

1 Latitudinal variations of $\delta^{30}\text{Si}$ and $\delta^{15}\text{N}$ signatures along 2 the Peruvian shelf: quantifying the effects of nutrient 3 utilization versus denitrification over the past 600 years

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14 Abstract

15 The sedimentary stable nitrogen isotope compositions of bulk organic matter ($\delta^{15}\text{N}_{\text{bulk}}$) and silicon
16 isotope composition of diatoms ($\delta^{30}\text{Si}_{\text{BSi}}$) both mainly reflect the degree of past nutrient utilization by
17 primary producers. However, in ocean areas where anoxic and suboxic conditions prevail, the $\delta^{15}\text{N}_{\text{bulk}}$
18 signal ultimately recorded within the sediments is also influenced by water column denitrification
19 causing an increase in the subsurface $\delta^{15}\text{N}$ signature of dissolved nitrate ($\delta^{15}\text{NO}_3^-$) upwelled to the
20 surface. Such conditions are found in the oxygen minimum zone off Peru, where at present an increase
21 in subsurface $\delta^{15}\text{NO}_3^-$ from North to South along the shelf is observed due to ongoing denitrification
22 within the pole-ward flowing subsurface waters, while the $\delta^{30}\text{Si}$ signature of silicic acid ($\delta^{30}\text{Si}(\text{OH})_4$) at
23 the same time remains unchanged.

24 Here, we present three new $\delta^{30}\text{Si}_{\text{BSi}}$ records between 11°S and 15°S and compare these to
25 previously published $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ records from Peru covering the past 600 years. We present a
26 new approach to calculate past subsurface $\delta^{15}\text{NO}_3^-$ signatures based on the direct comparison of $\delta^{30}\text{Si}_{\text{BSi}}$
27 and $\delta^{15}\text{N}_{\text{bulk}}$ signatures at a latitudinal resolution for different time periods. Our results show that, during
28 the Current Warm Period (CWP, since 1800 AD) and prior short-term arid events, source water $\delta^{15}\text{NO}_3^-$
29 compositions have been close to modern values increasing southward from 7 to 10‰ (between 11°S and
30 15°S). In contrast, during the Little Ice Age (LIA) we calculate low $\delta^{15}\text{NO}_3^-$ values between 6 and 7.5‰.
31 Furthermore, the direct $\delta^{30}\text{Si}_{\text{BSi}}$ versus $\delta^{15}\text{N}_{\text{bulk}}$ comparison also enables us to relate the short-term
32 variability in both isotope compositions to changes in the ratio of nutrients (NO_3^- : $\text{Si}(\text{OH})_4$) taken up by
33 different dominating phytoplankton groups (diatoms and non-siliceous phytoplankton) under the variable
34 climatic conditions of the past 600 years. Accordingly, we estimate a shift from a 1:1 (or 1:2) ratio during
35 the CWP and a 2:1 (up to 15:1) ratio during the LIA, associated with a shift from overall high nutrient
36 utilization to NO_3^- dominated (and thus non-siliceous phytoplankton) utilization.

37 1. Introduction

38 Investigations of the isotopic compositions of the macro-nutrients, such as silicic acid (Si(OH)_4) and
39 nitrate (NO_3^-), have been used to infer changes of biogeochemical cycles in the past (Brunelle et al.,
40 2007; Horn et al., 2011; Robinson et al., 2014). The preferential incorporation of the lighter isotopes ^{14}N
41 and ^{28}Si into organic matter (OM) and biogenic opal (BSi), respectively, during primary production in
42 surface waters leads to an increase in the $\delta^{15}\text{N}$ and $\delta^{30}\text{Si}$ in the remaining dissolved nutrients (i.e. $\delta^{15}\text{NO}_3^-$
43 and $\delta^{30}\text{Si(OH)}_4$) as a result of progressive consumption of the nutrient pools (Altabet et al., 1991; De La
44 Rocha et al., 1997; Wada and Hattori, 1978). This preferential incorporation is associated with an
45 approximate enrichment factor of -5‰ for NO_3^- (Waser et al., 1998) and -1.1‰ for Si(OH)_4 (De La
46 Rocha et al., 1997), which agree well with estimates for the Peruvian shelf (Ehlert et al., 2012; Mollier-
47 Vogel et al., 2012; Grasse et al., 2016). While a potential fractionation of $\delta^{30}\text{Si}$ signatures of biogenic
48 opal during dissolution of -0.55‰ has been reported previously (Demarest 2009), [investigations from](#)
49 [the water column of the Southern Ocean did not find significant difference between the \$\delta^{30}\text{Si}\$ values of](#)
50 [particles in the water column and in surface sediments](#) (Varela et al., 2004; Fripiat et al., 2012; Closset
51 et al., 2015). Furthermore, field studies and laboratory experiments based on sediments have so far
52 indicated that $\delta^{30}\text{Si}$ signatures of diatoms within the sediments are generally unaffected by diagenetic
53 alteration (e.g. Egan et al., 2012; Wetzel et al., 2014; Ehlert et al., 2016). Accordingly, the degree of
54 utilization of NO_3^- and Si(OH)_4 is recorded in the $\delta^{15}\text{N}_{\text{bulk}}$ and $\delta^{30}\text{Si}_{\text{BSi}}$ of the OM and BSi produced. In
55 combination with parameters such as organic carbon, BSi or barium accumulation rates, both $\delta^{15}\text{N}_{\text{bulk}}$
56 and $\delta^{30}\text{Si}_{\text{BSi}}$ have been employed as proxies for the evaluation of past productivity and corresponding
57 nutrient utilization (De La Rocha et al., 1998; François et al., 1992; Horn et al., 2011; Pichevin et al.,
58 2005).

59 However, in coastal upwelling areas, where upwelling of nutrient-rich subsurface waters causes
60 high surface productivity, subsequent degradation of the high amounts of OM leads to extensive oxygen
61 consumption in the water column (Pennington et al., 2006; Zuta and Guillén, 1970). As a result of the
62 low oxygen concentrations, NO_3^- is used as an oxidant during OM degradation and is transferred to N_2
63 leading to a net loss of bio-available nitrogen (e.g., denitrification and anaerobe ammonium-oxidation;
64 (Codispoti, 2006; Lam et al., 2009). Due to the high isotope fractionation factor ($\sim -20\%$) associated
65 with denitrification, the $\delta^{15}\text{NO}_3^-$ signatures of subsurface waters strongly increase and consequently
66 supply a heavy $\delta^{15}\text{NO}_3^-$ signal to surface waters during upwelling (Cline and Kaplan, 1975). This ^{15}N -
67 enriched NO_3^- is incorporated by phytoplankton and ultimately deposited and buried in marine sediments.
68 Accordingly, although $\delta^{15}\text{N}_{\text{bulk}}$ also varied in phase with productivity proxies, elevated $\delta^{15}\text{N}_{\text{bulk}}$ values in
69 highly productive and poorly ventilated regions including most of the coastal upwelling areas, have been
70 generally interpreted as the consequence of stronger denitrification associated with intense oxygen
71 depletion (Agnihotri et al., 2006; 2008; De Pol-Holz et al., 2007; Fleury et al., 2015; Gutiérrez et al.,
72 2009; Mollier-Vogel et al., 2012; Salvatelli et al., 2014b). However, given that dissolved $\delta^{15}\text{NO}_3^-$ is
73 influenced by both nutrient utilization and denitrification – associated with water column de-oxygenation
74 - both processes should also influence the $\delta^{15}\text{N}_{\text{bulk}}$ signatures recorded by the sedimentary OM.

75 In contrast, $\delta^{30}\text{Si}_{\text{BSi}}$ signatures are primarily controlled by surface water diatom productivity and
76 Si(OH)_4 utilization (Brzezinski, 2002; De La Rocha et al., 1998) closely coupled to the amount of

77 upwelling strength in the study area (Doering et al., 2016; Ehlert et al., 2013; 2015; 2012; Grasse et al.,
78 2013). Accordingly, downcore records of $\delta^{30}\text{Si}_{\text{BSi}}$ off Peru are closely coupled to changes in the diatom
79 assemblage with high signatures (>1‰) reflecting strong upwelling conditions and lower signatures (0.5-
80 1‰) reflecting weak upwelling conditions (Doering et al., 2016). This coupling was previously shown
81 to be mainly the consequence of changes in the relative abundance of different diatom groups during
82 diatom succession linked to different upwelling strength (Doering et al., 2016) rather than potential
83 species-specific fractionation (Sutton et al., 2013).

84 Thus, the combination of both $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ compositions in the water column and late
85 Quaternary sediments off Peru has been applied as a measure to disentangle modern and past nutrient
86 utilization and denitrification processes (Ehlert et al., 2015; Grasse et al., 2016). Comparison of modern
87 dissolved $\text{Si}(\text{OH})_4$ and NO_3^- distributions and their corresponding isotopic ratios has shown that $\text{Si}(\text{OH})_4$
88 and NO_3^- concentrations and their stable isotopic signatures are strongly correlated within the surface
89 mixed layer at near-shore and offshore areas, indicating that the signal preserved in the sediments
90 depends on the degree of utilization of both nutrients (Grasse et al., 2016). Similarly, an initial
91 comparison for the past 600 years based on one sediment core indicated that both isotope compositions
92 were largely influenced by nutrient utilization suggesting that denitrification in the water column only
93 had a significant influence since ~1850 AD (Ehlert et al., 2015) thus partly contradicting previous
94 interpretations of N-loss having been the main driver of changes in past $\delta^{15}\text{N}_{\text{bulk}}$ records.

95 At present the features of the Peruvian upwelling system vary significantly with El Niño-
96 Southern Oscillation (ENSO) on interannual time scales. During warm phases of ENSO (El Niño) a
97 weakening of the trade winds over the equatorial Pacific and an eastward displacement of West Pacific
98 warm pool (Picaut et al., 1996) cause warmer sea surface temperature anomalies in the Central and
99 Eastern Pacific Ocean. Off Peru this causes the mixed layer (and thermocline/nutricline) depth to
100 increase, decreasing the nutrient content (NO_3^- and iron (Fe)) of upwelled waters and leading to a
101 decrease in phytoplankton (mainly diatoms) abundance and productivity (Barber and Chávez, 1983;
102 Chavez, 1989; Espinoza-Morriberón et al., 2017; Sanchez et al., 2000). In contrast, the cold phases of
103 ENSO (La Niña) are associated with a stronger Walker circulation (west-east or zonal) and upwelling-
104 favorable winds off Peru, resulting in negative sea surface temperature (SST) anomalies (Morón, 2000),
105 a thermocline shoaling and higher phytoplankton productivity (Espinoza-Morriberón et al., 2017).
106 Similar conditions have been reported to alternate on the multicentennial time scales during Northern
107 Hemisphere cold and warm periods. These so-called El Niño- and La Niña-like mean states reflect larger-
108 scale oceanographic and climatic changes (Fleury et al., 2015; Rein, 2004; Yan et al., 2011).
109 Accordingly, the climate of the last 600 years can be divided into two climatic phases consisting of the
110 Current Warm Period (CWP, since 1800 AD) and the Little Ice Age (LIA, ca. 1400 to 1800 AD). Off
111 Peru, the CWP has been characterized by dry (arid) conditions, strong upwelling intensity, as well as
112 high productivity and intense N-loss processes, reflecting overall dominant La-Niña conditions (Fleury
113 et al., 2015; Salvattecchi et al., 2014b; Sifeddine et al., 2008). In contrast, within the present day main
114 upwelling area between 10°S and 15°S, the LIA was characterized by lower productivity and low
115 denitrification intensity for the present day main upwelling area between 10°S and 15°S (Díaz-Ochoa et
116 al., 2009; Salvattecchi et al., 2014b; Sifeddine et al., 2008). Previous paleo-reconstructions agreed that
117 these conditions were induced by weakening of the Walker circulation and reduction of the South Pacific

118 subtropical High (SPSH), as well as by a southward shift of the mean position of the Intertropical
119 Convergence Zone (ITCZ) and the associated precipitation belt (Fleury et al., 2015; Sachs et al., 2009;
120 Salvattecchi et al., 2014b; Sifeddine et al., 2008). These changes resulted in reduced LIA surface
121 productivity and more oxygenated subsurface waters off Peru, as reflected by lower sedimentary BSi and
122 TOC concentrations (Ehlert et al., 2015; Gutiérrez et al., 2009; Salvattecchi et al., 2014a) and Si/Fe ratios
123 (Fleury et al., 2015), and supported by a marked reduction in the sedimentary concentrations of redox
124 sensitive trace metals such as molybdenum and rhenium (Salvattecchi et al., 2014b; Sifeddine et al., 2008).
125 However, these conditions did not prevail continuously but instead short-term variations during both the
126 LIA and the CWP are for example mirrored by changes in diatom abundances, productivity sensitive
127 element ratios indicative of productivity changes (Br/Fe) and $\delta^{15}\text{N}_{\text{bulk}}$ values (Fleury et al., 2015). These
128 proxy records indicate multidecadal shifts between arid/humid conditions during the CWP and
129 particularly during the LIA when pronounced short-term periods of arid conditions occurred (Fleury et
130 al., 2015). The well-studied biogeochemical evolution of the Peruvian shelf over the last 600 years and
131 the significant differences in productivity and subsurface oxygenation between the CWP and the LIA
132 form the basis for our study to gain new insights into the relationship between nutrient utilization and
133 denitrification via $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ records.

134 Here, our goal is to verify whether the southward increase of $\delta^{15}\text{NO}_3^-$ due to denitrification
135 observed in the present day has persisted during the marked changes in upwelling intensity during the
136 LIA and CWP, and therefore under different ENSO conditions, based on comparison of $\delta^{30}\text{Si}_{\text{BSi}}$ and
137 $\delta^{15}\text{N}_{\text{bulk}}$ signatures of four different sediment cores retrieved along the entire gradient of upwelling
138 strength of the southern Peruvian shelf. More specifically, we aim to detect the extent of variability in
139 $\delta^{15}\text{N}_{\text{bulk}}$ caused as a function of denitrification and nutrient utilization during specific time periods (i.e.
140 LIA and CWP). Therefore, we present three new records for $\delta^{30}\text{Si}_{\text{BSi}}$ and BSi concentrations from the
141 Peruvian shelf between 11°S and 15°S covering the last 600 years. These are compared to previously
142 published $\delta^{15}\text{N}_{\text{bulk}}$ data obtained from the same cores (Fleury et al., 2015) and $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ records
143 from a fourth core from 14°S (Fig. 1; Ehlert et al., 2015).

144 **Regional Setting**

145 Along the Peruvian margin the main source for the high amounts of upwelled nutrients ($30 \mu\text{mol L}^{-1}$ for
146 both $\text{Si}(\text{OH})_4$ and NO_3^- ; Bruland et al., 2005) is the subsurface Peru-Chile Undercurrent (PCUC), which
147 flows southward along the continental slope and outer shelf between 4°S and 14°S at a depth between
148 50 and 150 m, before it detaches from the shelf south of 15°S (Brink et al., 1983; Chaigneau et al., 2013;
149 Toggweiler et al., 1991). Eastward flowing subsurface waters of the Equatorial Undercurrent (EUC) and
150 the Southern Subsurface Counter Current (SSCC) (see Fig. 1) feed the PCUC. These subsurface currents
151 deliver $\text{Si}(\text{OH})_4$ and NO_3^- with mean preformed source signatures for $\delta^{30}\text{Si}(\text{OH})_4$ of $1.5 \pm 0.2\text{‰}$ (Beucher
152 et al., 2011; Ehlert et al., 2012; Grasse et al., 2013) and for $\delta^{15}\text{NO}_3^-$ of $7.1 \pm 0.3\text{‰}$ (1SD; Rafter et al.,
153 2012; Rafter and Sigman, 2016) for the EUC. Within the SSCC preformed $\delta^{15}\text{NO}_3^-$ values of $5.5 \pm 0.3\text{‰}$
154 (Rafter et al., 2012) are about 1.6‰ lower than the EUC, resulting in an approximate average PCUC
155 value of $\sim 6\text{‰}$ (Fig. 2a; Mollier-Vogel et al., 2012).

156 The dissolved $\delta^{15}\text{NO}_3^-$ of subsurface waters (50-150 m water depth) increases southward (EQ
157 to 17°S; Mollier-Vogel et al., 2012) as a consequence of water column denitrification, while the dissolved
158 $\delta^{30}\text{Si}(\text{OH})_4$ signature remains close to the source value of 1.5‰ for the PCUC (Fig. 2a; Ehlert et al.,
159 2012). This difference in the evolution of the isotopic signature from North to South is caused by the
160 anoxic conditions off Peru only increasing the $\delta^{15}\text{NO}_3^-$ signatures via denitrification in the subsurface,
161 but not affecting the $\delta^{30}\text{Si}(\text{OH})_4$ signatures. Accordingly, at the northern shelf between 1°N and 10°S,
162 where subsurface O_2 concentrations $[\text{O}_2]$ are $>20 \mu\text{mol L}^{-1}$, N-loss is not observed and the $\delta^{15}\text{N}_{\text{bulk}}$ values
163 in the sediments range between 4 and 5‰ close to the $\delta^{15}\text{NO}_3^-$ source value of 6‰, thus indicating a high
164 degree of NO_3^- utilization (Fig. 2b; Mollier-Vogel et al., 2012). In contrast, the $\delta^{30}\text{Si}_{\text{BSi}}$ signatures north
165 of 10°S are more variable reflecting an overall lower degree of $\text{Si}(\text{OH})_4$ utilization (Doering et al., 2016;
166 Ehlert et al., 2012). At the central Peruvian shelf (10-12°S), where subsurface $[\text{O}_2]$ is $<20 \mu\text{mol L}^{-1}$ (Fig.
167 2a), the subsurface source value of $\delta^{15}\text{NO}_3^-$ increases to 8.6‰ due to denitrification (Mollier-Vogel et
168 al., 2012). The $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ values both increase as a consequence of higher $\text{Si}(\text{OH})_4$ utilization
169 but a decrease in NO_3^- utilization compared to the northern part of the study area (Fig. 2b) which reflects
170 the interplay between increased upwelling intensity, high nutrient re-supply and higher consumption via
171 diatom productivity. In the southernmost part of the shelf (13-16°S), highest productivity and upwelling
172 intensity prevail today, leading to a further increase in the subsurface $\delta^{15}\text{NO}_3^-$ signature of up to 12.5‰
173 at 15°S, whereas surface sediment mean $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ values further increase reflecting moderate
174 utilization of both $\text{Si}(\text{OH})_4$ and NO_3^- (Figs. 2a-b). The supply of dissolved $\text{Si}(\text{OH})_4$ strongly increases
175 from the northern shelf to the southern shelf area (Fig. 2c), reflecting the strength of the upwelling
176 conditions. This increase in upwelling and productivity between 10-15°S results in high accumulation
177 rates of BSi ($0.4\text{-}0.6 \text{ g cm}^{-2} \text{ yr}^{-1}$; Ehlert et al., 2012) and total nitrogen (TN, $0.026\text{-}0.035 \text{ g cm}^{-2} \text{ yr}^{-1}$;
178 Mollier-Vogel et al., 2012) in the sediment (based on accumulation rates of Gutierréz et al., 2009).
179 However, the NO_3^- supply, as indicated by subsurface (50-150 m) NO_3^- concentrations in the water
180 column, slightly decreases from North to South, reflecting the loss of NO_3^- via denitrification.

181 2. Sample locations, methods and calculations

182 2.1 Core locations and age models

183 The new data in this study were obtained from three short, fine-laminated trigger cores retrieved from
184 the main upwelling region off the Peruvian margin during the German R/V Meteor cruise M77/2 in 2008
185 as part of the Collaborative Research Center (SFB) 754 (Fig. 1). New records of $\delta^{30}\text{Si}_{\text{BSi}}$ and BSi
186 concentrations were generated for cores M77/2-024-5TC (024-5TC; 11°05'S, 78°00'W, 210 m water
187 depth), M77/2-005-3TC (005-3TC; 12°05'S, 77°40'W, 214 m water depth) and core M77/2-003-2TC
188 (003-2TC; 15°06'S, 75°41'W, 271 m water depth). One cm slices of the sediment cores were sampled
189 for BSi and Si isotope measurements to ensure the availability of sufficient amounts of diatoms for silicon
190 isotope analysis (Tab. 1). For core 003-2TC additional BSi concentration measurements of material the
191 extracted from individual laminations was possible (Fleury et al., 2015). As previously published $\delta^{15}\text{N}_{\text{bulk}}$
192 values are based on samples from single laminations these were averaged to 1 cm resolution when

193 directly compared to the $\delta^{30}\text{Si}$ data in the following. Core locations are shown in Fig. 1. The age models
194 were published before in Fleury et al. (2015). The age models for all cores are given years AD.

195 **2.2 Biogenic opal and silicon isotope analyses**

196 The amount of BSi in the sediments was measured following an automated leaching method using
197 sodium hydroxide (DeMaster, 1981; Müller and Schneider, 1993) with a precision of 1-2% (1SD).
198 Unfortunately, no material was left of the cores studied here to estimate dry bulk densities to calculate
199 mass accumulation rates (MAR). Therefore, MAR values were used from nearby cores BO413 (12 °S)
200 and BO406 (14°S; Gutiérrez et al. 2009), which were generally close to 0.02 ($\text{g cm}^{-2} \text{yr}^{-1}$) during the LIA
201 and 0.03 $\text{g cm}^{-2} \text{yr}^{-1}$ during the CWP. The exact bulk MAR values ($\text{g cm}^{-2} \text{yr}^{-1}$) for each time period were
202 multiplied by the fractional concentration of BSi and TN (Fleury et al., 2015) to calculate the MAR BSi
203 and MAR TN (Figs. 2c and 6).

204 For the Si isotope measurements diatoms were extracted from the sediment by chemical and
205 physical cleaning (11 and 32 μm sieve; heavy liquid separation with a sodium polytungstate solution set
206 at 2.15 g mL^{-1}) as described in detail in Ehlert et al. (2012; 2013) and Doering et al. (2016). For all
207 samples the purity of the small diatom fraction (11-32 μm) was evaluated via light microscopy prior to
208 dissolution and only pure (>95%) diatom samples were treated further. All samples were dissolved in 1
209 mL 0.1 M NaOH and treated with 200 μL concentrated H_2O_2 (Suprapur). Sample solutions were diluted
210 with 4 mL MQ water and neutralized with 0.1 mL 1 M HCl (Reynolds et al., 2008), followed by a
211 chromatographic purification using 1 mL pre-cleaned AG50W-X8 cation exchange resin (BioRad, mesh
212 200-400) (de Souza et al., 2012). The Si isotopic compositions were determined in 0.6 ppm sample
213 solutions on a *NuPlasma HR* MC-ICPMS at GEOMAR applying a standard-sample bracketing method
214 (Albarède et al., 2004). Silicon isotopic compositions are reported in the δ -notation relative to the
215 reference standard NBS28 in parts per thousand: $\delta^{30}\text{Si} = ((R_{\text{sample}}/R_{\text{standard}})-1)*1000$, where R_{sample} is the
216 $^{30}\text{Si}/^{28}\text{Si}$ ratio of the sample and R_{standard} is the $^{30}\text{Si}/^{28}\text{Si}$ ratio of the NBS28. All $\delta^{30}\text{Si}$ measurements were
217 run at least in triplicates, with uncertainties ranging between 0.05‰ and 0.27‰ (2SD). Repeated
218 measurements of an in-house diatom matrix standard gave average $\delta^{30}\text{Si}$ values of $1.03 \pm 0.21\text{‰}$ (2SD
219 $n=15$). Long-term repeated measurements of the reference materials NBS28, IRMM018, and Big Batch
220 gave average $\delta^{30}\text{Si}$ values of $0.00 \pm 0.24\text{‰}$ (2SD), $-1.40 \pm 0.21\text{‰}$ (2 SD, $n=15$) and $-10.60 \pm 0.24\text{‰}$
221 (2SD, $n=15$), respectively, in good agreement with literature values (Reynolds et al., 2007).

222 **2.3 Diatom assemblage data**

223 Diatom analysis of cores M77/2-024-5TC, 005-3TC and 003-2TC were published previously based on
224 three slides per sample and counting of a minimum of 300 valves for each sample (for details see Fleury
225 et al., 2015). The diatom abundances are presented here for three groups representing different
226 environmental conditions (Fig. 4e-g): Upwelling species – *Chaetoceros* sp., *Skeletonema costatum*,
227 *Thalassionema nitzschioides* var. *nitzschioides*; Coastal planktonic – *Actinocyclus* spp., *Atinoptychus*
228 spp, *Asteromphalus* spp., and *Coscinodiscus* sp.; Other diatom species – *Nitzschia* spp., *Rhizosolenia*
229 spp. and *Thalassiosira* spp., *Cyclotella* spp., *Cocconeis* sp.;

230 The diatom assemblage abundance is compared to $\delta^{30}\text{Si}_{\text{BSi}}$ compositions for cores M77/2-024-
231 5TC, 005-4TC and 003-2TC to investigate if changes in the assemblage have influenced the isotopic

232 record. While diatom counts have been performed on bulk sediment samples $\delta^{30}\text{Si}_{\text{BSi}}$ was measured on
 233 the 11-32 μm size fraction. However, it was shown previously that this size range closely resembles the
 234 main assemblage, which allows studying the influence of changes in the diatom assemblage on the
 235 $\delta^{30}\text{Si}_{\text{BSi}}$ record (Ehlert et al., 2012; 2013).

236 2.4 Nutrient utilization

237 The degree of nutrient utilization can be described assuming either Rayleigh-type (single input followed
 238 by no additional nutrients newly supplied to a particular parcel of water followed by fractional loss as a
 239 function of production and export) or steady-state (continuous supply and partial consumption of
 240 nutrients causing a dynamic equilibrium of the dissolved nutrient concentration and the product)
 241 fractionation behavior (Mariotti et al., 1981). For means of simplification we will only provide the values
 242 derived from steady state fractionation, which was shown to better reflect upwelling conditions off Peru
 243 (Ehlert et al., 2012).

$$244 (1) \% \text{Si}(\text{OH})_4 \text{ consumed} = 1 - \left(\left(\delta^{30}\text{Si} - \delta^{30}\text{Si}(\text{OH})_{4 \text{ source}} \right) / {}^{30}\epsilon \right) * 100$$

$$245 \% \text{NO}_3^- \text{ consumed} = [1 - (\delta^{15}\text{N} - \delta^{15}\text{NO}_3^-) / {}^{15}\epsilon] * 100$$

246 with $\% \text{Si}(\text{OH})_4 \text{ consumed}$ or $\% \text{NO}_3^- \text{ consumed}$ being the percentages of the supplied $\text{Si}(\text{OH})_4$ and NO_3^- that have
 247 been utilized. For this calculation we apply enrichment factors of -1.1‰ ${}^{30}\epsilon$ ($\delta^{30}\text{Si}$, (De La Rocha et al.,
 248 1997) and -5‰ ${}^{15}\epsilon$ ($\delta^{15}\text{N}$) and assume a constant source water signature of 1.5‰ for $\delta^{30}\text{Si}(\text{OH})_{4 \text{ source}}$
 249 (i.e. the mean $\delta^{30}\text{Si}(\text{OH})_4$ of the PCUC). [The here calculated nutrient utilization for surface sediments is](#)
 250 [identical to the original publications \(Fig. 2b; Mollier-Vogel et al., 2012; Ehlert et al., 2012\)](#). To evaluate
 251 the impact of changes in ${}^{30}\epsilon$ on the $\delta^{30}\text{Si}$ signatures the potential influence of species-specific
 252 fractionation was tested based on the impact of a -2.1‰ enrichment factors of *Chaetoceros brevis* (Sutton
 253 et al., 2013). However, the estimated impact on past $\delta^{30}\text{Si}_{\text{BSi}}$ records due to a change in the amount of
 254 *Chaetoceros* sp. present in the sediment was less than 5% for all cores (M77/2-024-5TC, 005-3TC and
 255 003-2TC) and thus did not alter the assumed ${}^{30}\epsilon$ of -1.1‰ substantially (based on calculations presented
 256 in Doering et al., (2016); not shown). The impact of denitrification on the $\delta^{15}\text{NO}_3^-$ signatures of the past
 257 is assessed in the following section before calculating past NO_3^- utilization for the respective latitudes.

258 2.5 Calculation of the $\delta^{15}\text{NO}_3^-$ source signatures

259 Based on modern observations from the water column it is known that NO_3^- and $\text{Si}(\text{OH})_4$ are incorporated
 260 in a 1:1 ratio when diatoms dominate the phytoplankton assemblage (Brzezinski, 1985; Ragueneau et al.,
 261 2000). [The ratio of nutrients in the water column can, however, vary between 2:1 and 1:2 on the shallow](#)
 262 [Peruvian shelf \(Grasse et al., 2016\)](#). Assuming a strict 1:1 uptake ratio of nutrients, the respective $\delta^{30}\text{Si}_{\text{BSi}}$
 263 [and \$\delta^{15}\text{N}_{\text{Bulk}}\$ values in the underlying sediments should also reflect a 1:1 ratio \(indicated by white star '1'](#)
 264 [in Fig. 3a\)](#). Based on the known $\delta^{30}\text{Si}(\text{OH})_4$ and NO_3^- source signatures of modern subsurface waters, we
 265 can calculate the actual nutrient utilization (see section 2.4) and estimate the uptake ratio for NO_3^-
 266 [:Si\(OH\)₄ \(Fig. 3b\)](#). However, it is not possible to observe a significant correlation for the entire shelf
 267 [area, given that there are only a few data points for the areas along the shelf \(Figs. 2, 5a\)](#). We calculate
 268 [past nutrient utilization and estimate the influence of denitrification on the \$\delta^{15}\text{N}_{\text{bulk}}\$ values based on the](#)
 269 [fact that on the shelf \$\delta^{30}\text{Si}_{\text{BSi}}\$ and \$\delta^{15}\text{N}_{\text{bulk}}\$ values generally follow a positive linear regression \(Figs. 3b,](#)

270 5a). In order to estimate past changes in the $\delta^{15}\text{NO}_3^-$ source values, the $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ values were
 271 separately plotted against each other for the time periods of the CWP and the LIA, arid and humid (Fig.
 272 5 b-d). Accordingly, the $\delta^{15}\text{NO}_3^-$ source value for each period was calculated based on the linear function
 273 assuming that the source $\delta^{30}\text{Si}(\text{OH})_4$ signature always remained stable at 1.5‰ over time:

274 (2) $\delta^{30}\text{Si}(\text{OH})_4 = a * \delta^{15}\text{NO}_3^- + b$, or

275 (3) $\delta^{15}\text{NO}_3^- = (\delta^{30}\text{Si}(\text{OH})_4 - b) / a$

276 with a indicating the slope of the line and b the intercept. For $\delta^{30}\text{Si}(\text{OH})_4$ we used the value of 0.4‰
 277 representing near-0% utilization (= source water $\delta^{30}\text{Si}(\text{OH})_4$ of 1.5‰ of the PCUC – 1.1‰ fractionation
 278 during uptake) to estimate the $\delta^{15}\text{NO}_3^-$ source. Accordingly, the values estimated by equation (3)
 279 represent the $\delta^{15}\text{NO}_3^-$ source value assuming also near-0% utilization of NO_3^-

280 We calculated the linear regression based on all samples of the different cores from the different
 281 latitudes (11°S, 12° S, 14°S and 15°S) during the CWP and LIA. We also further differentiated between
 282 short-term productive phases (arid phases) and the generally prevailing humid El-Niño like conditions
 283 during the LIA (grey shadings in Fig. 4), and resolved the resulting equation based on eq. (2) to estimate
 284 $\delta^{15}\text{NO}_3^-$. Only for the LIA (humid) phases it was not possible to directly calculate $\delta^{15}\text{NO}_3^-$ values based
 285 on the linear function from eq. (2), due to near horizontal alignment of the $\delta^{15}\text{N}_{\text{bulk}}$ versus $\delta^{30}\text{Si}_{\text{BSi}}$ values
 286 (Fig. 5b). Therefore, for this time period the highest $\delta^{15}\text{N}_{\text{bulk}}$ value for each latitude was assumed to
 287 reflect ~100% utilization and was thus used as $\delta^{15}\text{NO}_3^-$ source value. This assumption might slightly
 288 overestimate the maximum utilization, which is only ~80% today (Fig. 2b), and therefore might
 289 underestimate the source value slightly. For all time periods and latitudes, the linear regressions as well
 290 as correlation coefficient (r^2) are given in the supplements (Fig. S1). The results are presented in the
 291 following as the resulting $\delta^{15}\text{NO}_3^-$ source values and the theoretical ratio of nutrient utilization (i.e. 1:1
 292 or 2:1, 15:1, etc.; Fig. 5. b-d) for each latitudinal range to compare the latitudinal trends between the
 293 CWP and LIA.

294 2.6 Calculation of Nutrient supply

295 Based on these calculated subsurface $\delta^{15}\text{NO}_3^-$ values we further calculated the change in nutrient
 296 utilization as well as nutrient supply for the different latitudes. Past nutrient utilization was calculated
 297 following equation (1). Given the estimate of nutrient demand and export productivity it is further
 298 possible to estimate changes in the supply with the relationship $\Delta\text{supply} = \Delta\text{demand}/\Delta\text{utilization}$ by
 299 applying the equation of (Horn et al., 2011) given by:

300 (4)
$$\text{Nutrient supply} = \frac{F_{\text{BSi/TN}}^{\text{sample}} / F_{\text{BSi/TN}}^{\text{present}}}{\% \text{nutrient}_{\text{consumed}}^{\text{sample}} / \% \text{nutrient}_{\text{consumed}}^{\text{present}}}$$

301 $F_{\text{opal/TN}}$ is the flux of BSi or TN and $\% \text{nutrient}_{\text{consumed}}$ is the percent of the $\text{Si}(\text{OH})_4$ or NO_3^- supply
 302 consumed (i.e. nutrient utilization). Given that there are no accumulation rates available for either the
 303 surface sediment samples or for any of the cores studied here to directly determine the export productivity
 304 directly, we used the BSi and TN values previously published (surface sediments; Mollier-Vogel et al.,
 305 2012; Ehlert et al., 2012) and the new BSi values presented in this study together with mass accumulation
 306 rates ($\text{g cm}^{-2} \text{yr}^{-1}$) for cores BO406-13 and 406-5 from Gutierrez et al. 2009 to calculate the accumulation
 307 rates of BSi and TN (MAR; $\text{g cm}^{-2} \text{yr}^{-1}$). For the different time periods mean values for MAR BSi and

308 MAR TN were calculated and the respective nutrient supply was calculated based on equation (4),
309 indicating changes in the nutrient supply compared to modern values.

310 **3. Results**

311 **3.1 Biogenic opal and silicon isotope signatures**

312 The data of the sediment cores from the shelf area between 12°S and 15°S presented here show an
313 increase in BSi content from mean values of 13-23% during the LIA to values of 21-29% during the
314 CWP. The $\delta^{30}\text{Si}_{\text{BSi}}$ records follow a similar trend of lower mean $\delta^{30}\text{Si}_{\text{BSi}}$ values of $0.8 \pm 0.2\text{‰}$ (2SD, 12°S),
315 $0.8 \pm 0.1\text{‰}$ (14°S) and $1 \pm 0.2\text{‰}$ (15°S) during the LIA to more variable and higher mean values of 1.3
316 $\pm 0.4\text{‰}$ (12°S), $0.8 \pm 0.4\text{‰}$ (14°S) and $1.5 \pm 0.2\text{‰}$ (15°S) during the CWP (Fig. 3 a-d; Table 1).

317 The diatom assemblages (Fig. 4e-g; based on Fleury et al., 2015) show an association of the
318 amount of upwelling species and $\delta^{30}\text{Si}_{\text{BSi}}$ signatures, with decreases of up to 20% in upwelling species
319 often accompanied by a reduction of $\delta^{30}\text{Si}_{\text{BSi}}$ by about 0.5-1‰. However, not every decrease in $\delta^{30}\text{Si}_{\text{BSi}}$
320 is mirrored by a change in the diatom assemblage and vice versa (e.g. Fig. 4f at 1650 AD). Overall the
321 diatom assemblage data indicate little changes in the mean conditions and a slight reduction of upwelling
322 strength at 12°S and 15°S during the LIA in comparison to the CWP (Fig. 6). The most distinct shift of
323 lower abundances of upwelling species (~50%) to higher values during the CWP (~70%) is found at
324 15°S (003-2TC) corresponding to the strongest changes in BSi and $\delta^{30}\text{Si}_{\text{BSi}}$ at this location.

325 The sedimentary BSi concentrations and $\delta^{30}\text{Si}_{\text{BSi}}$ signatures at 12°S (005-3TC) and 15°S (003-
326 2TC) were lowest during the LIA (Fig. 4c,e), in agreement with previously published records from 11°S
327 (M77/1-470; Fig. 4a) and 14°S (Ehlert et al., 2015; Fig. 4d). An exception is core 024-5TC (Fig. 4a) from
328 11°S, where $\delta^{30}\text{Si}$ mean values of the LIA ($1.3 \pm 0.4\text{‰}$) are similar to CWP mean values ($1.4 \pm 0.1\text{‰}$).
329 Furthermore, both the BSi concentrations and $\delta^{30}\text{Si}_{\text{BSi}}$ signatures of core 024-5TC were significantly
330 higher during the LIA than at nearby core M77/1-470 (Fig. 4a; Ehlert et al. 2015). However, comparison
331 with the cumulative diatom assemblage indicates overall little difference in the amount of upwelling and
332 coastal planktonic diatom species between the LIA and the CWP at 11°S (Fig. 4f), with intervals of
333 reduced abundances of upwelling species generally lasting less than 50 years, much shorter than the 100
334 to 150 years intervals observed at 12°S and 15°S. Furthermore, the finely laminated sediment layers do
335 indicate short periods of higher productivity during the LIA in phase with more arid conditions (Fig. 4,
336 grey shadings; for details see Fleury et al., 2015). Accordingly, the high mean BSi and $\delta^{30}\text{Si}_{\text{BSi}}$ values
337 obtained from core 024-5TC may be an artifact of low sampling resolution with only two $\delta^{30}\text{Si}_{\text{BSi}}$ samples
338 representing the time period between 1700 and 1800 AD and $\delta^{30}\text{Si}_{\text{BSi}}$ analyses not evenly covering all
339 the short events (~50 years) of reductions in the abundance of upwelling diatom species (Fig. 4f).
340 Alternatively, the increase in $\text{Si}(\text{OH})_4$ utilization decoupled from an increase in diatom abundance
341 (Fleury et al., 2015; not shown here) may indicate stronger silicification of the diatom frustules, as often
342 observed under Fe-deficient conditions and associated with an increase in the $\text{Si}(\text{OH})_4:\text{NO}_3^-$ incorporated
343 by the diatoms (De La Rocha et al., 2000; Takeda, 1998; Wilken et al., 2011).

344 As previously shown the $\delta^{15}\text{N}_{\text{bulk}}$ values of the three cores (M77/2-024-5TC, 005-3TC and 003-
345 2TC) presented in this study were on average 0.8‰ lower during the LIA than during the CWP (Fleury

346 et al., 2015). The $\delta^{15}\text{N}_{\text{bulk}}$ values reported for core 005-3TC (12°S) are close to values of nearby core
347 B0406-13 (Gutiérrez et al., 2009). Similarly, the $\delta^{15}\text{N}_{\text{bulk}}$ values of core 003-2TC (15°S) agree well with
348 previously published $\delta^{15}\text{N}_{\text{bulk}}$ record of core B0405-6 (14°S, Fig. 4 j, k; Gutiérrez et al., 2009).

349 **3.2 $\delta^{15}\text{NO}_3^-$ source signatures, nutrient utilization and supply**

350 During the humid phases of the LIA the calculated $\delta^{15}\text{NO}_3^-$ source values were lower reaching values of
351 6‰ between 11°S and 12°S and 7.5‰ between 14°S and 15°S (Fig. 5b, 6a). The calculated NO_3^-
352 utilization was higher during this time reaching values between 70 and 90%, while $\text{Si}(\text{OH})_4$ utilization
353 ranged between 6 and 60%. The MAR TN was lowest ($<0.02 \text{ g cm}^{-2} \text{ yr}^{-1}$) during the LIA, however, with
354 little difference between humid and arid phases (Fig. 6 a+c, right side). The MAR BSi values were similar
355 to today during the LIA (humid) ranging between 0.2 - 0.5 $\text{g cm}^{-2} \text{ yr}^{-1}$ (Figs. 2, 6a right side). The
356 calculated NO_3^- supply was lowest during the LIA (humid) ranging between 0.3 and 0.7 with little change
357 over latitude in accordance with the prevalence of more oxygenated waters, whereas the $\text{Si}(\text{OH})_4$ supply
358 strongly increased from 0.5 to 3.8 at 12°S (Fig. 6a).

359 During the CWP the calculated $\delta^{15}\text{NO}_3^-$ source signatures based on eq. (2) and (3) result in
360 values of 7.6‰ at 11°S, 8.6‰ at 12°S and 10.4‰ between 14°S and 15°S during the CWP (Figs. 5c, 6b;
361 S1), which reflects a southward increase in $\delta^{15}\text{NO}_3^-$ source signatures as observed today (Fig. 2a). Based
362 on these $\delta^{15}\text{NO}_3^-$ values the nutrient utilizations estimated based on eq. (1) range between 30-90% for
363 NO_3^- and 40-100% for $\text{Si}(\text{OH})_4$ (Fig. 6b). During the LIA (arid) similar values are calculated with a
364 $\delta^{15}\text{NO}_3^-$ mean value of 8‰ between 11°S and 12°S, increasing to a value of 9‰ between 14°S and 15°S
365 (Fig. 6c). The respective nutrient utilization ranges between 2 to 70% for NO_3^- and 20 to 85% for
366 $\text{Si}(\text{OH})_4$. The MAR TN were by about 0.02 ($\text{g cm}^{-2} \text{ yr}^{-1}$) lower during the CWP than today and MAR BSi
367 values were generally higher by about 0.1 - 0.35 ($\text{g cm}^{-2} \text{ yr}^{-1}$). The calculated $\text{Si}(\text{OH})_4$ supply indicates a
368 slight increase compared to today (as indicated by positive values) but has remained rather stable around
369 1 over all latitudes, while the and NO_3^- supply also indicate values of ~1 at 11°S and 15°S but the supply
370 increased to 2 at 12°S (Fig. 6b, right side). During the LIA (arid) MARs of TN and BSi were both lower
371 in comparison to the CWP, ranging between 0.014 - 0.017 ($\text{g cm}^{-2} \text{ yr}^{-1}$) and 0.25 - 0.7 ($\text{g cm}^{-2} \text{ yr}^{-1}$),
372 respectively. The $\text{Si}(\text{OH})_4$ supply was similarly stable as observed during the CWP but slightly higher
373 ranging from 0.6 to 1.55, while the NO_3^- supply was lower and decreased from North to South from 1 to
374 0.3.

375 **4. Discussion**

376 The aim of this study is to reconstruct the extent of variability in $\delta^{15}\text{N}_{\text{bulk}}$ caused as a function of
377 denitrification versus nutrient utilization during specific time periods, i.e. the CWP and recurring short-
378 term arid/humid periods during the LIA. The combination of $\delta^{15}\text{N}_{\text{Bulk}}$ and $\delta^{30}\text{Si}_{\text{BSi}}$ signatures enables us
379 to calculate the $\delta^{15}\text{NO}_3^-$ source signatures during these time periods of time, enabled us to estimate the
380 extent of NO_3^- utilization additional contributing to the $\delta^{15}\text{N}_{\text{bulk}}$ recorded in the sediments. These data are
381 combined with the $\delta^{30}\text{Si}_{\text{BSi}}$ signatures, calculated $\text{Si}(\text{OH})_4$ utilization calculations and nutrient supply,
382 will be discussed in the following (1) in comparison to modern conditions, and (2) in the context of

383 consistency with ENSO variability observed off Peru and the Eastern Equatorial Pacific (EEP) during
384 the last 600 years. Due to similar conditions prevailing during the CWP and arid phases of the LIA we
385 will discuss these time periods together in the following.

386 **4.1. Disentangling nutrient supply, utilization and N-loss processes: Changes in the source water** 387 **nitrate isotopic composition**

388 **Humid conditions of the Little Ice Age**

389 During the humid LIA the $\delta^{30}\text{Si}_{\text{BSi}}$ values remain remarkably stable, whereas $\delta^{15}\text{N}_{\text{bulk}}$ values show a wide
390 range potentially reflecting enhanced NO_3^- limitation prevailing during humid phases (Fig. 5b). Such a
391 shift towards increasing $\delta^{15}\text{N}_{\text{bulk}}$ values with consistently low $\delta^{30}\text{Si}_{\text{BSi}}$ values is indicative of weaker
392 denitrification due to the higher subsurface oxygenation (only suboxic and not anoxic conditions) in
393 agreement with reconstructions of redox conditions (Salvatteci et al., 2014b; Sifeddine et al., 2008). This
394 is in agreement with the lower $\delta^{15}\text{NO}_3^-$ source signatures (6-7.5 ‰) and a decrease in the abundance of
395 upwelling-indicating diatom species and *Chaetoceros* sp. (Figs. 4e-f and 6a; data from Fleury et al.,
396 2015). Furthermore, our results indicate much higher NO_3^- utilization over $\text{Si}(\text{OH})_4$ utilization with ratios
397 of up to 15:1 (Fig. 5b, 7a). This is in agreement with phytoplankton assemblage analyses during El-Niño
398 events when productivity has been reported to be dominated by non-siliceous phytoplankton groups
399 (Sanchez et al., 2000), which is also observed today further off the coast of Peru (Fig. 3a; Grasse et al.,
400 2016). Accordingly, with prevalence of non-siliceous phytoplankton groups more NO_3^- than $\text{Si}(\text{OH})_4$ is
401 utilized (Conley and Malone, 1992; Wilkerson and Dugdale, 1996) and the ratio might shift to ratios of
402 up to 15:1 (Fig. 3b, 7a; Grasse et al., 2016). However, the conditions found offshore today are based on
403 surface waters that originate from the shelf area where diatom blooms prevail, thus being already
404 depleted in $\text{Si}(\text{OH})_4$ and might not provide an adequate analogue for the conditions prevailing during the
405 humid LIA phases (Fig. 5b, 6a). The calculated NO_3^- supply was lowest with little change over latitude
406 in accordance with prevalence of more oxygenated waters, whereas the $\text{Si}(\text{OH})_4$ supply strongly
407 increased especially at 12°S (Fig. 6a). However, the calculated increased $\text{Si}(\text{OH})_4$ supply likely reflects
408 the change in nutrient uptake (i.e. nutrient ratio) due to stratification and potentially Fe limitation rather
409 than an actual increase in $\text{Si}(\text{OH})_4$ supply reaching surface waters. Accordingly, we observe a high
410 $\text{Si}(\text{OH})_4$ supply but low utilization, reflecting a low $\text{Si}(\text{OH})_4$ demand at the time. The NO_3^- supply appears
411 to be lower than today but the strongly enhanced NO_3^- utilization indicates a higher NO_3^- demand. This
412 shift towards a decreased $\text{Si}(\text{OH})_4$ but an increased NO_3^- demand further supports a change in the nutrient
413 uptake ratio by phytoplankton (NO_3^- : $\text{Si}(\text{OH})_4$ = 2:1 or 15:1, Fig. 5b, 7a). Regarding the high Si supply
414 it is also possible that it was actually bound by non-siliceous phytoplankton species, such as
415 *Synechococcus* and not by diatoms as observed further offshore today (Fig 3a; Grasse et al., 2016).
416 However, these species are more likely to be recycled within the water column and Si stored within their
417 cells is thus remineralized and not transported to the sediment. This might be the reason we observe low
418 BSi (%) values and the $\delta^{30}\text{Si}_{\text{BSi}}$ remain equally low (Fig. 4, 5b).

419 **Current Warm Period and arid phases of the Little Ice Age**

420 The calculated $\delta^{15}\text{NO}_3^-$ source values based on linear regression between $\delta^{15}\text{N}_{\text{Bulk}}$ and $\delta^{30}\text{Si}_{\text{BSi}}$ indicate
421 an increase in the $\delta^{15}\text{NO}_3^-$ source signatures of upwelled subsurface waters from North to South from

422 ~7‰ to 10‰ during the CWP and arid phases of the LIA similar to those observations for modern
423 conditions (Figs. 2a, 5c-d, 7b). This is in agreement with high contributions of upwelling diatoms and
424 *Chaetoceros* sp. during both time periods (Figs. 4e-g. and 6b-c; data from Fleury et al., 2015). The
425 calculated Si(OH)₄ and NO₃⁻ supplies indicate a slight increase compared to today with Si(OH)₄ supply
426 increasing and NO₃⁻ supply decreasing towards the southern shelf. The latter agrees with continuous
427 denitrification in the southern area causing loss of NO₃⁻. Furthermore, nutrient utilization for both NO₃⁻
428 and Si(OH)₄ were moderate to high (~30-90%; Fig. 6b-c, 7b), similar to modern values between 10°S
429 and 15°S (Fig. 2b; Mollier-Vogel et al., 2012; Ehlert et al., 2012). Due to the incomplete utilization of
430 NO₃⁻ the increasing δ¹⁵N<sub>NO₃⁻ source values are also only partially reflected in the δ¹⁵N_{Bulk} signatures for
431 the CWP and LIA (arid) as previously reported for signatures from surface sediments (Mollier-Vogel et
432 al., 2012). Especially during the CWP, we calculate about 20-40 % lower NO₃⁻ utilization compared to
433 today (Fig. 2b) but at the same time NO₃⁻ supply increased, while Si(OH)₄ supply was only slightly higher
434 compared to today and remained rather stable with latitude (Fig. 6b, right side). Apparently, the nutrient
435 concentration of upwelled waters during the CWP has been different from today, which is also supported
436 by a difference in the ratio of NO₃⁻:Si(OH)₄ utilization (Fig. 5c). Accordingly, unlike today's surface
437 sediment data, the cores at 11°S and 12°S show substantially higher δ³⁰Si_{BSi} values during both the CWP
438 and LIA (arid) (Fig. 5c-d). These higher δ³⁰Si_{BSi} signatures result in a NO₃⁻:Si(OH)₄ utilization that has
439 shifted towards a 1:2 ratio, indicating enhanced utilization of Si(OH)₄ over NO₃⁻ potentially leading to
440 Si(OH)₄ limitation, in agreement with the lower Si(OH)₄ supply in comparison to NO₃⁻ and higher
441 Si(OH)₄ than NO₃⁻ utilization rates (Fig. 6b-c). Such a decoupling of Si and N within diatoms can be
442 caused by biogeochemical changes, such as Fe availability altering the Si:N uptake dynamics (Hutchins
443 and Bruland, 1998; Takeda, 1998) whereby elevated Si:N ratios are characteristic for Fe-limited diatom
444 communities (Takeda, 1998). Accordingly, increased uptake of Si over N can lead to a Si(OH)₄ limitation
445 as found during the CWP and LIA arid phases at 11°S to 12°S (Figs. 5c-d, 6b-c, 7b). The reason may
446 have been that less Fe was upwelled at the narrow shelf between 11°S and 16°S, which led to Fe-
447 limitation during progressing diatom blooms (Doering et al., 2016).</sub>

448 **4.2 The coupling between the biogeochemical cycle and ENSO variability**

449 Recent evidence shows that a cool EEP plays a key role in climate change due to its linkage to a
450 slowdown in global warming (England et al., 2014; Kosaka and Xie, 2013) highlighting the importance
451 to understand Pacific climate variability in the past (Rustic et al., 2015). The last millennium has been
452 divided into warmer global conditions over the Medieval Warm Period (MWP), colder temperatures over
453 the LIA and rising temperatures since the beginning of the CWP (Mann et al., 1999). The transition
454 between the MWP and LIA (~1150 to 1500 AD) has been associated with an anomalous strong zonal
455 SST gradient and with transitional Northern Hemisphere (NH) cooling into the LIA as evidenced by
456 cooler SSTs at Galápagos (Rustic et al., 2015). After ~1500 AD, the EEP cooling trend ended and local
457 SSTs began to increase until around 1600 AD an anomalous weak zonal gradient was established when
458 the EEP temperatures reversed from cooling to warming. This reversal occurred when the NH descended
459 into the coldest part of the LIA and persisted throughout most of the LIA resulting in an extended El
460 Niño-like mean state (Mann et al., 2009). Evidence links the ITCZ to hemispheric warming and cooling
461 cycles implying southward ITCZ displacements during NH cold periods (Chiang and Bitz, 2005;

462 Schneider et al., 2014). Accordingly a southward shift of the ITCZ during the MWP-LIA transition has
463 been proposed for the Atlantic and Pacific (Haug et al., 2001; Peterson and Haug, 2006; Sachs et al.,
464 2009). The El Niño-like conditions during the LIA have been associated to a gradual intensification of
465 the fluvial input of sediments to the continental shelf as reflected by an increase in the terrigenous
466 sediment flux (Briceño-Zuluaga et al., 2016; Gutiérrez et al., 2009; Sifeddine et al., 2008), changes of
467 the radiogenic isotopic composition of the terrigenous fraction due to changes in the provenance and
468 material transport (Ehlert et al., 2015), as well as better oxygenation and a lower productivity in the
469 Peruvian upwelling area (Gutiérrez et al., 2009; Salvattecí et al., 2014b; Sifeddine et al., 2008).
470 Accordingly, most of the LIA i.e., the humid phases, have been characterized by low productivity and
471 weak denitrification intensity between 10°S and 15°S (Díaz-Ochoa et al., 2009; Salvattecí et al., 2014b;
472 Sifeddine et al., 2008), which is supported by the absence of a significant southward increase in the
473 source value of $\delta^{15}\text{NO}_3^-$ reconstructed from our records (Fig. 5b, 6a). Correspondingly, high $\delta^{15}\text{N}_{\text{bulk}}$ and
474 little change in reconstructed NO_3^- supply indicate more complete NO_3^- utilization during the LIA
475 (humid), while $\delta^{30}\text{Si}_{\text{BSi}}$ signatures and utilization remained low and Si supply high (Fig. 6a). This
476 indicates a shift towards a dominance of non-siliceous phytoplankton productivity causing NO_3^-
477 limitation and low uptake of Si. This is in agreement with modern conditions during El Niño events for
478 which physical-biogeochemical models together with in-situ and satellite observations (1958-2008) have
479 shown that the temperatures and sea level increase, the thermocline/nutricline deepens, and the
480 phytoplankton (mainly diatoms) and nutrient concentration decrease along the Peruvian coast (Espinoza-
481 Morriberón et al., 2017). Coastal trapped waves propagating along the coast can seasonally increase the
482 depth of thermocline and nutricline, decreasing the NO_3^- vertical flux into the surface layer. The NO_3^-
483 and Fe content of the upwelling source waters may also strongly decline (Espinoza-Morriberón et al.,
484 2017). Our calculations show that phases of lower productivity during so-called El Niño like-conditions
485 during the LIA (humid), indeed have a $\delta^{15}\text{NO}_3^-$ source delivered to the Peru upwelling area similar to
486 today (Fig. 6a), but due to less or no denitrification $\delta^{15}\text{NO}_3^-$ source does not increase southward (Fig. 5b
487 6a). Instead $\delta^{15}\text{N}_{\text{Bulk}}$ values are mainly affected by variability of NO_3^- concentrations, which seem to be
488 the limiting factor for PP similar as observed during El Niño events today (Espinoza-Morriberón et al.,
489 2017). Potentially the stronger stratification due to deepening of the nutricline does not allow for
490 similarly efficient N remineralization (or N is transported offshore due to eddy activity, Espinoza-
491 Morriberón et al., 2017) and may result in NO_3^- to be utilized more strongly than $\text{Si}(\text{OH})_4$ (Fig. 7a).
492 Accordingly, the NO_3^- supply was diminished while $\text{Si}(\text{OH})_4$ was still available.

493 Finely laminated sediment from the LIA from the Oxygen Minimum Zones (OMZ), which have
494 also been used in this study, resolve multidecadal variations in precipitation over the continent, and of
495 variations in detrital and biogenic fluxes in relation to precipitation and upwelling intensity (Briceño-
496 Zuluaga et al., 2016, Díaz-Ochoa et al., 2009; Fleury et al., 2015; 2016; Salvattecí et al., 2014a). And
497 stable oxygen isotope compositions of individual planktic foraminifera point to greater ENSO activity
498 (high frequency between alternating La Niña and El Niño conditions) in the EEP based on records from
499 Galapagos (Rustic et al., 2015). It was shown by coupled models that such multi-decadal variation in
500 ENSO amplitude can arise from episodic strengthening and weakening of the thermocline feedback
501 (Borlace et al., 2013). The difference we observed in the isotopic evolution of nutrients ($\delta^{15}\text{N}$ and $\delta^{30}\text{Si}$)
502 between the arid and humid phases during the LIA support the development of multidecadal phases of

503 prevailing La Niña- or El Niño-like conditions. Similar interannual variance has been observed based on
504 organic carbon and carbonate proxies during the LIA within the California current system, which the
505 authors related to large ENSO events in contrast to an apparent reduction in such variability during the
506 CWP (Abella-Gutiérrez and Herguera, 2016).

507 This El Niño-like mean state appears to have ended at the beginning of the CWP (Rustic et al.,
508 2015). Evidence for increasing precipitation off the coast of Panama after 1700 AD likely reflects the
509 northward shift of the ITCZ (Linsley et al., 1994) from its more southerly LIA position. During the CWP
510 the OMZ intensified and marine productivity increased together with surface temperature cooling and
511 increase in terrigenous material input (Briceño-Zuluaga et al., 2016; Gutiérrez et al., 2011). We find that
512 the CWP and LIA (arid), are characterized by high upwelling intensity, productivity and N-loss processes
513 (Fleury et al., 2015; Salvatelli et al., 2014b; Sifeddine et al., 2008), are associated with southward
514 increasing $\delta^{15}\text{NO}_3^-$ source signatures caused by denitrification, reflecting moderate NO_3^- utilization and
515 moderate to high $\text{Si}(\text{OH})_4$ utilization (Fig. 7b). Highest $\delta^{30}\text{Si}_{\text{BSi}}$ and utilization values at 15°S are
516 potentially caused by progressive Fe limitation during diatom blooms, causing a $\text{NO}_3^-:\text{Si}(\text{OH})_4$ ratio of
517 up to 1:2. Southward increasing $\delta^{15}\text{N}_{\text{bulk}}$ values and calculated $\delta^{15}\text{NO}_3^-$ demonstrate the consistent
518 incorporation of higher isotopic compositions due to subsurface denitrification under anoxic subsurface
519 conditions in agreement with decreasing NO_3^- supply illustrating the N-loss process.

520 Conclusions

521 Based on a compilation of new and previously published $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ records of several short
522 sediment cores from the southern Peruvian shelf (11-15°S) we present a new evaluation of the impact of
523 denitrification on the isotopic source signature of NO_3^- and subsequent utilization. As denitrification
524 increases southward along the shelf today, we applied a latitudinal comparison between $\delta^{30}\text{Si}_{\text{BSi}}$ and
525 $\delta^{15}\text{N}_{\text{bulk}}$ signatures in modern surface and latest Holocene sediments. Given that during the last 600 years
526 both proxies have mainly been influenced by nutrient utilization we performed a novel calculation of
527 subsurface $\delta^{15}\text{NO}_3^-$ based on the linear regression of $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ signatures for the CWP and
528 LIA (arid versus humid conditions). Our results show that low productivity and higher subsurface
529 oxygenation (suboxic conditions) during the humid phases of LIA were associated with low $\delta^{30}\text{Si}_{\text{BSi}}$ and
530 $\delta^{15}\text{N}_{\text{bulk}}$ signatures. The latitudinal comparison of $\delta^{30}\text{Si}_{\text{BSi}}$ versus $\delta^{15}\text{N}_{\text{bulk}}$ signatures supports decreased
531 influence of subsurface denitrification on the NO_3^- isotope distribution with lower and more uniform
532 $\delta^{15}\text{NO}_3^-$ source signatures between 6 and 7.5‰. However, NO_3^- utilization was significantly higher,
533 while $\text{Si}(\text{OH})_4$ utilization was lower because the $\text{Si}(\text{OH})_4$ supply was higher compared to the demand.
534 This change in nutrient utilization is reflected by a $\text{NO}_3^-:\text{Si}(\text{OH})_4$ uptake ratio of up to 15:1, suggesting
535 a shift from a diatom-dominated regime to one dominated by non-siliceous phytoplankton. This agrees
536 with El-Niño-like conditions prevailing during most of the LIA accompanied by a deepening of the
537 thermocline and lower nutrient availability. During the CWP and sporadic arid conditions during the LIA
538 the isotopic compositions of NO_3^- have increased southward due to subsurface denitrification under
539 strong oxygen depletion, similar to modern conditions. Furthermore, enhanced $\text{Si}(\text{OH})_4$ over NO_3^- uptake
540 characterized nutrient utilization over NO_3^- uptake, reflecting strong diatom blooms as observed today,
541 potentially leading to progressive Fe limitation increasing the Si:N uptake ratio of diatoms to 2:1.

542 In summary, our results constitute an improvement of the application of combined $\delta^{30}\text{Si}_{\text{BSi}}$ and
543 $\delta^{15}\text{N}_{\text{bulk}}$ signatures as a powerful tool to differentiate between past changes in subsurface denitrification,
544 nutrient utilization and supply but also changes in the nutrient ratios as a result of either micro-(Fe) or
545 macro-nutrient limitation.

546 **Data availability**

547 All data will be uploaded at www.pangea.de upon publication

548 **Author contributions**

549 S. Fleury and K. Doering conducted the sampling of the sediment cores at Bordeaux University. K.
550 Doering prepared the samples and performed the isotope measurements. K. Doering wrote the
551 manuscript with contributions from all co-authors.

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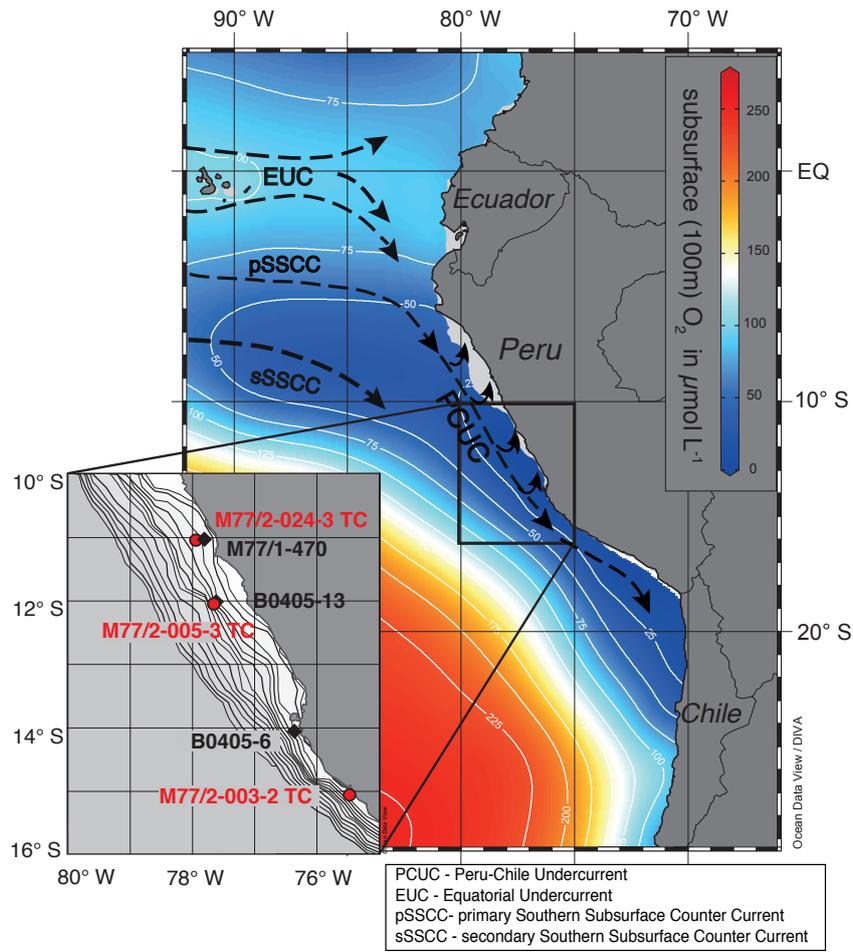
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Table 1: Downcore record of core M77/2-024-5TC, M77/2-005-3TC and M77/2-003-2TC for $\delta^{30}\text{Si}_{\text{BSi}}$ (‰) and BSi content (wt%). The 2 SD represents the external reproducibility of repeated sample measurements.

Core	Age yrs BP	Depth (mm)	BSi (wt%)	$\delta^{30}\text{Si}_{\text{BSi}}$ (‰)	2SD
24-5TC	42	0	16.2	1.50	0.23
	101	42	16.1	1.26	0.17
	154	104	34.3	1.50	0.18
	170	134	29.3	1.43	0.15
	187	161	23.7	1.47	0.05
	243	213	30.7	1.35	0.21
	304	264	28.1	1.40	0.09
	376	301	21.0	1.38	0.16
	422	390	10.1	0.81	0.19
	441	432	24.6	1.51	0.16
483	473	23.8	1.61	0.08	
005-3TC	46	0	15.9	1.07	0.09
	73	35	15.0	1.37	0.11
	95	69	25.4	1.46	0.21
	217	128	18.8	1.03	0.18
	250	165	17.3	0.80	0.22
	259	185	15.1	0.93	0.13
	303	241	13.1	0.44	0.27
	340	296	14.0	0.50	0.15
	358	323	11.6	0.47	0.20
	450	369	14.5	1.24	0.24
464	389	25.0	1.60	0.19	
003-2TC	22	0	39.2	1.63	0.24
	146	97	40.5	1.48	0.05
	245	174	41.9	1.30	0.26
	288	208	20.8	0.65	0.23
	327	239	23.9	0.74	0.13
	411	304	19.4	0.73	0.27
	474	353	46.7	1.38	0.17
	581	437	29.1	0.63	0.12

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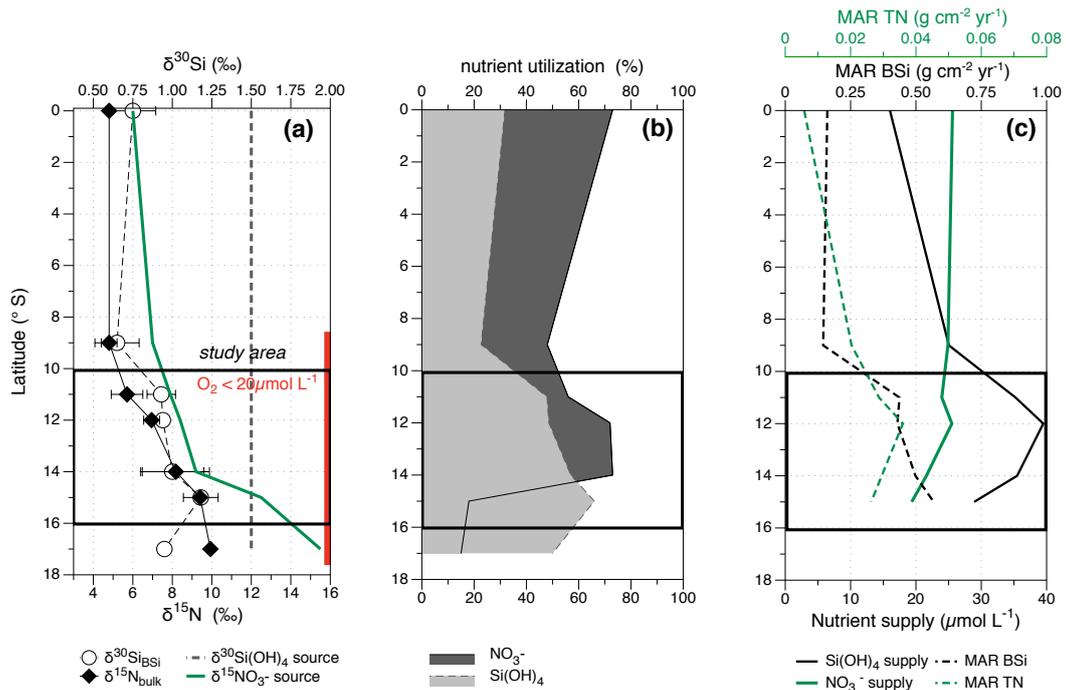
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808 **Figure 1: Subsurface (100 m) oxygen concentration and current directions in the Eastern Equatorial Pacific.**
 809 **Inset map shows locations of cores M77/2-024-3 TC, M77/2-005-3 TC, M77/2-003-2 TC (this study) and**
 810 **M77/1-470, B0405-13 and B0405-6 (Ehlert et al., 2015; Gutiérrez et al., 2009) in more detail. The bathymetry**
 811 **is given for 0 to 1000 m water depth in 50 m increments.**

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814 **Figure 2: Latitudinal overview of present day (a) mean $\delta^{15}\text{N}_{\text{bulk}}$ (‰, black diamonds, 2 SD error bars) and**
 815 **$\delta^{30}\text{Si}_{\text{BSi}}$ (‰, white circles, 2SD error bars), the black dashed line indicates the subsurface $\delta^{30}\text{Si}(\text{OH})_4$ source**
 816 **value of 1.5 ‰, the green solid line marks the $\delta^{15}\text{NO}_3^-$ source value, increasing southwards from 6‰ (EQ-8°S),**
 817 **to about 8‰ (10-12°S) and 12.5‰ (15°S). The red bar indicates the area of suboxic conditions in subsurface**
 818 **waters. The black rectangle marks the study area for downcore reconstruction (see also Fig.1). (b) Nutrient**
 819 **utilization for NO_3^- (%, dark grey area) and $\text{Si}(\text{OH})_4$ (%, dashed area). (c) MAR TN ($\text{g cm}^{-2} \text{ yr}^{-1}$) and MAR**
 820 **BSi ($\text{g cm}^{-2} \text{ yr}^{-1}$; for calculation see section 2.6) and nutrient supply (modified after Mollier-Vogel et al., 2012**
 821 **and Ehlert et al., 2012).**

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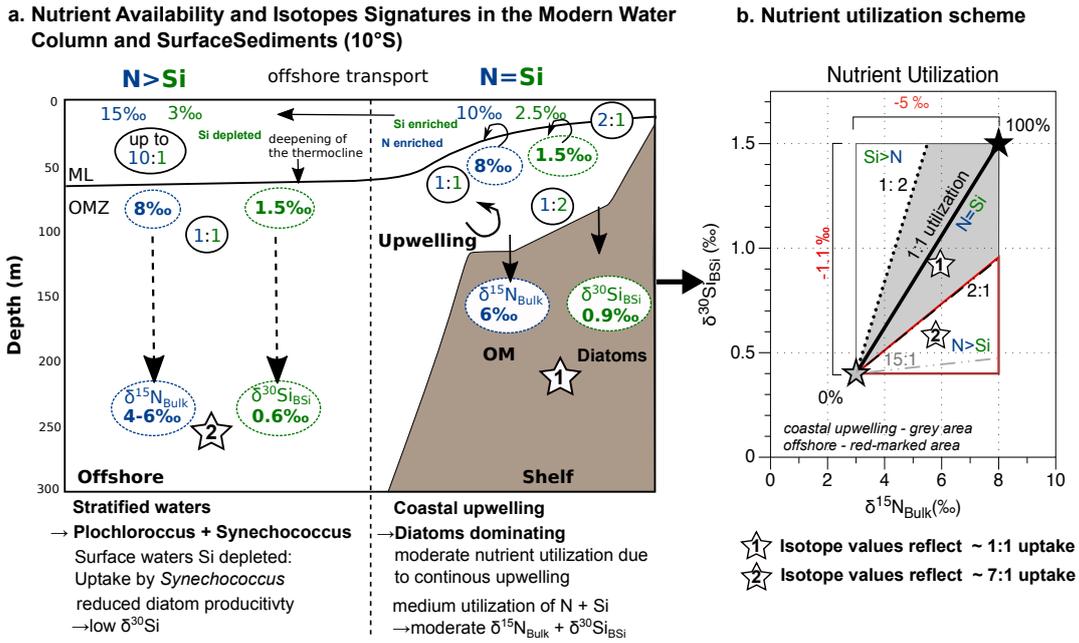
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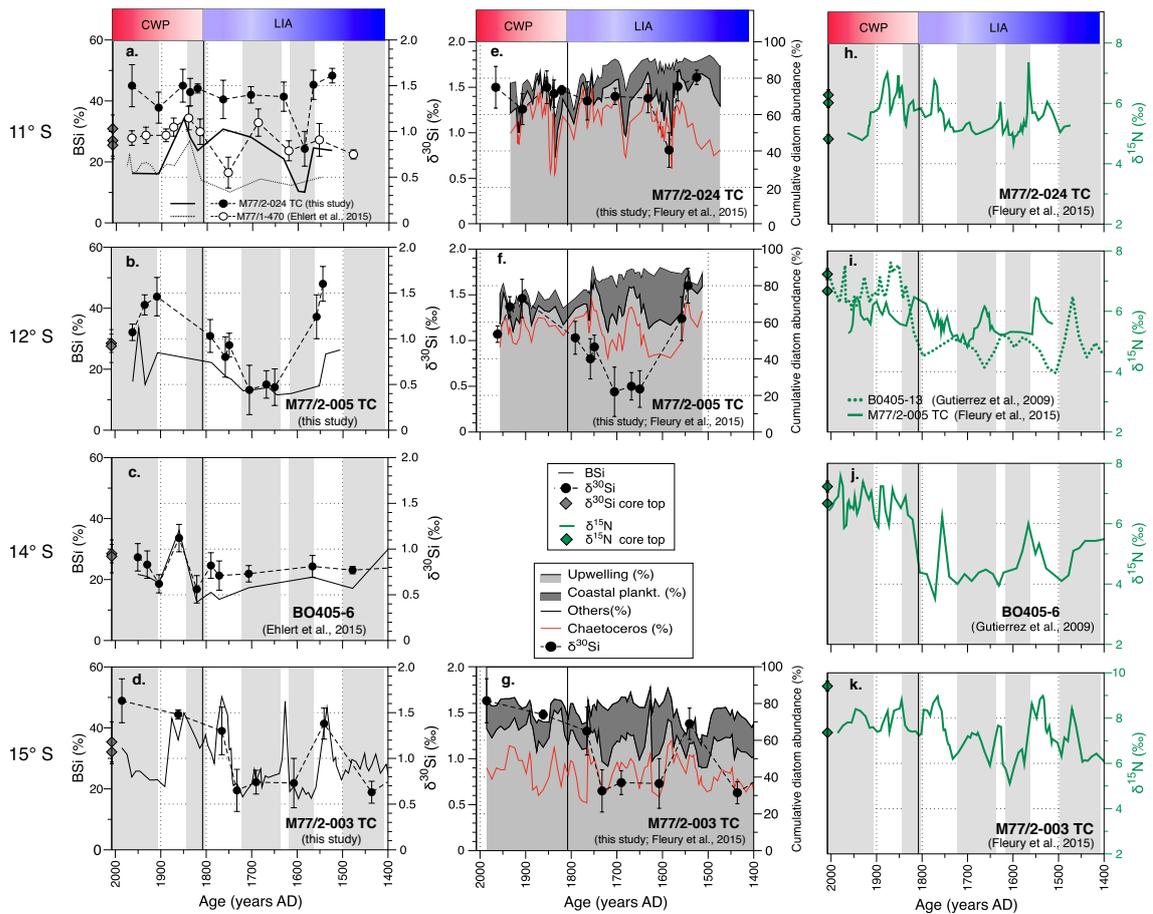
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831 **Figure 3: a. Simplified schematic figure of the 10°S transect off Peru indicating the concentrations of $Si(OH)_4$**
 832 **(green) and NO_3^- (blue; given as enriched or depleted) together with the $NO_3^-:Si(OH)_4$ ratios (N:Si). The**
 833 **stable isotope composition in the water column given as $\delta^{30}Si(OH)_4$ and $\delta^{15}NO_3^-$ and the $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{Bulk}$**
 834 **signatures in underlying sediments. Diatoms are dominant on the shelf, whereas non-siliceous organisms**
 835 **(Synechococcus, Plochlorococcus) dominate the offshore productivity (modified from Grasse et al., 2016);**
 836 **Schematic overview of nutrient utilization, the black star marks the source signature (or 100% utilization)**
 837 **for $\delta^{15}NO_3^-$ (8‰) and for $\delta^{30}Si(OH)_4$ (1.5‰) at the location, the grey star marks the theoretical isotopic**
 838 **compositions for ~0% utilization, the thick black solid line indicates the 1:1 utilization for N=Si, respectively.**
 839 **The $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{Bulk}$ signatures from the shelf (white star 1) reflect an N:S uptake close to 1:1 while**
 840 **offshore signatures (white star 2) indicate higher N over Si utilization (N>Si). The rectangle indicates the total**
 841 **range of possible isotopic values. The respective fractionation factors are given in red.**
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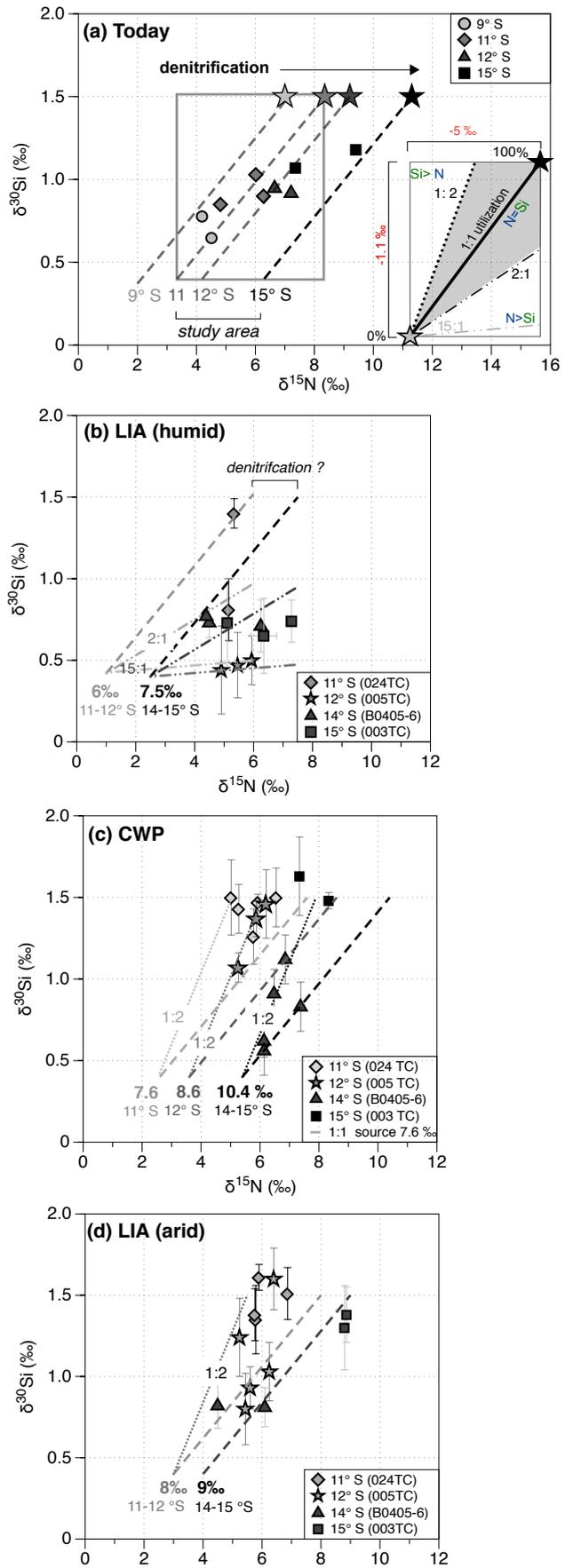
846 **Figure 4: Downcore records of BSi (wt%), $\delta^{30}\text{Si}_{\text{BSi}}$ (‰, 2 SD error bar of repeated sample measurements)**
 847 **records of cores: (a) M77/2-024-5TC and M77/1-470 (Ehlert et al., 2015) (b) M77/2-005-3TC (c) BO405-6**
 848 **(Ehlert et al., 2015; Gutiérrez et al., 2009) and (d) M77/2-003-2TC. The cumulative diatom assemblages are**
 849 **compared to $\delta^{30}\text{Si}$ for core e.) M77/2-024-5TC, f.) M77/2-005-3TC and g.) M77/2-003-2TC: Upwelling species**
 850 **- light gray; Coastal planktonic - gray; Other species - white; *Chaetoceros* sp. - red dashed line; $\delta^{30}\text{Si}_{\text{BSi}}$ -**
 851 **black dots; the black line indicates the transition between the LIA and the CWP. For comparison previously**
 852 **published $\delta^{15}\text{N}_{\text{bulk}}$ (‰) are shown for cores h.) M77/2-024-5TC (Fleury et al., 2015), i.) M77/2-005-3TC (Fleury**
 853 **et al., 2015) and BO405-13 (Gutiérrez et al., 2009), j.) BO405-6 (Gutiérrez et al., 2009) and k.) M77/2-003-2TC**
 854 **(Fleury et al., 2015). All records are sorted by latitude from top (11°S) to bottom (15°S). The time intervals**
 855 **for the CWP (red) and the LIA (blue) are highlighted in (a); the horizontal grey shading indicates humid**
 856 **periods (Fleury et al., 2015).**

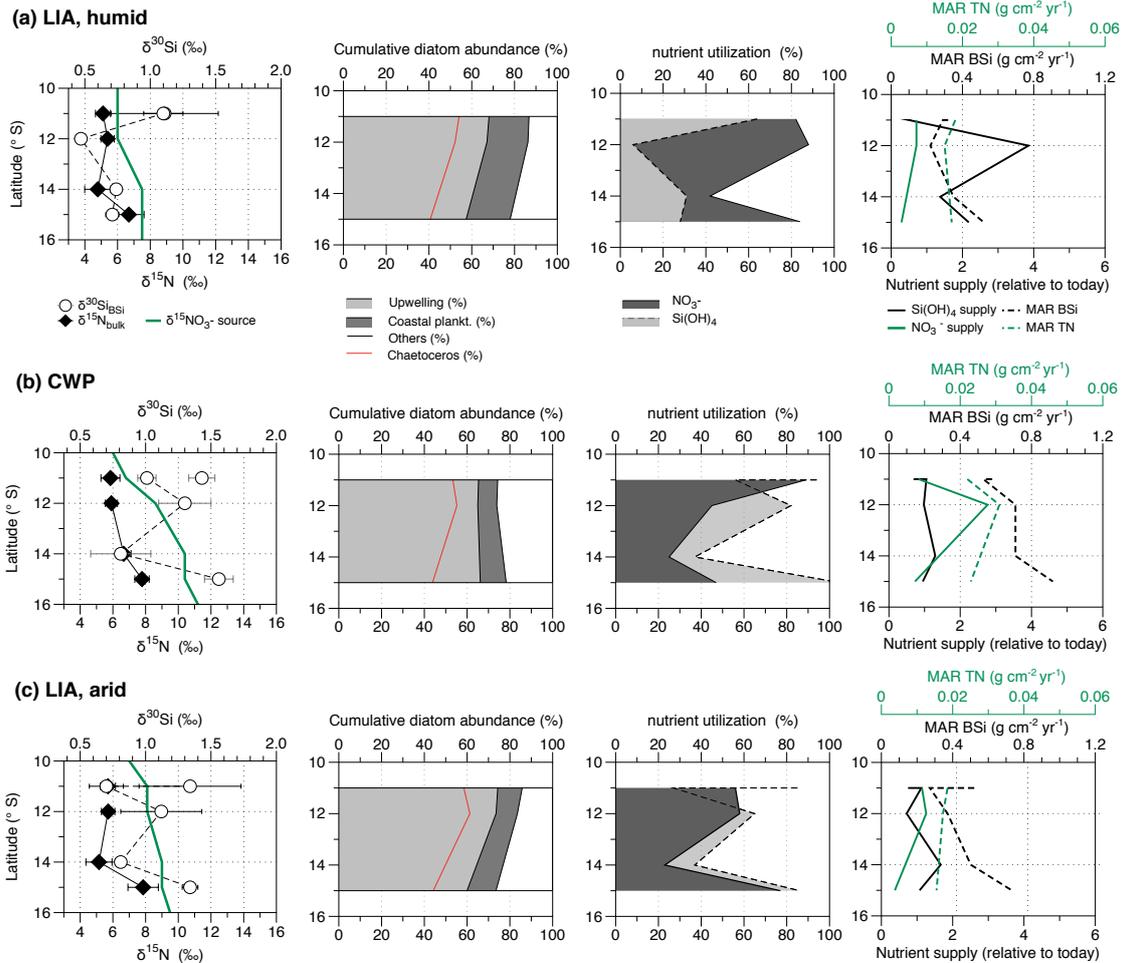
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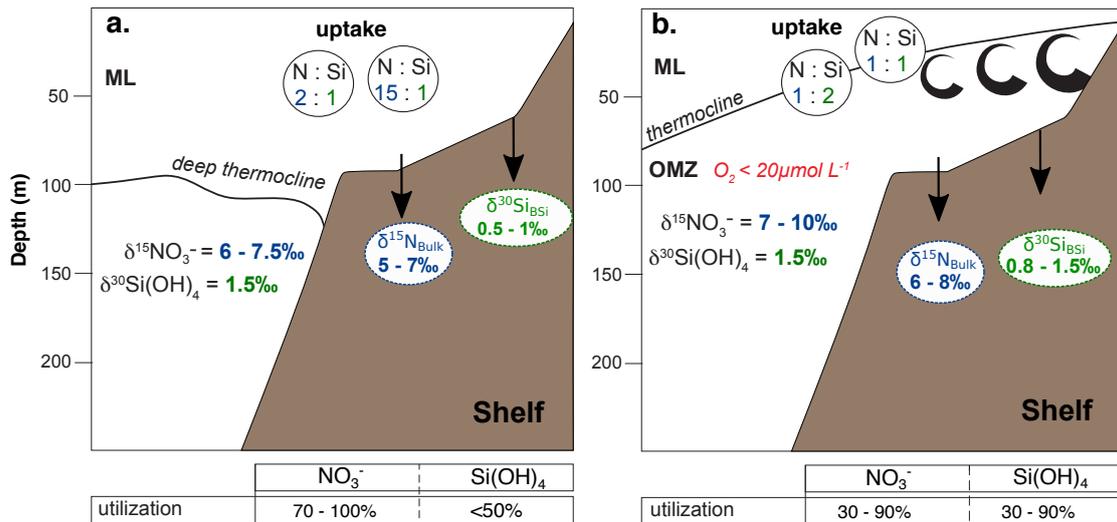
860 **Figure 5: (a) Direct comparison of $\delta^{15}\text{N}_{\text{bulk}}$**
 861 **versus $\delta^{30}\text{Si}_{\text{BSi}}$ for modern surface sediments**
 862 **(modified from Ehlert et al., 2015): The**
 863 **dashed lines indicate 1:1 utilization of**
 864 **different $\delta^{15}\text{NO}_3^-$ source values (7‰, 7.9‰,**
 865 **8.35‰ and 11.3‰) between 9°S and 15°S**
 866 **(based on Mollier-Vogel et al., 2012), the**
 867 **rectangle marks the respective range of**
 868 **isotope values that can be expected in**
 869 **sediment samples for nutrient utilization**
 870 **with source values of 1.5‰ ($\delta^{30}\text{Si}(\text{OH})_4$) and**
 871 **8.35‰ ($\delta^{15}\text{NO}_3^-$); (inset) Schematic overview**
 872 **of nutrient utilization associated with**
 873 **changes in the isotopic compositions of both**
 874 **$\delta^{15}\text{N}$ and $\delta^{30}\text{Si}$: the black star marks the**
 875 **source signature (or 100% utilization) for**
 876 **$\delta^{15}\text{N}$ and for $\delta^{30}\text{Si}$, the grey star marks the**
 877 **respective isotopic compositions for 0% utilization, the black dashed line indicates the**
 878 **1:1 utilization for $\text{NO}_3^-:\text{Si}(\text{OH})_4$, respectively.**
 879 **Ratios that plot above the utilization lines**
 880 **reflect $\text{Si}(\text{OH})_4$ limitation, as indicated by the**
 881 **dark grey and light grey dotted line**
 882 **representing ratios of 1:2, whereas data**
 883 **points below record stronger NO_3^- limitation,**
 884 **as indicated by the dark grey and light grey**
 885 **dashed lines representing ratios of 2:1 and**
 886 **15:1. The rectangle indicates the total range**
 887 **of possible isotopic values. (b-d) Downcore**
 888 **comparison of $\delta^{15}\text{N}_{\text{bulk}}$ and $\delta^{30}\text{Si}_{\text{BSi}}$ for cores**
 889 **024TC (diamonds), 005TC (grey stars),**
 890 **003TC (grey squares) and B0405-6 (grey**
 891 **triangles; Ehlert et al., 2015), for the CWP**
 892 **and the LIA. For the LIA the sample values**
 893 **are separated into arid (d) and humid (b)**
 894 **periods (b).**
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900 **Figure 6: Latitudinal comparison of (from left to right) mean $\delta^{15}\text{N}_{\text{bulk}}$ (‰, black diamonds) and $\delta^{30}\text{Si}_{\text{BSi}}$ (‰,**
 901 **white circles) and the calculated $\delta^{15}\text{NO}_3^-$ source values (green line), the mean cumulative diatom abundance**
 902 **(%; calculated from Fleury et al., 2015), the respective nutrient utilization of NO_3^- (grey, solid line) and**
 903 **$\text{Si}(\text{OH})_4$ (dashed area and line), and MAR TN ($\text{g cm}^{-2} \text{yr}^{-1}$) and MAR BSi ($\text{g cm}^{-2} \text{yr}^{-1}$) together with nutrient**
 904 **supply relative to today for (a) the humid phases of the LIA, (b) the CWP and (c) the arid phases of the LIA**
 905 **and . Please note that for $\delta^{15}\text{N}_{\text{bulk}}$ values the mean was calculated for all available values for each time period**
 906 **and not only for samples, for which also $\delta^{30}\text{Si}_{\text{BSi}}$ values are available. Error bars mark the 1 SD of the mean**
 907 **values.**



LIA (humid): El-Niño-like conditions, deep thermocline, low productivity
 non-siliceous phytoplankton
 no nutrient-rich upwelling
 suboxic subsurface waters → reduced N-loss

Today, CWP and LIA (arid): La-Niña-like conditions, strong upwelling, high productivity
 siliceous phytoplankton (diatoms)
 anoxic subsurface condition
 N-loss (denitrification + anammox)

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Figure 7: Schematic nutrient (Si(OH)₄ and NO₃⁻) cycle models for the Peruvian mixed layer (ML) and Oxygen Minimum Zone (OMZ) along the shelf area (0-200m water depth) during the last 600 years. The NO₃⁻:Si(OH)₄ (N:Si) indicates the ratio in which both nutrients are taken up during biological production in surface waters.