paleontological study of ecosystem response to global change. As a basic requisite for their application as paleoceanographic proxies it is necessary to maximize the retrieval of paleoecological information from coccolithophore species, and to enhance the understanding of their ecology as a plankton group. Knowing how the present-day environment influences their spatial and temporal distribution, we could use the fossil record of such organisms to reconstruct the state and variation of past environments (Kucera et al., 2005). One of the modern ocean's most productive upwelling conditions occur all along the Chilean margin (Strub et al., 1998; Abrantes et al., 2007). In coastal upwelling domains, the dominant primary producers are diatoms, although coccolithophores are also significant contributors to the total phytoplankton community (e.g., Mitchell-Innes and Winter, 1987; Giraudeau et al., 2000; Boeckel and Baumann, 2004). However, there are very few modern studies on coccolithophores ecology and calibration to climate proxies in the Southeast (SE) Pacific, and most of them are based on plankton samples (e.g., Beaufort et al., 2007; Beaufort et al., 2008; Beaufort et al., 2011) or on sediment trap samples (e.g., González et al., 2004; Köbrich, 2008). So far, only a small number of surface sediment studies were performed by Saavedra-Pellitero et al. (i.e., 2010; 2011). In such studies the ecological optima of the most important species of coccolithophores in the Pacific sector was studied in order to produced feasible transfer functions to reconstruct climate changes in the past. In this work the focus was on coccolithophore surface sediment assemblages since they represent the former living communities and with that, the overlying surface water conditions (Andruleit et al., 2004). While relative abundances indicate dominance of a certain ecological habitat, absolute fluxes represent more realistic living conditions in the water column, thus providing a more detailed reconstruction of hydrography (Ravelo et al., 1990). Coccolith accumulation rate (CAR) data could furthermore complement and in some cases improve upon the relative abundance data, whereas also comparing with modern flux estimates derived from sediment trap studies.

The estimation of past environmental parameters using micropaleontological data has became a very useful tool from the development of statistical transfer function techniques (IKM - Imbrie and Kipp Method) in which the authors originally used planktonic foraminifera (Imbrie and Kipp, 1971; Klovan and Imbrie, 1971). It provides quantitative estimations of hydrographical parameters (e.g., sea surface temperature, SST) preserved in the recent sedimentary record (e.g., CLIMAP 1976, 1981, Ortiz and Mix 1997, Pisias et al., 1997; Mix et al., 1999; Kucera et al., 2005; Morey et al., 2005; Abrantes et al., 2007). Different statistical techniques were already applied to coccolith census counts from surface sediments of the North and Equatorial Pacific (Geitzenauer et al., 1977; Roth and Coulbourn, 1982; Roth, 1994), of the North Atlantic (Geitzenauer et al., 1977) as well as of the Benguela upwelling system (Giraudeau and Rogers, 1994). However the different sample coverage, the different taxonomies (of traditional broad species) as well

as the exclusion of species in some of those investigations prevented any transfer function to be properly defined. Consequently, a well established calibration of modern coccolithophore assemblages to surface mixed-layer temperatures has only been previously achieved at a few locations. These were performed at the Benguela and the Peru-Chile upwelling systems (Giraudeau and Rogers, 1994; Saavedra-Pellitero et al., 2010; 2011) and differ from ours by being based on species relative abundances. The main goal of the present study was to investigate whether the modern regional gradients of sea surface productivity and temperature can be detected by studying (a) coccolith accumulation rates and (b) coccolithophore derived temperature estimates.

1.1. Regional setting

The SE Pacific is dominated by the Peru-Chile current system (Strub et al., 1998), one of the most productive eastern boundary systems in the world. Off southern Chile, cool waters from the Antarctic Circumpolar Current reach the continent and split in two branches, the southward-flowing Cape Horn Current and the northward-flowing Peru Current (Fig. 1A). Coastal upwelling, driven by persistent southerly winds along the coast brings cold and nutrient-rich waters to the sea surface along the coast of Chile and Peru towards the equator (Wyrtki, 1981; Bryden and Brady, 1985; Strub et al., 1998). Phytoplankton biomass is high throughout the year in this coastal upwelling system (Rojas de Mendiola, 1981). However, from 15°S to 30°S, minimum chlorophyll seasonality offshore Chile is observed, despite strong seasonality in wind forcing between 20°S and 30°S. South of this area, chlorophyll reaches maxima during austral summer

and minima in austral winter, in phase with the seasonal wind forcing (Thomas et al., 2004).

Precipitation patterns in Chile, the most important climate factor driving continental erosion, show one of the most pronounced latitudinal gradients on Earth (Kaiser, 2005; Hebbeln et al., 2007). Rainfall rates rapidly increases from almost zero in the hyper-arid Atacama desert (north of 27°S) over intermediate precipitation in the semi-arid Mediterranean-type climate of central Chile (from 31°S to 37°S) to year round humid conditions with extraordinary high annual precipitation south of 42°S (Miller, 1976; New et al., 2002). Major atmospheric circulation patterns, specifically the SE Pacific anticyclone in the north and the rain-bearing Southern Westerlies in the south, are responsible for this marked N-S gradient along Chile (Hebbeln et al., 2007, see Fig. 1B). However, expected differences in mass accumulation rates along the Chilean continental margin depend not only on the different hydrological regimes, but also on the topography of margin and on the latitudinal variability of primary productivity and upwelling (Muñoz et al., 2004).

2. Material and Methods

For this study we considered 74 out of 106 surface sediment samples located from 22.80°S to 44.28°S and from 70.49°W to 75.86°W offshore Chile. Previous studies (Saavedra-Pellitero et al., 2010; 2011) allowed us to select the best preserved samples and to exclude the samples where coccoliths were poorly preserved. The uppermost centimetre from the undisturbed surface sediment samples (boxcores and multicores), has

been used for the analyses reported here. They were retrieved during Genesis III Cruise, RR9702A onboard the American R/V Roger Revelle and during R/V SONNE Cruise SO-156 Valparaiso-Talcahuano (Hebbeln and cruise participants, 2001) onboard the German R/V Sonne.

2.1. Coccolith counts and estimations of CARs

- Coccolith absolute abundance counts were already available from a previous study (Saavedra-Pellitero et al., 2010) although only relative abundances were published in that paper. Slides for coccolith counts were prepared using the standard settling methodology of Flores and Sierro (1997). Coccolith identification was done using a Leica DMRXE and a Nikon Eclipse 80i polarized microscopes at a magnification of X1000, occasionally X1250. In order to ensure statistical reliability a minimum of 400 coccoliths per sample were counted. This procedure allowed us to estimate the total number of coccoliths per gram of sediment for each of the coccolithophore species and species CARs. We followed the taxonomy established by Hine and Weaver (1998), Bown and Young (1998) and the internet site www.nannotax.org. Some additional considerations were also taken into account (i.e., the group of *Gephyrocapsa* <3µm defined by Flores et al., 1997). The formula used to calculate CARs is:
- $CAR = [(n \cdot R^2 \cdot V^2)/(r^2 \cdot g \cdot v)] \cdot DBD \cdot SR$
- where n is the number of coccoliths counted in a random light microscope scanned area; R is the radius of the Petri dish used; V is the volume of the water added to the dry sediment; r is the radius of the visual field used in the counting; g is the dry sediment

weight; v is the volume of mixture withdrawn with the micropipette; DBD is the estimated dry density of the sediment, and SR is the linear sedimentation rate.

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2.2. Sedimentation rate estimates and dry bulk densities

Sedimentation rates (SRs) and sediment dry bulk densities (DBD) are required to estimate CARs. However the lack of these measurements for the majority of the samples considered in this study led us to design an approach to estimate them. To calculate the SR along the Chilean continental margin, we considered the recent SR data based on ²¹⁰Pb (Muñoz et al., 2004; Fig. 2A) available from a subset of samples spanning across a broad range of sedimentation regimes which correspond to some of the samples studied here (Figs. 1B and 2, Table 1). Owing to the fact that the samples cover very distinct areas and stations are quite sparsely distributed, we normalized the number of coccoliths per gram of sediment instead of directly interpolating the SR data from Muñoz et al. (2004; see Fig. 2). This designed approach consists of comparing the bulk chemistry analyses done by inductively coupled plasma atomic emission spectrometry (ICP-MS, Stuut et al., 2007), with the SR based on ²¹⁰Pb (Muñoz et al., 2004) using multiple regression analysis. Mesh grids were created for Al, Fe, K, Mg, and Ti derived by ICP-MS measurements with MatlabTM and the values for the 17 stations indicated in Table 1 were used for the calibration.

Stepwise multiple regression is a systematic method for choosing predictors (or independent variables) of a particular dependent variable on the basis of statistical criteria (Howitt and Cramer, 2008). This procedure determines which independent variable is the best predictor, the second best predictor, etc. After regressing our independent or predictor variables (Al, Fe, K, Mg, and Ti ICP-MS values, in our case) against the dependent variable (SR, in our case) with MatlabTM software, we found out that only Ti is positively correlated to SR (R²=0.61, Fig. 2B and supplementary material). This relationship reflects the recent sedimentation patterns on the Chilean continental slope. A lack of significant precipitation limits the denudation in the Atacama Desert (Stuut et al., 2007) restricting the sediment supply to the Chilean margin and therefore the high SRs and Ti contents offshore North Chile. On the contrary, humid conditions and stronger erosion in South Chile (Miller, 1976) favors the higher SR and Ti contents at the southermost surface sediment samples. The linear equation obtained allowed us to estimate SR from Ti measurements for the specific case of the study area.

 $SR=(0.1089 \cdot Ti)-0.274$

This formula provided a way to estimate SR for the surface sediment samples studied (Table 2, Fig. 3A) with a root mean squared error (RMSE) of 0.047 for the 64 samples where ICP-MS were performed, all of them GeoB samples. Concerning the 10 non-GeoB stations of the database (RR-), euclidean distances between each station and the GeoB stations were calculated and the smallest one was chosen. For the four samples located further offshore, different SR values were considered (Table 1).

To estimate sediment DBDs, the closest value from Muñoz et al. (2004) was chosen (Table 1 for original measurements and Table 2 for estimates), except for the four further offshore stations, where the same criteria as for SR was followed.

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2.3. Oceanographic variables of the surface waters

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The modern oceanographic properties chosen for this work are sea surface temperature (SST in °C, Locarnini et al., 2006), sea surface salinity (SSS in PSU, Antonov et al., 2006), nitrate (micromole/l), phosphate (micromole/l), silicate (micromole/l, all data from Garcia et al., 2006) and chlorophyll concentrations (microgram/l, Levitus, 1982; Conkright and Boyer, 2002) expressed as an annual average from 0 m to 75 m water depth. In addition, depth of the mixing layer (m) and primary productivity (mg $C/m^2/day$) were considered. All these parameters were obtained from the World Ocean Atlas 2005, from the World Ocean Atlas 2001 Data Sets, National Oceanographic Data Centre, Washington DC (see http://ingrid.ldgo.columbia.edu/SOURCES/.NOAA/.NODC), and **Productivity** from Ocean (http://www.science.oregonstate.edu/ocean.productivity/index.php). Euclidean distances between each station and World Ocean Atlas database (1° grid) were calculated and the smallest one was chosen using MatlabTM. All the contour maps were generated using Ocean Data View (ODV) software (Schlitzer, 2011). The main model was generated with R software (for further details see section 3.2) and ordination was performed using the Vegan package for R (Oksanen et al., 2006).

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3. Results

3.1. Coccolith accumulation rates

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Maximum numbers of 2.21·10⁹ coccoliths/g and highest CARs of 6.9·10⁷ coccoliths/cm²/yr are reached at different locations in the northernmost stations while minimum numbers of 2.10·10⁶ coccoliths/g and CARs of 9.2·10⁴ coccoliths/cm²/yr are reached offshore southern Chile (44.06°S, 75.13°W, Fig. 3B, C). The 14 most common taxa or groups of coccoliths regarded in this study are Calciosolenia spp., Calcidiscus leptoporus, Coccolithus pelagicus, Emiliania huxleyi, Gephyrocapsa muellerae, Florisphaera profunda, *Gephyrocapsa* Helicosphaera carteri, Rhabdosphaera clavigera, small Gephyrocapsa (Gephyrocapsa <3µm), Syracosphaera spp., Umbellosphaera spp., Umbilicosphaera spp. and Oolithotus spp. In the following we briefly describe the main features observed in the contour maps (Fig. 4) ranging from highest CARs average to lowest ones for each coccolithophore taxa. Small Gephyrocapsa is the most abundant group (average of 1.94·10⁶ coccoliths/cm²/yr) which reaches abundances of 1.69·10⁷ coccoliths/cm²/yr at 26°S, although high numbers are also recorded in other parts of the Chilean upwelling area (Fig. 4A). C. leptoporus shows an average CAR of 1.48·10⁶ coccoliths/cm²/yr. Maximum CARs of up to 1.5·10⁷ coccoliths/cm²/yr for this species are reached in the samples located in the north of the study area and decrease towards the South (Fig. 4B). An average of 1.3·10⁶ coccoliths/cm²/vr was estimated for F. profunda (Fig. 4C). CARs for this lower photic zone dweller fluctuates considerably, decreasing broadly southwards; maximum values are reached at 26°S (1.08·10⁷ coccoliths/cm²) and minimum at the southernmost locations

offshore Chile (8.59·10³ coccoliths/cm²/yr). E. huxleyi, with an average of 1.21·10⁶ 229 230 coccoliths/cm²/yr, diplays a similar distribution pattern to small Gephyrocapsa with maximum CAR of 8.81·10⁶ coccoliths/cm² (Fig. 4D). 231 G. muellerae occurs in average CARs of 1.10·10⁶ coccoliths/cm²/yr. This species 232 fluctuates along the Chilean upwelling region; it reaches a maximum of 7.42·10⁶ 233 coccoliths/cm²/yr in the northern part of the study area and high CARs at the 234 southernmost locations (Fig. 4E). G. oceanica, with an average of 1.08·10⁶ 235 coccoliths/cm²/yr, reaches maximum CARs (9.74·10⁶ coccoliths/cm²/yr) at the northern 236 237 part of the study area and progressively decreases southwards (Fig. 4F). H. carteri shows average CARs of 5.24·10⁵ coccoliths/cm²/yr. Maximum CARs of this 238 species are clearly reached in central and north offshore Chile (6.19·10⁶) 239 coccoliths/cm²/yr, Fig. 4G). C. pelagicus reaches average CARs of 9.73·10⁴ 240 coccoliths/cm²/yr and its maxima (7.19·10⁵ coccoliths/cm²/yr) at the southernmost 241 242 locations of the Chilean upwelling (Fig. 4H). *Umbellosphaera* spp. shows average CARs of 8.86·10³ coccoliths/cm²/yr with maximum of 2.47·10⁵ coccoliths/cm²/yr (Fig. 4I). 243 244 Results corresponding to the rest of the coccolithophore species are not listed here either 245 owing to their low numbers or to the non-relevance for the SST estimates. This refers to Syracosphaera spp. (average of 3.67·10⁴ coccoliths/cm²/yr), Oolithotus spp. (average of 246 $1.98 \cdot 10^4$ coccoliths/cm²/yr), $1.06 \cdot 10^5$ 247 Umbilicosphaera spp. (average of coccoliths/cm²/yr), R. clavigera (average of 5.19·10³ coccoliths/cm²/yr) and 248 Calciosolenia spp. (average of $4.18 \cdot 10^3$ coccoliths/cm²/yr). 249

3.2. Statistical analysis and SST transfer function

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A preliminary detrended correspondence analysis (DCA) on the coccolithophore assemblage resulted in a gradient shorter than 2 Standard Deviation (SD) units, suggesting a linear response (ter Braak, 1987). Then, principal component analysis (PCA) was used to analyze the relationship between coccolithophore assemblage and environmental properties, where the latter variables have been entered passively, and to identify outlying samples with unusual assemblages (ter, Braak, 1987). There were no unusual samples, as indicated by the PCA. The significance of PCA axes was assessed using the broken-stick model, resulting in just one significant axis explaining 78.9% of the variance, and being highly correlated with SST. These results are in agreement with Saavedra-Pellitero (2011) who found out that SST was the dominant oceanographic parameter controlling certain coccolithophore species (grouped into a factor) offshore Chile. CARs were square transformed to standardize their variances. Rare species were downweighted because the square root transformation increases their weight and they can have undue influence on the ordination. To establish a SST-sensitive transfer function based on CAR, we performed a multiple linear regression. The number of parameters in the fitted model were determined using a Akaike's information criterion. Thus, the species eventually included in the minimal adequate model were: F. profunda (F.pro), H. carteri (H.car), G. muellerae (G.mue), Umbellosphaera spp. (Umbe) and C. pelagicus (C.pel). The minimal adequate regression and final calibration model showed a residual standard error of 0.803 on 66 degrees of freedom and adjusted R² of 0.7021. We obtained the following equation to estimate SST using CARs:

- 273 SST=12.98+[0.0015557•(F.pro) + 0.0011031•(H.car) -0.0009193•(G.mue)
- 274 0.0032570•(Umbe)-0.0024363•(C.pel)]

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A root mean squared error of prediction (RMSEP) was assessed by (bootstrapping and jackknifing) cross-validation (99 permutation cycles) in order to assess the predictive power of our transfer function (Table 3). The final model was examined for potential outliers, because these can strongly affect transfer function coefficients and may markedly decrease the predictive ability of the model. Outliers were identified as samples having an absolute residual (observed minus estimated) higher than the SD of the environmental variable of interest and a low influence on the model indicated by Cook's D (Cook's D <4/n, Fig 5D). Based on this criterion, the samples GeoB 7108 and RR 52 mc3 were excluded. The SST residuals (the difference between the observed minus the estimated SST) were tested for homoscedasticity (constant variance). This condition ensures that the bestfitting line works well for all relevant values of SST estimated, not just in certain areas. In the scatter plot of the standardized residuals against the SST estimated values (Fig. 5C) the spread in the residuals stays almost the same throughout, addressing the homoscedasticity condition. In general, the SST residuals are relatively low (most of them are between -1 and 1) and without any significant correlation or trend with the estimated SSTs (Fig. 5A). Our results based on CARs reveal good reproducibility of the SST World Ocean Atlas 2005 (see Fig. 6 and supplementary material). Even though we regarded annual averages to avoid any influence of seasonality, seasonal changes in oceanographic conditions can strongly influence the coccolithophore fluxes. Therefore SST residuals were also compared with the SST difference between summer and winter in the study area (Fig. 7A). A slight trend can be observed between SST difference and SST residuals (Fig. 7B)

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4. Discussion

4.1. CARs estimates

Coccolith distribution patterns and coccolith numbers from surface sediment samples are dependent on coccolithophore productivity, on dissolution and on dilution by terrigenous material, which influences sedimentation rates. Due to the enormous differences in mass accumulation rates along the Chilean continental margin, CARs compliment and in some cases improve the relative data to reconstruct gradients in coccolithophore productivity off Chile. Highest total CARs are found in the stations located off north-central Chilean coast (22.8°S-30°S, Fig. 3), where seasonal upwelling takes place (18°S-27°S; Strub et al., 1998) and where Abrantes et al. (2007) observed samples barren of diatoms. However, a marked decrease in CARs is observed further offshore at surface sediment samples around ~23°S (Fig. 3C). At these locations high numbers of coccoliths per gram of sediment are noted (Fig. 3B), yet CARs notably decrease with respect to more coastal samples at similar latitude, probably driven by low SRs estimates. High coccolithophore diversity is also recorded off north-central Chilean continental margin, as displayed by the presence of different placolith bearing species (i.e., small Gephyrocapsa, C. leptoporus, E. huxleyi, G. muellerae and G. oceanica) together with other coccolith forms (e.g., F. profunda, H. carteri and Umbellosphaera spp.). Offshore central-south Chile, upwelling-favorable conditions occur from late spring to early fall, corresponding to the most persistent upwelling extending from 35°S to 38°S (Strub et al., 1998). Due to the fact that underneath these high productive zones degradational processes of organic matter may favor enhanced carbonate dissolution (Boeckel and Baumann, 2004), samples barren of coccolithophores or highly affected by dissolution (which were excluded in our model) are mainly located in areas from 35.5°S to 39°S (Saavedra-Pellitero et al., 2010). A drop in the total CARs and in all the species numbers are observed in the area from 36.5°S to 38°S (Fig. 3) nearby the persistent upwelling cell off point Concepción (Strub et al., 1998) coincident with the highest diatom abundance values (valves/g) and organic carbon recorded in the same region by Abrantes et al. (2007). The only coccoliths recorded in this area (around ~36°S) belong to *F. profunda* and *G. oceanica*, and in a lesser extent *E. huxleyi*, small *Gephyrocapsa*. and *G. muellerae*. The tongue of low-salinity water characteristic from the fjord region off south Chile (e.g., Lamy et al., 2002) has been recognized by maxima in the abundance of freshwater diatoms (Abrantes et al., 2007) and by the factors derived from the coccolith percentage dataset (Saavedra-Pellitero et al., 2010), but is not clearly defined by the CARs. The most prominent coccolithophore species in this area are *C. pelagicus* and *G. muellerae*, but small placoliths, such as small *Gephyrocapsa* and *E. huxleyi* are also present.

A comparison of the observed CARs with the coccolith flux collected from a sediment trap located offshore Chile (30°S, 73°11'W, Fig. 4) showed that numbers differ, although they are still comparable. A total CAR of 6.8·10⁶ coccoliths/cm²/yr, was obtained for the closest surface sediment sample in our dataset (29.72°S, 72.17°W), a minimum flux of 9.86·10⁶ coccoliths/cm²/yr was estimated during El Niño conditions (1997-1998) and an average of 1.59·10⁸ coccoliths/cm²/yr during non-El Niño conditions (1993-1994; Köbrich, 2008); at least the calculated CAR is in the order of the minimum flux during El Niño conditions. Owing to the fact that the surface sediment sample was not retrieved

directly underneath the mooring location and that dissolution processes are likely to affect primarily deep sediments, differences between the CAR estimates and the sediment trap fluxes appear to be reasonable. In addition, the sediment trap recorded seasonal and annual variations while the surface sediment samples provided averaged data on a wider time interval of tens to hundreds of years.

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4.2. Reliability of the SST reconstruction

The present SST estimation is adding to a series of previously published transfer functions in the SE Pacific realm based on data from different siliceous and calcareous microfossils, with the innovation of using species CARs from surface sediment samples instead of relative abundances. The results of our SST transfer function based on CARs reveal good reproducibility of the SST World Ocean Atlas 2005 (Locarnini et al., 2006) data; the estimated and measured SST values are highly correlated ($R^2=0.723$, Fig. 8B). We improved the spatial resolution offshore Chile, especially compared with previous works based on radiolarian census (Pisias et al., 1997; Pisias et al., 2006) and planktonic foraminifera (Mix et al., 1999; Feldberg and Mix, 2002; Kucera et al., 2005; Morey et al., 2005) which considered very few samples for the whole study area (see Fig. 8A). Abrantes et al. (2007) added some samples to previously collected databases (e.g., Schuette and Schrader, 1979; Romero and Hebbeln, 2003) and successfully obtained a SST diatom transfer function based directly on species percentages. Many of those samples were also used by Saavedra-Pellitero et al. (2011) to estimate SST using multivariate statistical analyses performed on modern coccolithophore census data from 15°N to 50.6°S and from 71°W to 93°W. With our work we covered an existing gap in

the north-central Chilean coast (from ~23°S to ~33°S) due to the lack of preserved diatoms in the samples (Fig. 8A). A comparison of the SST estimates derived from our model (using CARs) with previous SST transfer functions based on planktonic foraminifera (Kucera et al., 2005) and diatoms (Abrantes et al., 2007) was performed and they resulted in close agreement (Fig. 8A). Nevertheless, even if the three reconstructions follow the same trend, our SST estimates are always lower than the other two because we considered an annual SST average from 0 m to 75 m water depth, instead of 0 m (chosen for diatoms) or 10 m (chosen for planktonic foraminifera) SST annual averages. Those differences are indeed higher offshore north-central Chile and become smaller offshore central-south Chile, specifically at intense upwelling areas (e.g., around 36°S, Fig. 8A). The underestimation of SST further offshore Chile around ~23°S (Figs. 6C and 8A) would be linked to the calculation of SR at those locations. A SST average (from 0 m to 75 m) was considered due to the fact that coccolithophore production can also happen at deeper depths (e.g., F. profunda); this choice also allowed us directly to compare with the SST estimates based on coccolith percentages (Saavedra-Pellitero et al., 2011). Both reconstructions based on coccolithophores follow the same trend as the SST observed, although the SST CAR estimates fits better (see Fig. 8A), especially from ~26°S to ~36°S. In any case, it should be noted that SST estimates using different coccolith datasets and statistical approaches offshore Chile resulted in close agreement, as shown by the high correlation ($R^2=0.71$) between the SST coccolith percentage estimates and the SST CAR estimates (supplementary material).

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Focusing more on the CAR transfer function, it can be noted that negative SST residuals indicate that the model overestimated the mean annual SST while positive residuals indicate that the model estimates underestimated this parameter. Although SST residuals calculated here are low, the contour map of SST residuals (Fig. 6C) shows that our model tends to underestimate SSTs at the northernmost locations and overestimate SSTs at the southernmost ones together with those stations from the area between ~34.5°S and ~36.5°S which are under the influence of the persistent upwelling region described by Strub et al. (1998). Abrantes et al. (2007) also got SST overestimates and SST underestimates at the northern- and southernmost locations of our study area, but not offshore central Chile. This can be just explained by the ecological dominance of diatoms over coccolithophores and/or by coccolith carbonate preservation which could affect coccolithophore species composition in the upwelling region near Concepción (from 35°S to 38°S). The slight trend observed between SST summer-winter difference and SST residuals (Fig. 7B) suggest that samples with SST underestimates (high positive residuals) are more affected by seasonality than samples with SST overestimates (low negative residuals). Therefore seasonality has, to some extent, an influence on the warmwater and cold-water coccolithophore taxa preserved in the surface sediment samples. Even considering the limitations of our regional approach, both the total and species CAR estimates give a general idea of the number of coccoliths/cm²/yr preserved in the surface sediments offshore Chile, an upwelling region mainly dominated by diatoms, and furthermore allowed us to obtain an accurate SST reconstruction.

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5. Conclusions

413 offshore Chile were detected by studying (a) coccolith accumulation rates (CARs) and (b) 414 coccolithophore derived sea surface temperature (SST) estimates. The main findings are 415 as follows: (1) CARs, calculated by using estimated sedimentation rates based on recent ²¹⁰Pb and 416 417 bulk chemistry analyses of surface samples from the Chilean margin, clearly reveal that 418 the accumulation of coccolithophores shows a strong statistical relationship to SST. 419 Rigorous numerical methods have been used to quantify the inherent error of the model 420 and to asses the reliability of the quantitative reconstruction for the average temperatures 421 of the uppermost 75 m of the water column. 422 (2) Total CARs and species CARs reflect the regional upwelling conditions along the 423 Chilean continental margin. Highest total CARs were found off north-central Chile, 424 where seasonal upwelling occurs. 425 (3) There are five key coccolithophore species which as show by our model record SST 426 information; these are Florisphaera profunda, Helicosphaera carteri, Gephyrocapsa 427 muellerae, Umbellosphaera spp. and Coccolithus pelagicus. 428 (4) Differences between observed and estimated SST coincide with a persistent upwelling 429 region between ~34.5°S and ~36.5°S, yielding warmer temperatures than expected. 430 (5) In short, our results demonstrate the good reconstructive skill of observed SSTs and 431 are in close agreement to a series of previously published SST transfer functions in the 432 Southeast Pacific realm based on species percentages from different siliceous and

In this study the modern regional gradients of sea surface productivity and temperature

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calcareous microfossils.

Acknowledgements

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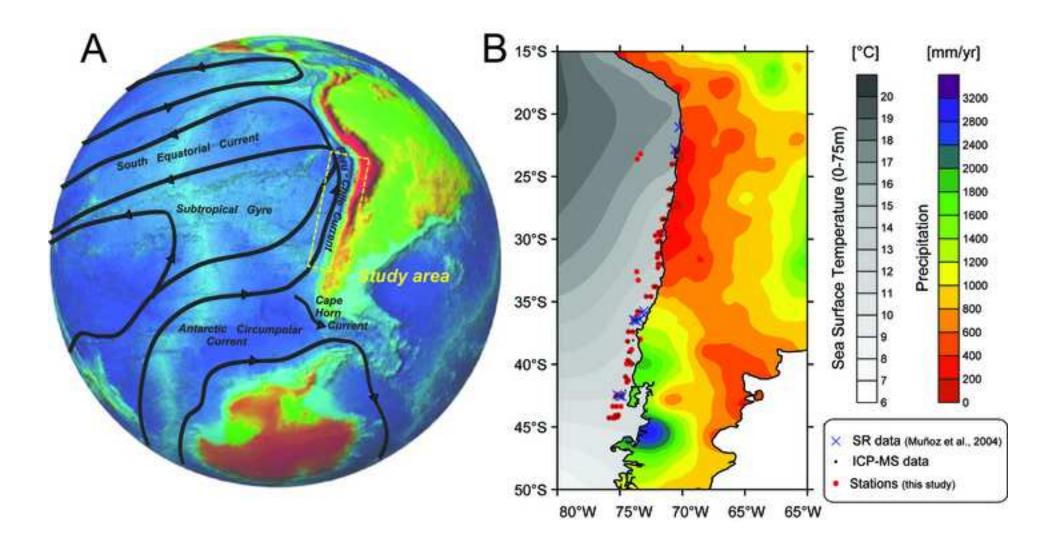
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Figure. 1. A. Map of the Pacific and adjacent areas showing major surface currents (after Tomczak and Godfrey, 2003; modified from Lamy and Kaiser, 2009). The study area has been indicated with yellow rectangle.

B. Sea Surface Temperature (SST in °C, Locarnini et al., 2006) expressed as an annual average from 0 m to 75 m water depth and annual mean precipitation (mm/yr) over parts of South America in 2000 (Beck et al., 2005).

The location of the sampling stations offshore Chile corresponding to recent sedimentation (SR) data available based on ²¹⁰Pb (Muñoz et al., 2004) is indicated with blue crosses, the sampling stations corresponding to ICP-MS measurements (Stuut et al., 2007) with black dots, and the 74 sea surface sediment samples used in this study with red dots.

Figure1
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- Figure 2. A. Sedimentation Rates (cm/yr) used in this work, from Muñoz et al. (2004), Lamy et al. (1999) and Ho et al. (2012).
- B. Sedimentation Rates (cm/yr) from Muñoz et al. (2004) versus Ti (‰) values from the bulk chemistry analyses done by inductively coupled plasma atomic emission spectrometry (ICP-MS; Stuut et al. 2007).
- C. Dry bulk densities (g/cm³) used in this work, from Muñoz et al. (2004), Hebbeln et al. (2004), Klump et al. (2004), Muñoz and Nuñez pers. comm.

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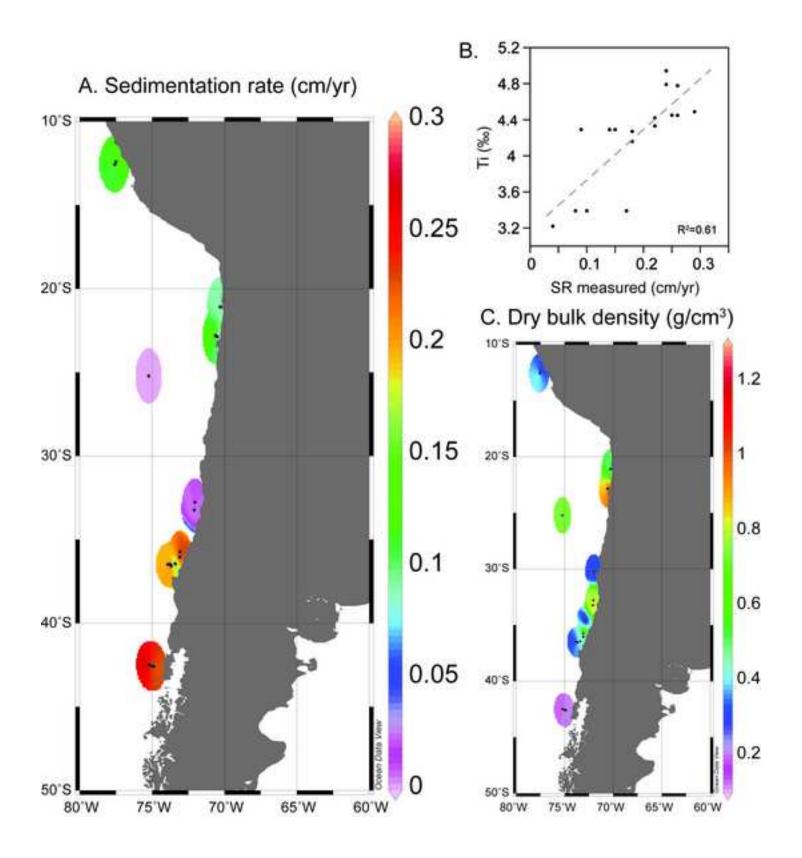


Figure Caption3

Figure 3. A. Sedimentation Rate estimates (cm/yr) for the study area using the present approach explained within the text. B. Total number of coccoliths per gram of sediment. C. Coccolith Accumulation Rate (CAR, coccoliths/cm²/yr). The 74 surface sediment sample locations are indicated here with black dots.

Figure3
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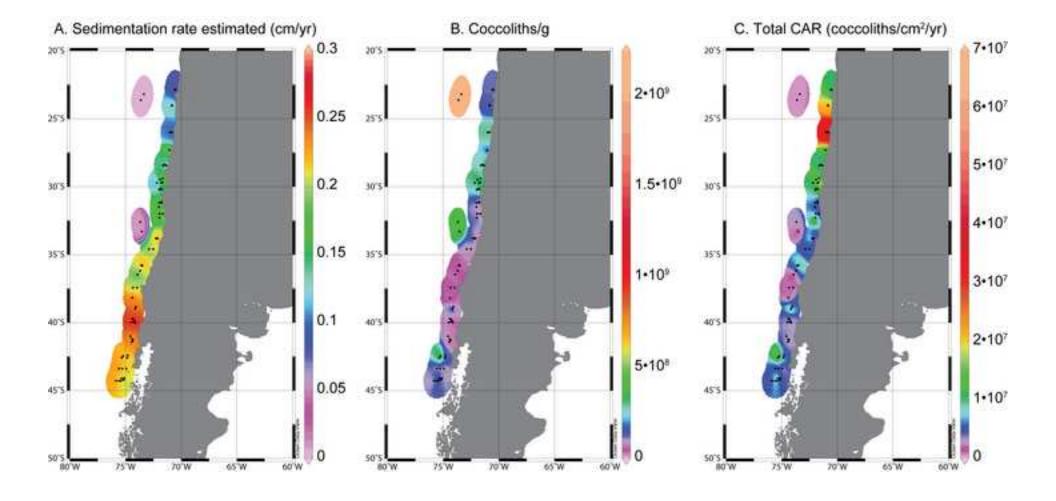


Figure Caption4

Figure 4. Distribution maps of Coccolith Accumulation Rates for the more important taxa or groups of coccoliths considered in the study area: A. "small" *Gephyrocapsa*, B. *Calcidiscus leptoporus*, *C. Florisphaera profunda*, D. *Emiliania huxleyi*, E. *Gephyrocapsa muellerae*, *F. Gephyrocapsa oceanica*, *G. Helicosphaera carteri*, *H. Coccolithus pelagicus* and I. *Umbellosphaera* spp. Stations are indicated with black dots. The gray star indicates the location of the sediment trap deployed off Chile (30°S, 73°11'W; González et al., 2004; Köbrich, 2008).

Figure4
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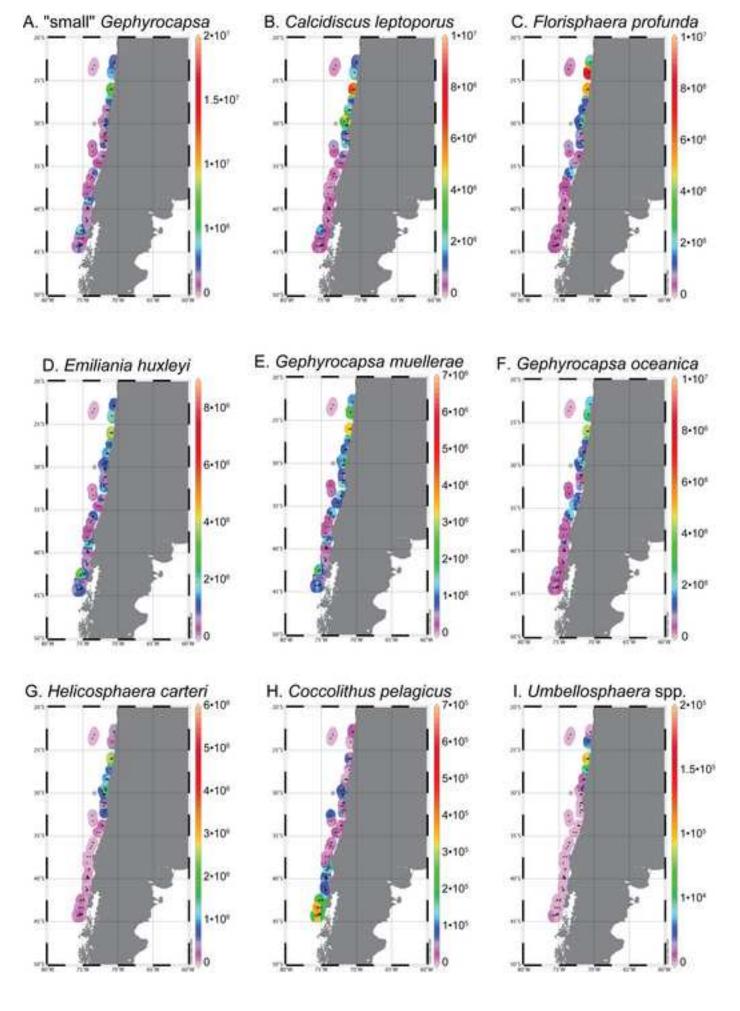


Figure Caption5

Figure 5. A. SST residuals versus SST estimated. B. Normal Q-Q. C. Scale location. D. SST residuals versus leverage.

Figure5
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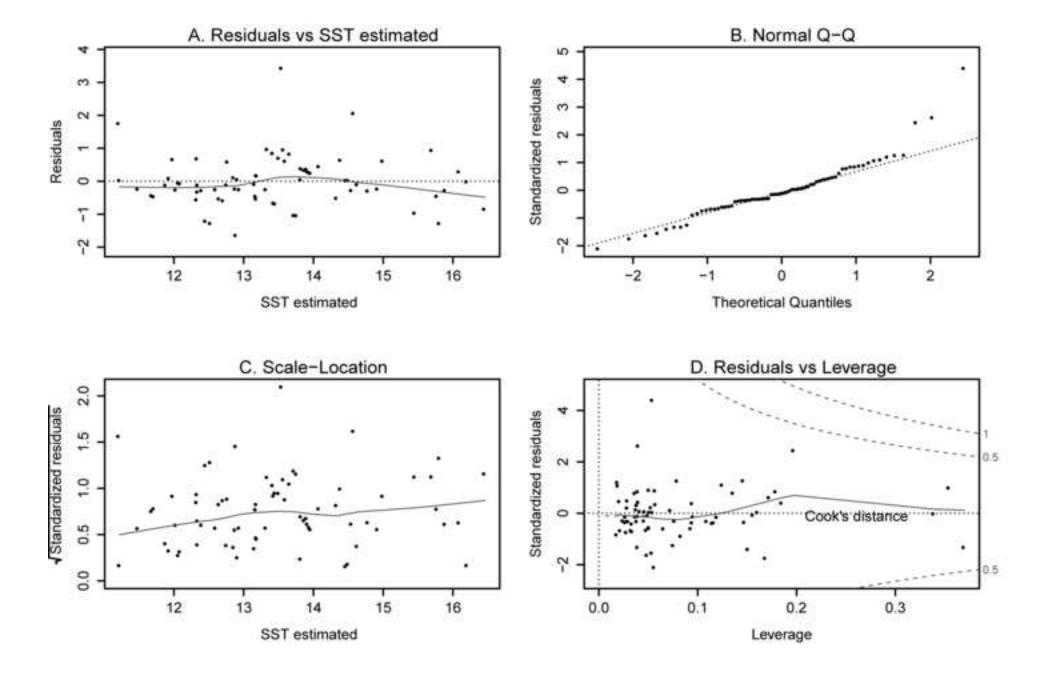


Figure Caption6

Figure 6. A. Annual 0-75 m SST average observed (in °C, from WOA05, Locarnini et al., 2006). B. Annual average 0-75 m SST estimated (in °C). C. Sea Surface Temperature residuals (SST estimated-SST observed). Stations are indicated with black dots.

Figure6
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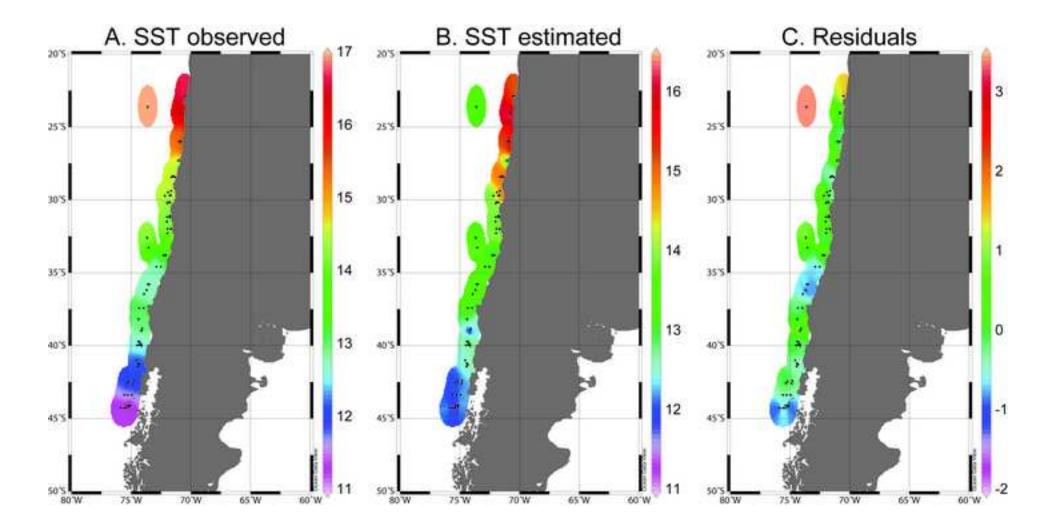


Figure Caption7

Figure 7. A. SST summer - SST winter (in °C). Data retrieved from WOA05 (Locarnini et al., 2006). The one-degree grid is indicated with black dots and stations with white dots. B. SST summer - SST winter versus SST residuals.

Figure7
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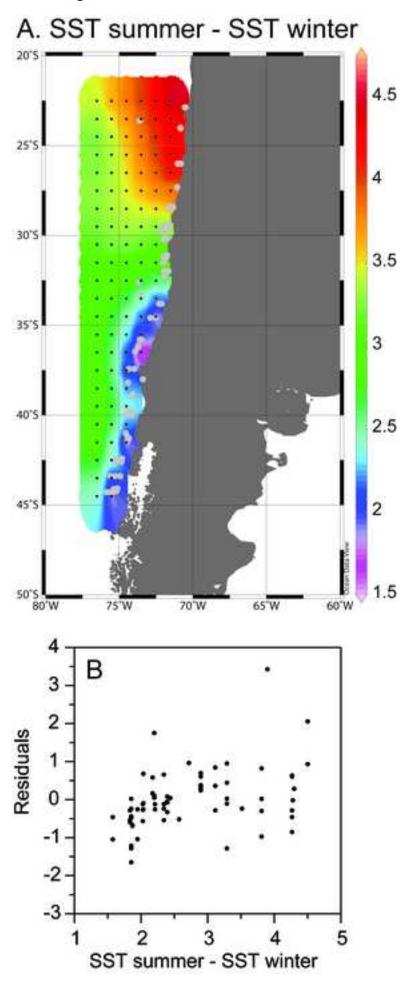


Figure 8. A. Sea Surface Temperature reconstruction (SST in °C, 0-75 m) using Coccolith Accumulation Rates (CARs) indicated with squares and pink line, SST observed (0-75 m, from WOA05, Locarnini et al., 2006) indicated with circles and orange line, SST reconstruction (0-75 m) using coccolithophore percentages (Saavedra-Pellitero et al., 2011) indicated with dashed line and green triangles, SST reconstruction with foraminifera at 10m (Kucera et al., 2005) indicated with blue squares with an asterisk inside and SST reconstruction with diatoms at 0 m depth (Abrantes et al., 2007). B. SST estimated versus SST observed (both in °C). The line represents the best fitting linear regression.

Figure8
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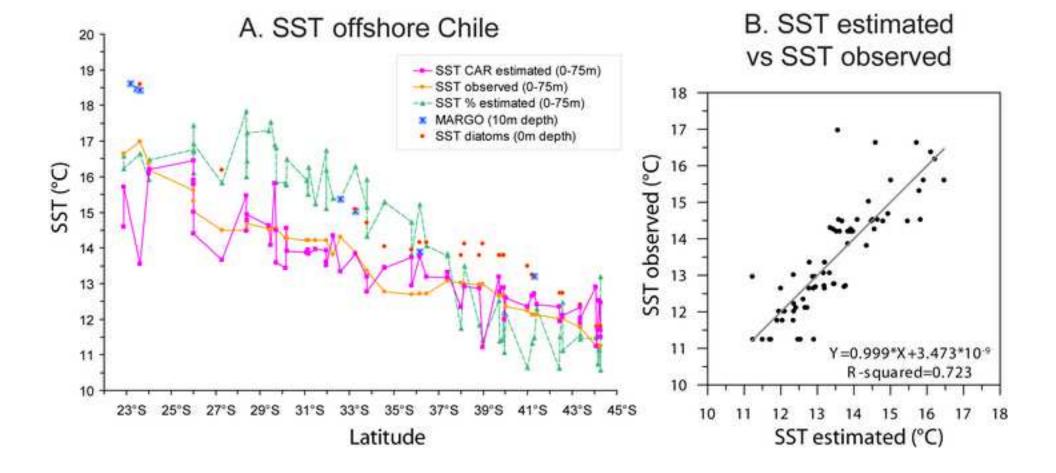


Table 1. Station, geographical position, measured sedimentation rate (SR, in cm/yr), authors of SR measurements, measurements of dry bulk density (DBD, in g/cm³), authors of DBD measurements, Al, Fe, K, Mg and Ti (‰) values selected from the bulk chemistry analyses done by inductively coupled plasma atomic emission spectrometry (ICP-MS; Stuut et al. 2007). Underlined stations were used for the SR-Ti approach.

Table 2. List of studied samples including geographical position as well as estimated Sedimentation Rates (SR, in cm/yr), estimated Dry Bulk Densities (DBDs, in g/cm³) and observed annual Sea Surface Temperature (SST in °C) average from 0 m to 75 m water depth (Locarnini et al., 2006). Asteriks indicate samples in which coccolithophore studies were not performed; for further details, see Saavedra-Pellitero et al. (2010). GeoB samples were retrieved during R/V SONNE Cruise SO-156 and RR samples during Genesis III Cruise RR9702A.

Table 3. Root mean squared error (RMSE), adjusted R², F-statistic, degrees of freedom and p-value of the 5 component model. Root mean squared error of prediction (RMSEP) of the model assessed by bootstrapping and jackknifing.

Station	Longitude	Latitude	SR measured (cm/yr)	Author (SR)	DBD measured (g/cm3)	Author (DBD)	AI (%)	Fe (%)	K (‰)	Mg (%)	Ti (‰)
Sta. A	-77.5	-12.4	0.13 ±0.02	Muñoz et al., 2004	0.18	Muñoz et al., 2004					
Sta. C	-77.6	-12.6	0.1 ±0.01	Muñoz et al., 2004	0.53	Muñoz et al., 2004					
Sta. 6	-70.2	-21.1	0.1 ±0.01	Muñoz et al., 2004	0.45	Muñoz et al., 2004	48.11	60.36	19.70	17.01	3.390
<u>Sta. 7</u>	-70.3	-21.1	0.08 ±0.01	Muñoz et al., 2004	0.54	Muñoz et al., 2004	48.11	60.36	19.70	17.01	3.390
GeoB 7104	-70.5	-22.9	0.04 ±0.01	Muñoz et al., 2004	1.22	Muñoz et al., 2004	46.21	31.41	12.86	15.15	3.220
GeoB 7106	-70.6	-22.8	0.17 ±0.003	Muñoz et al., 2004	0.67	Muñoz et al., 2004	48.11	60.36	19.70	17.01	3.390
<u>5d</u>	-73.1	-35.7	0.24 ±0.05	Muñoz et al., 2004	0.75	Muñoz et al., 2004	83.39	43.47	14.08	13.96	4.943
<u>4c</u>	-73.1	-36.0	0.26 ±0.03	Muñoz et al., 2004	0.44	Muñoz et al., 2004	80.86	41.90	13.29	14.55	4.778
GeoB 7160	-73.1	-36.0	0.24 ±0.07	Muñoz et al., 2004	0.42	Muñoz et al., 2004	80.93	42.09	13.31	14.61	4.791
<u> 26A</u>	-73.4	-36.4	0.09 ±0.01	Muñoz et al., 2004	0.32	Muñoz et al., 2004	74.93	43.41	10.40	15.24	4.291
<u>26B</u>	-73.4	-36.4	0.14 ±0.02	Muñoz et al., 2004	0.55	Muñoz et al., 2004	74.93	43.41	10.40	15.24	4.290
GeoB 7161	-73.4	-36.4	0.15 ±0.01	Muñoz et al., 2004	0.30	Muñoz et al., 2004	74.93	43.41	10.40	15.24	4.290
<u>3</u>	-73.7	-36.5	0.26 ±0.10	Muñoz et al., 2004	0.51	Muñoz et al., 2004	77.43	43.71	12.72	14.42	4.448
GeoB 7162	-73.7	-36.6	0.25 ±0.04	Muñoz et al., 2004	0.31	Muñoz et al., 2004	77.44	43.67	12.68	14.43	4.450
GeoB 7166	-73.8	-36.5	0.18 ±0.02	Muñoz et al., 2004	0.33	Muñoz et al., 2004	73.45	43.94	12.58	15.23	4.270
GeoB 7167	-73.9	-36.5	0.18 ±0.02	Muñoz et al., 2004	0.23	Muñoz et al., 2004	72.10	42.56	12.40	15.86	4.159
GeoB 7177	-74.8	-42.6	0.22 ±0.01	Muñoz et al., 2004	0.20	Muñoz et al., 2004	62.83	41.54	0.00	18.81	4.331
GeoB 7174	-75.0	-42.5	0.22 ±0.02	Muñoz et al., 2004	0.23	Muñoz et al., 2004	64.60	41.96	0.00	18.36	4.421
GeoB 7175	-75.2	-42.5	0.29 ±0.04	Muñoz et al., 2004	0.17	Muñoz et al., 2004	66.40	42.38	0.00	17.59	4.489
GeoB 7139	-72.0	-30.2	-		0.30	Muñoz, pers. comm.					
GeoB 7155	-72.9	-34.6	-		0.27	Muñoz, pers. comm.					
GIK 17748-2	-72.0	-32.8	0.009	Lamy et al., 1999	0.77	Hebbeln et al., 2004					
GIK 3302-1	-72.1	-33.2	0.006	Lamy et al., 1999	0.85	Klump et al., 2004					
GeoB 3388-1	-75.2	-25.2	0.0003	Ho et al., 2012	0.74	Nuñez Ricardo, pers comm.					

Table2

Station	Longitude	Latitude	Estimated SR	Estimated DBI	SST average (0-75 m)	Station	Longitude	Latitude	Estimated SR	Estimated DBI	SST average (0-75 m)
GeoB 7108 GeoB 7104	-70.6 -70.5	-22.8 -22.9	0.077 0.077	0.670 1.220	16.64 16.64	GeoB 7211 RR 20 mc4	-74.5	-39.9 -40.0	0.255 0.255	0.170 0.170	12.65
GeoB 7103	-70.5	-22.9 -23.2	0.077	1.220 0.740	16.64	RR 22 mc3		-40.0	0.255	0.200	
RR 52 mc3 RR 50 mc2	-73.4 -73.6	-23.2	0.0003 0.0003		16.98 16.98	GeoB 7197 GeoB 7195		-41.0 -41.2	0.240 0.234	0.170 0.200	
GeoB 7114	-70.8	-24.0	0.113	1.220	16.38	RR 24 mc3	-74.3	-41.3	0.234	0.200	12.12
GeoB 7112	-70.8	-24.0	0.148		16.19	GeoB 7194		-41.4	0.234	0.200	
GeoB 7118 GeoB 7122	-70.8 -70.8	-26.0 -26.0	0.100 0.100	1.220	15.61 15.61	GeoB 7172 GeoB 7175		-42.4 -42.5	0.227 0.215	0.200 0.170	
GeoB 7119	-70.9	-26.0	0.100		15.32	GeoB 7179		-42.6	0.213	0.170	
GeoB 7121	-70.9	-26.0	0.100	1.220	15.61	GeoB 7177		-42.6	0.197	0.200	
GeoB 7116	-71.0	-26.0	0.100		15.03	GeoB 7182		-43.4	0.212	0.200	
GeoB 7123 GeoB 7127	-71.1 -71.5	-27.3 -28.4	0.196 0.158		14.49 14.49	GeoB 7181 GeoB 7180		-43.4 -43.4	0.212 0.242	0.230 0.170	
GeoB 7127 GeoB 7131	-71.5 -71.5	-28.4	0.138		14.49	GeoB 7183		-43.4 -44.1	0.242	0.170	
GeoB 7129	-71.3	-28.4	0.103		14.49	GeoB 7192		-44.1	0.217	0.230	
GeoB 7130	-71.6	-28.4	0.138		14.69	GeoB 7186		-44.2	0.197	0.200	
GeoB 7133 GeoB 7132	-71.6 -71.9	-29.4	0.213 0.142		14.53	GeoB 7187 GeoB 7189		-44.2 -44.3	0.194	0.200	
GeoB 7132 GeoB 7135	-71.9 -71.7	-29.5 -29.7	0.142		14.53 14.53	GeoB 7191		-44.3 -44.3	0.216 0.209	0.230 0.230	
GeoB 7134	-71.8	-29.7	0.143		14.53	GeoB 7190		-44.3	0.232	0.230	
GeoB 7136	-72.2	-29.7	0.082		14.53	GeoB 7115 (*)		-24.0			
GeoB 7138 GeoB 7137	-71.9 -71.7	-30.1 -30.2	0.128 0.172		14.27 14.27	GeoB 7140 (*)		-31.0 -35.8			
GeoB 7137 GeoB 7139	-71.7 -72.0	-30.2	0.172		14.27	RR 44 mc2 (*) GeoB 7159 (*)		-35.8			
GeoB 7141	-71.8	-31.1	0.176		14.21	GeoB 7160 (*)		-36.0			
GeoB 7144	-72.0	-31.2	0.176		14.21	RR 39 mc2 (*)		-36.2			
GeoB 7142	-71.8	-31.2	0.176	0.300		GeoB 7161 (*)		-36.4			
GeoB 7149 GeoB 7146	-72.0 -71.6	-31.5 -32.0	0.158 0.202		14.21 14.21	GeoB 7163 (*) GeoB 7166 (*)		-36.4 -36.5			
GeoB 7148	-71.9	-32.0	0.174		14.21	RR 34 mc5 (*)		-36.5			
GeoB 7147	-71.7	-32.0	0.202	0.300	14.21	GeoB 7162 (*)		-36.5			
GeoB 7150	-72.0	-32.3	0.157		13.82	GeoB 7170 (*)		-37.4			
RR 48 mc4 RR 46 mc1	-73.7 -73.5	-32.6 -33.3	0.009 0.006	0.770 0.850	13.87	RR 31 mc2 (*) RR 29 mc2 (*)		-37.7 -37.8			
GeoB 7152	-72.1	-33.8	0.203		13.36	GeoB 7205 (*)		-38.0			
GeoB 7153	-72.2	-33.8	0.234		13.36	GeoB 7204 (*)		-38.0			
GeoB 7154	-72.3 -72.5	-33.8	0.201 0.207		13.36	GeoB 7203 (*) GeoB 7201 (*)		-38.0			
GeoB 7156 GeoB 7155	-72.5 -72.9	-34.6 -34.6	0.207		12.77 12.77	GeoB 7201 () GeoB 7202 (*)		-38.1 -38.1			
GeoB 7158	-73.5	-35.8	0.219		12.69	GeoB 7200 (*)		-38.2			
GeoB 7157	-73.6	-35.8	0.218		12.69	GeoB 7199 (*)		-38.2			
RR 42 mc1	-73.7	-36.2	0.197		12.72	GeoB 7219 (*)		-39.8			
GeoB 7167 GeoB 7171	-73.9 -74.0	-36.5 -37.4	0.179 0.202		12.72 13.07	RR 25 mc2 (*) GeoB 7218 (*)		-39.9 -39.9			
GeoB 7169	-74.3	-37.4	0.199		13.07	GeoB 7216 (*)		-40.1			
GeoB 7207	-73.4	-38.0	0.220		13.02	RR 27 mc4 (*)		-40.5			
GeoB 7198	-74.4	-38.2	0.239		12.97	GeoB 7173 (*)		-42.1			
GeoB 7215 GeoB 7209	-74.1 -74.2	-38.8 -39.0	0.239 0.239		12.97 12.97	GeoB 7174 (*) RR 12 mc2 (*)		-42.5 -43.4			
GeoB 7212	-74.4	-39.7	0.255		12.65	RR 14 mc2 (*)		-43.5			
GeoB 7213	-74.3	-39.7	0.255	0.170	12.65	RR 08 mc6 (*)	-76.7	-46.4			
GeoB 7214	-74.2	-39.9	0.255	0.170	12.65	RR 06 mc4 (*)	-76.6	-46.9			

Table3
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Prediction model (5 components)

RMSE Adjusted R-squared F-statistic Degrees of freedom p-value	0.803 0.702 34.470 66 < 2.2e ⁻¹⁶
RMSEP _{jacknifing}	0.848
RMSEP _{bootstrapping}	0.869