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interglacial  
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# Persistent millennial-scale link between Greenland climate and northern Pacific Oxygen Minimum Zone under interglacial conditions

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## Abstract

The intensity and/or extent of the northeastern Pacific Oxygen Minimum Zone (OMZ) varied in-phase with the Northern Hemisphere high latitude climate on millennial timescales during the last glacial period, indicating the presence of atmospheric and oceanic connections under glacial conditions. While millennial variability was observed for both the Greenland ice core and the northern Atlantic during the last interglacial period, the relationship with the northeastern Pacific OMZ has not yet been observed under warm interglacial conditions. Here we present a new geochemical dataset, spanning the past 120 kyr, for major components (terrigenous fraction, marine organic matter, biogenic opal, and carbonates) by X-ray fluorescence scanning alongside with biological productivity and redox sensitive trace element content (Mo, Ni, Cd) of sediment core MD02-2508 at 23° N, retrieved from the northern limit of the modern OMZ. We evidenced high biological productivity from opal based on Si/Ti, and from Cd/Al, and Ni/Al ratios during last interglacial period. Highly resolved opal reconstruction presents millennial variability corresponding to all the Dansgaard–Oeschger interstadial events over the last interglacial, while the Mo/Al ratio indicates reduced oxygenation during these intervals. Extremely high opal content during warm interstadials suggests high diatom productivity. Despite the different climatic and oceanic background between glacial and interglacial periods, rapid variability in the northeastern Pacific OMZ seems to be tightly related to Northern Hemisphere high latitude climate mainly via atmospheric processes.

## 1 Introduction

Oxygen Minimum Zones (OMZ) develop in areas where oxygen consumption by organic matter degradation in the water column and on the seafloor outmatches lateral/vertical advection/diffusion of dissolved oxygen. Thus, intermediate depth OMZ variations are mainly determined by (1) variations of the oxygen content in source in-

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intermediate water masses, (2) changes in rate of intermediate water formation and advection, and/or (3) oxygen consumption occurring during the flow of intermediate water masses toward the OMZ and within the OMZ itself (Karstensen et al., 2008; Paulmier and Ruiz-Pino, 2009; Stramma et al., 2010a). Oxygen consumption is related to the degradation of organic matter as it sinks through the water column and settles on the seafloor (Karstensen et al., 2008).

During the past decades, the scientific community has put considerable effort in understanding the past dynamics of the OMZ, owing to its potential role in the carbon cycle and greenhouse gas emission (Paulmier et al., 2008, 2011), or the global marine nitrogen cycle (Galbraith et al., 2004). The modern expansion of the OMZ, probably in relation to anthropogenic climate change (Stramma et al., 2008, 2010b), points out the importance of understanding the factors that influence OMZ dynamics in an abrupt climate change context, as it could behave as an internal feedback on the global climate (Altabet et al., 2002; Pichevin et al., 2007).

The variability of the mid-latitude north Pacific OMZ during the last glacial period has been extensively studied (Hendy and Pedersen, 2005; Dean, 2007; Hendy, 2010; Cartapanis et al., 2011, 2012). Most of these studies revealed a strong link between oxygen deficit in the northern Pacific and Northern Hemisphere high latitude climate on millennial timescales, with enhanced oxygen depletion and higher biological productivity during warm Dansgaard–Oeschger (DO) interstadial events, and enhanced oxygenation during Heinrich events (HE) of the last glacial period. Both biological productivity and oceanic ventilation are suspected to have influenced past OMZ variation (Hendy and Kennett, 2000; Hendy et al., 2004; Cartapanis et al., 2011, 2012).

Climate variability during the last interglacial (Marine Isotopic Stage = MIS 5) is particularly interesting because of climatic similarities with the Holocene. However, productivity and ventilation variations during MIS 5 have been poorly documented by now. Except for MIS5e, MIS5 is characterized by lower sea level than during full interglacial periods (e.g. Holocene and MIS5e), but higher sea level than during glacial (e.g. MIS2, 3 and 4) (Lambeck et al., 2002; Waelbroeck et al., 2002; Cutler et al., 2003; Hu et al.,

2010; Grant et al., 2012). This suggests the existence of a small but significant ice cap over Northern Hemisphere high latitude continents (Bonelli et al., 2009; Ganopolski et al., 2010). During MIS5, DO (Johnsen et al., 2001) and HE-like events (massive iceberg discharge in the north Atlantic) (McManus et al., 1994; Eynaud et al., 2000; Oppo et al., 2006) occurred together with rapid high amplitude sea level changes (Grant et al., 2012).

A few studies in eastern north Pacific suggested higher productivity (Ganeshram and Pedersen, 1998; Kienast et al., 2002) and lower oxygenation at intermediate depth (Nameroff et al., 2004) during MIS5 as compared to glacial periods (MIS2 to MIS4). However, the millennial scale variations of productivity and oxygenation in north Pacific OMZ over the last interglacial remain unknown because of scarce high-resolution records.

Siliceous organisms such as diatoms represents a significant proportion of the production in the Pacific, but the mechanisms responsible for spatial and temporal variations of diatoms productivity (e.g. wind driven upwelling, nutrient content of water masses, biological competition for nutrients use) remain controversial and are likely related to changes in atmospheric and oceanic circulation. While several studies displayed millennial and/or glacial/interglacial changes of the opal production at low latitude in the eastern Pacific (Ganeshram and Pedersen, 1998; Kienast et al., 2006; Dubois et al., 2010, 2011; Pichevin et al., 2010; Arellano-Torres et al., 2011; Romero et al., 2011a; Cartapanis et al., 2012), high temporal resolution opal records in eastern north Pacific are still limited.

Here we present a new geochemical dataset spanning the last 120kyr from the northern edge of the modern North Pacific OMZ. High-resolution X-ray fluorescence (XRF) measurements for major sediment components (marine organic carbon and opal), were performed on MD02-2508 core (MD08, northeastern coastal Pacific), in order to monitor the past productivity variation. Trace element response to productivity and bottom water oxygenation were measured by ICP-MS in an attempt to reconstruct past variability of the OMZ and to determine the factors driving its variations. High

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sedimentation rate at site MD08 during MIS5 (around  $35 \text{ cm kyr}^{-1}$ ) provides a unique opportunity to reconstruct the millennial scale variability of productivity and ventilation during the last interglacial period, and the mechanisms involved in linking high latitude climate variations to lower latitude climate, oceanic conditions, and biogeochemical cycles.

## 2 Materials and method

Core MD08 ( $23^{\circ} 27.91' \text{ N}$ ,  $111^{\circ} 35.74' \text{ W}$ , 606 m water depth, Fig. 1 was retrieved from the Baja California margin by the R/V *Marion Dufresne* during the coring campaign IM-AGES MD126-MONA. Detailed analytical procedures are shown in the previous study (Cartapanis et al., 2011). In order to trace the past OMZ dynamics, we measured Br and Si/Ti, representative of the marine organic matter (Mayer et al., 2007) and opal content respectively, and Ca and Ti, representative of the carbonates and the terrigenous sediment fractions respectively. We used XRF core scanner ITRAX (Cox Analytical Systems) with a Mo X-ray source and a Cr X-ray source at 30 kV and 45 mA, and at 35 kV and 35 mA respectively, with a counting time of 15 s. XRF measurement resolution was increased in the presence of lamination (from 0.5 cm to  $200 \mu\text{m}$ ) and is equivalent to 2 yr on average. Discrete bulk sediment samples were dissolved by acid digestion and elemental concentrations (Cd, Mo, Ni, Ti, Ca, and Al) were analyzed by ICP-MS (Agilent 7500ce). Trace elements contents (Cd, Mo, Ni) are normalized against Al to estimate authigenic enrichment. Temporal resolution of these measurements is better than 500 yr. While Cd and Ni are closely associated with biogenic sinking particles, Mo accumulation in the sediment is instead associated with redox condition at bottom water/sediment interface (Nameroff et al., 2002; Tribovillard et al., 2006; Cartapanis et al., 2011). We thus use Cd/Al and Ni/Al as productivity indicators, and Mo/Al as an oxygenation indicator. The terrigenous fraction of the sediment was calculated using Ti content in the mean Upper Continental Crust (UPC,  $4100 \mu\text{g g}^{-1}$ , McLennan, 2001). Total organic carbon (TOC) was determined using a FISONs NA 1500 elemental an-

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alyzer after carbonates were removed with 1M HCl. All the elemental analyses and organic carbon determination were carried out at CEREGE (Aix en Provence, France).

Samples for the analysis of opal were freeze-dried and ground in an agate mortar. Opal content was determined by the sequential leaching technique of DeMaster (1981) and by molybdate-blue spectrophotometry, with further modifications by Müller and Schneider (1993). Opal measurements were performed at MARUM (Bremen, Germany).

The age model of the core is based on previously published studies. Given a known relationship between sediment physical property variation and high latitude climate variability at southern Baja California margin (Ortiz et al., 2004; Dean et al., 2006; Dean, 2007; Marchitto et al., 2007), we used a visual correlation of wet bulk density obtained from the GEOTEK logger and lightness obtained by spectrophotometry (Beaufort et al., 2002) to the NGRIP isotopic oxygen record (Johnsen et al., 2001) for the past 70 kyr (see details in Leduc, 2007; Cartapanis et al., 2011 and in Table 1). One additional tie point was added for the Blake magnetic excursion (115–122 kyr) identified in MD08 core by Blanchet et al., (2007) (see crosses at the top of Fig. 2 and Table 1).

### 3 Study area

The intertropical Pacific hosts the most extended modern OMZ (Paulmier and Ruiz-Pino, 2009, see also Fig. 1). Oxygen depletion is even more pronounced in the northern Pacific, because of restrained North Pacific Intermediate Water (NPIW) formation in the Okhotsk sea (Talley, 1991; Shcherbina et al., 2003) as compared to the southern Pacific where Antarctic Intermediate Water (AAIW) ventilates the intermediate depth more efficiently. MD08 core was retrieved off the Baja California margin, at the southern limit of the NPIW in the eastern Pacific (Fig. 1, see details in Cartapanis et al., 2011). Further south, intermediate depths are occupied by the Equatorial Pacific Intermediate Waters, mainly derived from AAIW and Pacific Deep Waters (Bostock et al., 2010). At the surface, the California Current (CC) that transports relatively fresh and cold

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Subarctic Water (SW) along eastern Pacific coast is diverted westward and slowly sinks in the water column around 25° N, slightly north of MD08 core (Auaud et al., 2011).

Presently, the productivity of diatoms and small phytoplankton (as defined by Moore et al., 2004, and which include coccolithophoridae), is thought to be limited by nitrates content in surface waters (Moore et al., 2004). Wind driven upwelling activity related to atmospheric circulation is an important driver of the modern productivity along north eastern Pacific shores (Lynn and Simpson, 1987; Thomas et al., 2001; Zaytsev et al., 2003; Pennington et al., 2006). During summer, the North Pacific high-pressure cell strengthens and the continental low deepens, resulting in a high east-west pressure gradient inducing equatorward winds. Modern productivity off northeastern Pacific shores is consequently higher during summer months when alongshore southward winds are enhanced (Fig. 1, Thomas et al., 2001). Despite the influence of local bottom topography and angular orientation of the coastline, upwelling is stronger during early summer at MD08 core (Zaytsev et al., 2003; Cartapanis et al., 2011). Upwelled waters originate from up to 300 m depth along the California coast (van Geen and Husby, 1996), at the mixing zone between SW and NPIW. Thus, NPIW nutrient inventory related to tidal mixing at high northern latitude in the Pacific (Sarmiento et al., 2004), might influence surface productivity. High local productivity is thus associated with warm condition on seasonal timescales when the Intertropical Convergence Zone (ITCZ) is situated on its northern position.

## 4 Results

Highly resolved XRF Si/Ti (log-scale) is well correlated ( $R^2 = 0.93$ ) to opal content obtained by chemical leaching of bulk sediments (Fig. 2). Br is contained in marine organic matter, but also in pore water (Ziegler et al., 2008). Since pore water content in opal-rich sediment is strongly affected by opal concentration, we used Br/Cl ratio as indicator of marine organic matter to correct pore water contribution using Cl (Croudace et al., 2006). Log Br/Cl is well correlated ( $R^2 = 0.68$ ) to TOC content (Fig. 2). The MD08

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sediment column is divided in three different units (Fig. 2). The first unit (Unit I) that corresponds to the Holocene consists of laminated high TOC ( $\approx 13\%$ ), relatively low carbonates ( $\approx 20\%$ ) and terrigenous compounds ( $\approx 45\%$ ) sapropelic mud (Fig. 2). The second unit (Unit II) was deposited during MIS 2, 3 and 4, and is composed of light homogenous calcareous clay (carbonates  $\approx 35\%$ , terrigenous  $\approx 60\%$ , and TOC  $\approx 7\%$ ). Interbeds of dark laminated sapropelic mud similar to Unit I (Fig. 2) were deposited during interstadial events (Cartapanis et al., 2011). Opal content within Units I and II is low (0 to 10%) but is higher within laminated intervals (up to 20%, Fig. 2). The third unit (Unit III) corresponds to MIS5 and mainly consists of laminated sapropelic diatom ooze (Fig. 3) with some homogenous layers composed of calcareous clays, similar to Unit II non-laminated sediment (Fig. 2). The millimetric to centimetric laminations in the Unit III are composed of light color biogenic remains, and dark colored organic matter mixed with terrigenous sediment (Fig. 3). Opal content rises up to 40% in MIS5 laminations and reaches over 80% in particular laminations (Fig. 2). Micro sedimentologic analyses suggest that high opal content laminae in Unit III were deposited abruptly, and could correspond to algal blooms during upwelling events or in the frontal zone between water masses of different densities (Murdmaa et al., 2010).

Trace element (Cd, Mo, Ni) to Al ratios show extremely high values relative to the so-called UPC values (McLennan, 2001, Table 2): the mean Ni/Al ratio is six times higher than in UPC, seventy times higher for Mo/Al, and more than three hundreds times higher for Cd/Al (Table 2). Even the lowest element to Al ratios, which occur mainly in Unit II, are higher than the corresponding value in UPC. The results indicate that significant part of these elements are not related to the input of terrigenous minerals, but rather to in-situ biogenic and authigenic enrichments. The highest values for elemental ratios and enrichments in MD08 core occur within laminated intervals, and are even higher within sedimentary Unit III as compared to Unit I (Fig. 2).

## 5 Discussion

A previous study of the MD08 core revealed the strong link between productivity in surface waters and OMZ variability during the last glacial period, in relation to changes in atmospheric circulation in Baja California driven by Northern Hemisphere high latitude climate variability (Cartapanis et al., 2011). High productivity may have led to reduced bottom water oxygenation at site MD08 during interstadials. Changes in the wind patterns were proposed as mechanisms for changes in the strength, duration, and frequency of upwelling events, leading to higher productivity during interstadials events of MIS3. Higher bottom water oxygenation during Heinrich events was suggested to be produced by changes in oxygen advection by NPIW, formed in the northern Pacific. In light of the new datasets on MD08 core, that now cover the past 120 kyr, we will focus our discussion on the oceanic and climatic millennial scale variability of the last interglacial period (MIS5).

### 5.1 Millennial-scale productivity variations during MIS5

The high-resolution records of opal, terrigenous, and carbonate fractions in the MD08 core display striking similarities with the NGRIP  $\delta^{18}\text{O}$  record on millennial timescales across the last interglacial period, despite limited age constraint earlier than 60 kyr (Fig. 2). The MD08 record shows higher opal content within laminated intervals that likely correspond to DO interstades 25 to 19 (Figs. 2 and 4). The opal content is extremely high during interstadials 25 to 21 (up to more than 40%), while TOC remains rather stable (around 8%, Fig. 2). The opposite pattern is observed for DO interstades 20 and 19 (higher TOC and lower opal content). This difference probably reflects dilution of TOC by opal from interstades 25 to 21. Carbonates and terrigenous fractions show low values during Greenland interstades 25 to 19, most likely due to dilution by opal and TOC as well as carbonates dissolution. Both Cd/Al and Ni/Al, closely related to biogenic compounds (Nameroff et al., 2002), show increased values within laminated intervals. In summary, marine organic matter, opal, Cd/Al, and Ni/Al variations

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suggest higher productivity during the intervals corresponding to Greenland warm DO interstadials of MIS5 (Fig. 4). This observation is consistent with the occurrence of upwelling-related diatom blooms in the laminated intervals of MD08 (Murdmaa et al., 2010).

The good match between productivity and oxygenations at MD08 with Greenland temperature records (Figs. 2 and 3) suggest strong connections between Northern Hemisphere high latitude climate and northeastern Pacific OMZ on the millennial-scale during MIS5 via atmospheric and/or oceanic pathways. In the following section, we discuss possible processes responsible for high opal content during MIS5 interstadials compared to Holocene and MIS3 interstadials.

## 5.2 Atmospheric circulation impact on productivity

Despite different climatic settings, cold Northern Hemisphere high latitude intervals (MIS2 and MIS4 as well as stadials of MIS3 and MIS5) were generally less productive than warmer interglacial and DO interstadial periods at site MD08. Considering that modern productivity over site MD08 is driven by wind, changes in local wind fields may have possibly influenced productivity during MIS5 (Fig. 4). During cold events simulated by fresh water perturbation under pre-industrial conditions, low temperatures in the northern Pacific enhance the Aleutian Low (Mikolajewicz et al., 1997; Okumura et al., 2009). Cold temperatures over the North American continent favor the establishment of anticyclonic circulation (Kutzbach and Wright Jr, 1985; Romanova et al., 2006). These mechanisms could have reduced the southward wind intensity over the studied site during MIS5 stadials. Substantial millennial-scale changes in the volume, surface extent, and height of the north American ice sheet suggested by high amplitude sea level changes (Fig. 5) (Lambeck and Chappell, 2001; Siddall et al., 2007; Grant et al., 2012; Medina-Elizalde, 2013), could have been responsible for variations in atmospheric circulation (Romanova et al., 2006).

Continental records indicate millennial-scale variability in atmospheric circulation over the North American continent during MIS5. A multiproxy study in Lake Owens

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(southeastern California) suggests reduced rainfall and/or warmer conditions during interstadial events of MIS5 (e.g.  $\delta^{18}\text{O}$  of Owens Lake sediment, Figs. 1 and 3, Li et al., 2004), consistent with variations of isotopic composition of Goshute cave stalagmite (NE Nevada, Denniston et al., 2007, Figs. 1 and 3). Previous studies in the southwestern United States over the last glacial interpreted millennial-scale speleothem  $\delta^{18}\text{O}$  variations to reflect latitudinal migrations of storm tracks and rainfall associated to the Polar Jet Stream and the ITCZ, implying atmospheric circulation changes, at least, in the Northern Hemisphere (Asmerom et al., 2010; Wagner et al., 2010). During warm interstadials, both polar jet and Northern Hemisphere summer ITCZ were proposed to have shifted northward (Asmerom et al., 2010; Wagner et al., 2010; Wang et al., 2012). By affecting upwelling intensity, duration or frequency, this atmospheric circulation change may have triggered productivity variability at MD08 (Cartapanis et al., 2011), as well as in the Panama Basin (Romero et al., 2011a; Cartapanis et al., 2012). Based on the fact that millennial-scale ITCZ latitudinal shifts existed during MIS5a (Peterson et al., 2000), we infer the similar processes have operated over the whole MIS5.

### 5.3 Oceanic circulation impact on oxygenation and productivity

High Mo/Al during MIS5 interstadials suggest reduced oxygenation of bottom water (Figs. 2 and 5). The good correlation between Mn and terrigenous element contents ( $R^2 = 0.97$  between Mn and Ti) indicates that Mn oxides were dissolved in the sediment, and that bottom waters had never been oxic, even during stadial events (not shown). Changes in oceanic circulation could have also impacted the OMZ dynamic by changing ventilation. Oceanic circulation variations could have also modified the nutrient content of the upwelled water over site MD08, affecting biological productivity and oxygen consumption in the OMZ. Modeling studies indicate that reduction of North Atlantic Deep Water formation during Heinrich events and associated global oceanic circulation modifications could have increased the NPIW formation (Saenko et al., 2004; Timmermann et al., 2005; Schmittner et al., 2007; Okazaki et al., 2010), which was confirmed by observational studies for the last glacial period (Okazaki et al.,

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2010; Cartapanis et al., 2011; Rella et al., 2012). Considering that Heinrich-like events probably occurred during the MIS5 (Fig. 5) (McManus et al., 1994; Eynaud et al., 2000; Oppo et al., 2006), changes in the ventilation at Baja California cannot be ruled out.

5 Silicic acid and nitrate inventory in subsurface waters of the northern Pacific is partly related to the upward advection of nutrient-rich Pacific Deep Water toward NPIW at high northern latitudes (Sarmiento et al., 2004). The enhanced NPIW formation during HE and stadials related to oceanic circulation changes (Saenko et al., 2004; Timmermann et al., 2005; Schmittner et al., 2007; Okazaki et al., 2010), possibly reduced the upward advection of deep, old, oxygen poor and nutrient rich water toward NPIW (Sarmiento et al., 2004; Rella et al., 2012). Considering that NPIW is probably the source for upwelling water in the northeastern Pacific (van Geen and Husby, 1996), stronger NPIW production could have lowered the productivity at site MD08, reduced oxygen consumption in NPIW, and enhanced oxygen advection toward the OMZ. This scenario would explain the correlation between productivity and bottom water oxygenation proxies (Fig. 5) along the NE Pacific margin as both oxygen advection and productivity (thus oxygen consumption) would have been related to NPIW formation. Alternatively, atmospheric connections (Harada et al., 2006; Clement and Peterson, 2008) altered surface hydrological conditions in NPIW formation zones (such as Okhotsk and Bering Seas), which affected the NPIW formation (Sarmiento et al., 2004; Rella et al., 2012), and thus the ventilation and/or the nutrient availability at MD08 core site during stadials/interstadials and Heinrich events.

15 A fundamental difference in oceanic circulation conditions between the MIS5 and the last glacial period is related to sea level, which affected the communication between the Arctic Ocean and the northern Pacific through the Bering Strait (De Boer and Nof, 2004). Modeling studies indicate that the impact of Heinrich-like events on oceanic circulation over both northern Atlantic and Pacific oceans might have been reduced during interglacial periods (De Boer and Nof, 2004; Hu et al., 2012). During sea level high stands, any increase of the freshwater inputs in the northern Atlantic was partially diverted toward the northern Pacific through the still open Bering Strait, thus weak-

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ening the impact of HE on the North Atlantic Deep Water (De Boer and Nof, 2004; Hu et al., 2012). At the same time, freshwater influx into the northern Pacific probably reduced NPIW formation. Moreover, global reorganization of oceanic circulation, that favored NPIW formation during glacial age HEs (Saenko et al., 2004; Timmermann et al., 2005), would have been weakened during MIS5. Consequently, Heinrich-like events during MIS5 should have had reduced impact on the NE Pacific OMZ as compared to glacial periods. In spite of this, no obvious differences in millennial-scale response of redox sensitive trace elements for glacial and interglacial periods in our records are seen (Fig. 2). This suggests that productivity is the main factor controlling millennial-scale variations of the bottom water oxygenation at core MD08 site throughout the MIS5. This scenario, however, depends on the sea level changes during MIS5 stadial/Heinrich-like events. The present depth of the Bering Strait is around 50 m, close to the reconstructed (Fig. 5) and simulated sea level during MIS5 (Lambeck et al., 2002; Waelbroeck et al., 2002; Cutler et al., 2003; Hu et al., 2010; Grant et al., 2012). This suggests that Arctic/Pacific water exchanges were probably limited like the present state. In order to address the Bering Strait influence on the past North Pacific climate and oceanic circulation, and furthermore, the global climate and oceanic circulation variation on both glacial/interglacial and millennial timescales (Okumura et al., 2009; Hu et al., 2012), it will be necessary to develop a well dated record of the opening and closure of the Bering Strait.

#### 5.4 High biogenic opal content in MIS5 sediments

One of the most striking features of the 120 kyr MD08 record is the extraordinary high opal content during the MIS5 (Fig. 2). The sediment deposited during MIS5 interstadial events has been identified as diatom-rich laminations (Murdmaa et al., 2010). The formation of this type of sediment structure may occur during major diatom blooms within active frontal zones, which favor the aggregation of diatoms and the rapid sinking of frustules downward (Kemp et al., 1996; Shimada et al., 2008; Romero et al., 2011b). Changes in the seasonal and latitudinal repartition of the insolation during MIS5 as

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compared to the Holocene could be responsible for changes in the atmospheric circulation (Montero-Serrano et al., 2011; Herold et al., 2012), wind driven upwelling, and productivity. However, high opal production extends at least over 40 kyr (120–80 kyr), during periods of different changes in the intensity and the latitudinal repartition of insolation. This suggests that insolation variation was not likely responsible for the buildup of mat deposits in Baja California.

Since site MD08 is located south of the modern limit of Subarctic Water transported by the California Current, the southward extension of the latter toward site MD08 (ca. 23° N) might have contributed to the build-up of diatom-rich laminations during MIS5. Opal content at the nearby site NH15P (ca. 22° N, 106° W, 420 m water depth, Fig. 1, Ganeshram and Pedersen, 1998) shows similar variability in opal content with increased values during interglacial periods. It is worth of noting that there is no obvious difference between Holocene and MIS5 opal content at site NH15P, which is consistent with the hypothesis of the southern limit of California Current was situated above MD08 during MIS5 whereas site NH15P was beyond of the influence of California Current for both MIS5 and Holocene.

Despite the fact that nitrate availability was thought to be the limiting factor for diatom production in surface waters overlying MD08 (Moore et al., 2004), shipboard seawater incubation experiments demonstrated that diatom production within upwelling zones along California margins was rather limited by iron (Hutchins and Bruland, 1998; Firme et al., 2003; Moore et al., 2013). Intense productivity could have led to total Fe utilization during upwelling events thus to transient Fe limitation at the end of an upwelling event (Hutchins and Bruland, 1998; Firme et al., 2003). Iron limitation can lead to reduced cellular organic matter production and increased silicification (high cellular Si : C and Si/N ratio) of diatoms (Baines et al., 2010, 2011; Brzezinski et al., 2011), high Si : C ratio in sinking biogenic particles, high opal flux (Hutchins and Bruland, 1998; Firme et al., 2003; Pichevin et al., 2012), and better frustule preservation in sediments. This scenario is consistent with the unvarying TOC contents in MD08 core across stadial/interstadials DO intervals of MIS5 (Fig. 2), and high biogenic Si to C ratio (Si bio/C,

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Fig. 5). Moreover, terrigenous element content during MIS5 is low in MD08 core, possibly because of reduced aeolian and fluvial inputs, suggesting reduced iron inputs to the surface waters. Dissolved Fe in upwelling areas also depends on interactions between upwelled waters and underlying shelf sediments (Elrod et al., 2004; Bruland et al., 2005), such as reduced Fe content in the sediment could have further enhanced Fe depletion in upwelled waters.

As suggested by (Romero et al., 2011b), change in nutrient availability and supply in the photic zone might have affected the buildup of diatoms mats deposits. In this scenario, changes in the intensity of processes described in Sect. 5.2 (wind driven upwelling) and Sect. 5.3 (oceanic circulation impact on nutrient availability) between Holocene and MIS5 could be responsible for higher diatom productivity during MIS5.

Regardless of the mechanism responsible (California Current position, nutrient inventory at subsurface or nutrient supply to the photic zone), we suggest that the climatic/oceanic setting might have led to high opal production during MIS5. Global ice volume (Lambeck et al., 2002; Waelbroeck et al., 2002; Cutler et al., 2003; Hu et al., 2010; Grant et al., 2012) suggests the existence of a small ice sheet over the north American continent during MIS5d to MIS5a (Bonelli et al., 2009; Ganopolski et al., 2010). Leaving aside millennial-scale variability, the presence of this ice sheet (absent during the Holocene and MIS5e) could have been responsible for high MIS5 opal content in MD08 as compared to Holocene, by either modifying local wind stress, California Current extension, or nutrient content of upwelling waters. In order to determine whether these specific features (higher opal during MIS5 than during Holocene) reflect regional or global processes rather than a local non-linear response to climatic variations, more records in upwelling zones of northeastern Pacific for the MIS5 will be required.

## 6 Conclusions

We studied core MD02-2508, retrieved off the Baja California margin, at present northern limit of the northeastern Pacific Oxygen Minimum Zone (OMZ), using high resolution XRF measurements (Si/Ti as a biogenic opal indicator, Ca as a biogenic carbonate indicator, Br as a marine organic carbon indicator, and Ti as a terrigenous fraction indicator) and ICP-MS trace elements measurements (Mo, Ni, Cd), for the last interglacial period (MIS5). The data allowed us to better constrain the millennial scale variability of past biological productivity and oxygenation at the core site over the studied period.

Opal, Ni/Al, and Cd/Al increased during the DO interstadial events identified in Greenland ice cores over the MIS5, strongly suggesting an increase in biological productivity. A high Mo/Al ratio within interstadials events indicates that the OMZ strengthened during these intervals.

Despite differences in the climatic and oceanic conditions, productivity and oxygenation during MIS5 displayed millennial-scale variability in relation to high northern latitude climates that are comparable to those over the last glacial period. Reduced communication between the Pacific and Arctic Ocean during MIS5 because of high sea level does not seem to have strongly modified the productivity and bottom water ventilation sensitivity. This suggests that atmospheric teleconnection was the major link between the mid-latitude productivity and ventilation variations, and the high latitude climate. Changes in atmospheric circulation, such as latitudinal shift of the polar jet stream, the storm track, and the ITCZ during DO-H events of the past 120 kyr probably affected wind driven upwelling and biological productivity.

Oxygenation variations at the core site were more likely related to changes in the biological productivity associated to atmospheric circulation changes, but also possibly to modifications of North Pacific Intermediate Water production because of atmospheric changes at Northern Hemisphere high latitudes in the Pacific, that affected oxygen inputs and nutrient availability in subsurface waters.

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**Table 1.** Tie points (corrected depth in cm, age in yr BP), method and references used to build the age model of MD02-2508 core in this study.

Corrected depth (cm)	Age (yr BP)	Method	Reference
0	0	NGRIP visual correlation	Cartapanis et al. (2011)
500	11 450	NGRIP visual correlation	Cartapanis et al. (2011)
592	14 550	NGRIP visual correlation	Cartapanis et al. (2011)
892	28 500	NGRIP visual correlation	Cartapanis et al. (2011)
980	33 500	NGRIP visual correlation	Cartapanis et al. (2011)
1014	35 300	NGRIP visual correlation	Cartapanis et al. (2011)
1082	38 250	NGRIP visual correlation	Cartapanis et al. (2011)
1168	41 700	NGRIP visual correlation	Cartapanis et al. (2011)
1218	43 600	NGRIP visual correlation	Cartapanis et al. (2011)
1306	47 300	NGRIP visual correlation	Cartapanis et al. (2011)
1514	54 950	NGRIP visual correlation	Cartapanis et al. (2011)
1656	59 100	NGRIP visual correlation	Cartapanis et al. (2011)
3689	117 000	Blake magnetic excursion	Blanchet et al. (2007)

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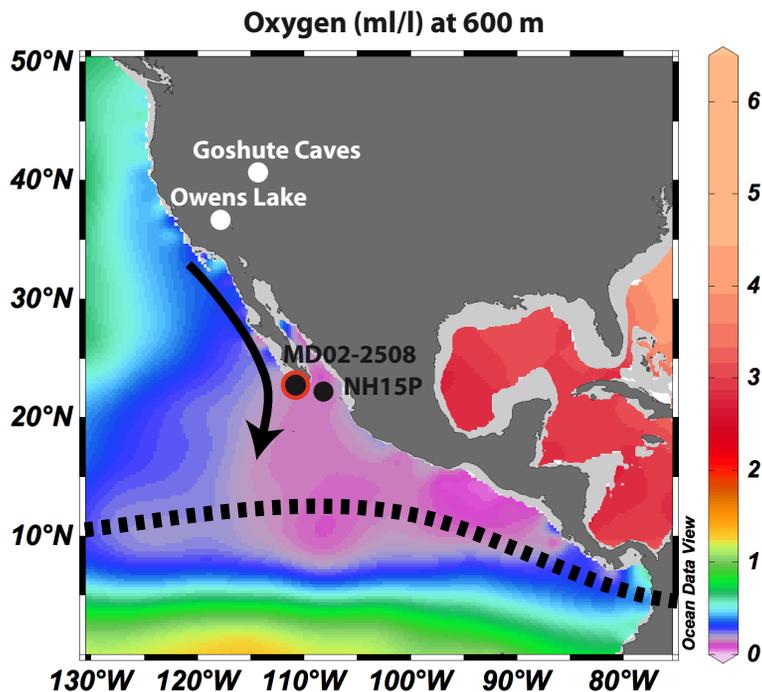
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**Table 2.** Minimal, maximal, and mean values for Al content ( $\mu\text{g g}^{-1}$ ), Cd/Al, Mo/Al, and Ni/Al in MD08 core. Mean values in Upper Continental Crust (McLennan, 2001) and mean enrichment factors ( $(\text{Mean Element/Al})_{\text{MD08}}/(\text{Element/Al})_{\text{UPC}}$ ) are displayed at the bottom of the table.

	Al ( $\mu\text{g g}^{-1}$ )	Cd/Al ( $\text{g g}^{-1}$ )	Mo/Al ( $\text{g g}^{-1}$ )	Ni/Al ( $\text{g g}^{-1}$ )
Min	3200	$2.77 \times 10^{-5}$	$1.32 \times 10^{-4}$	$1.38 \times 10^{-3}$
Max	51 813	$4.21 \times 10^{-3}$	$2.00 \times 10^{-2}$	$8.49 \times 10^{-3}$
Mean	32 343	$3.97 \times 10^{-4}$	$1.30 \times 10^{-3}$	$3.41 \times 10^{-3}$
UPC	80 400	$1.22 \times 10^{-6}$	$1.87 \times 10^{-5}$	$5.47 \times 10^{-4}$
Enrichment Factor		326	70	6

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**Fig. 1.** Dissolved oxygen content at 600 m in northeastern Pacific (World Ocean Atlas 09, Garcia et al., 2010) and positions of the records discussed in the text. Cores MD02-2508 (this study); NH15P (Ganeshram and Pedersen, 1998; Nameroff et al., 2004); Goshute Cave (Denniston et al., 2007); Owens Lake (Li et al., 2004). Black arrow indicates dominant winds during upwelling season and black dotted line represents ITCZ position during boreal summer. Figure 1 was generated using the Ocean Data View software <http://odv.awi.de>.

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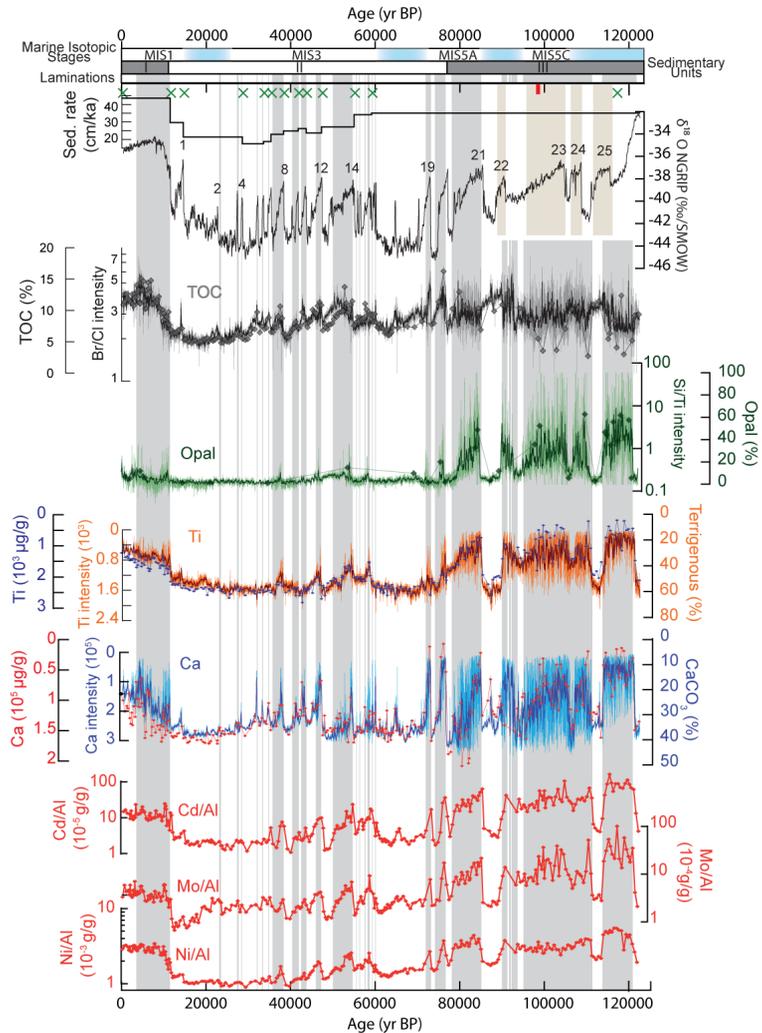
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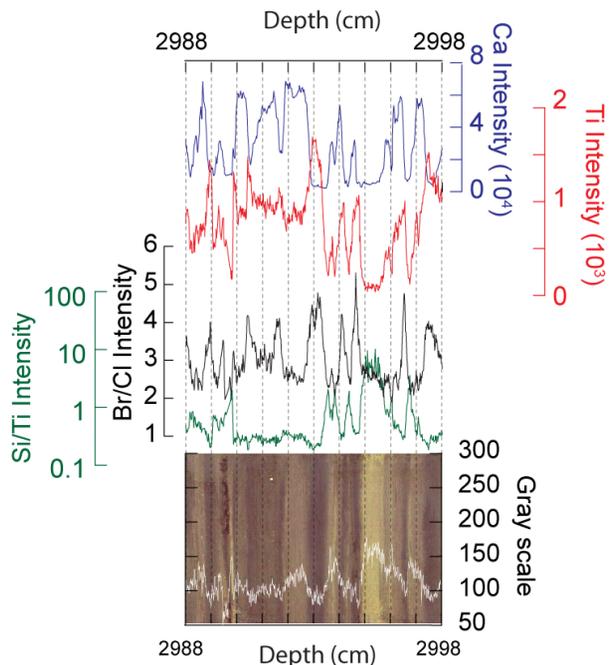
**Fig. 2.** The sedimentation rate in MD08 core; the isotopic composition of NGRIP ice core ( $\delta^{18}\text{O}\text{‰}/\text{SMOW}$ ) (NGRIP Members, 2004); the Br/Cl based marine organic matter high resolution record for MD02-2508 core calibrated using TOC measurements on the same core (the TOC data were first reported by Blanchet et al., (2007), and 40 additional TOC measurements were added from 120 to 60 kyr). Si/Ti record calibrated using opal measurements. Ca measurements (XRF scan and ICP-MS), converted into carbonate content considering that all the Ca belongs to the carbonate phase. Ti XRF and ICP-MS records converted into terrigenous matter content calculated using mean Ti content in the upper continental crust (McLennan, 2001). Note that Ca and Ti scales are reversed. Cd/Al, Mo/Al, and Ni/Al measured using ICP-MS on log scale. Green crosses at the top of the figure indicate tie points used to build the age model. Marine isotopic stages and sedimentary units as described in part 3 are indicated. Grey vertical bars highlight the laminated layers. Red tick at the top of the figure indicates the position of the sample displayed in Fig. 3.

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**Fig. 3.** The XRF intensities for Ca, Ti, Br/Cl, and Si/Ti (spatial resolution of 200  $\mu\text{m}$ ) of a 10 cm long sample of MD02-2508, representing roughly 300 yr of sediment deposition, and the corresponding photography of the core with gray scale analyses. Contrast and lightness of the image were slightly enhanced, and gray scale measurements were performed using ImageJ software. The position of the sample within the record is indicated with a red tick at the top of Fig. 2. Vertical dashed lines show 1 cm intervals.

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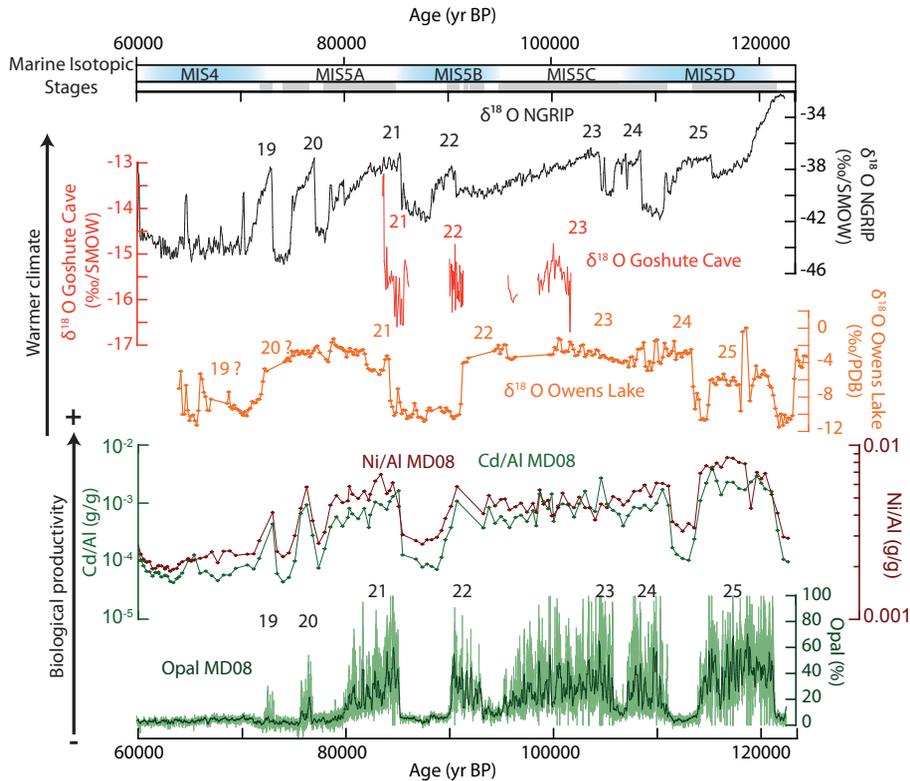
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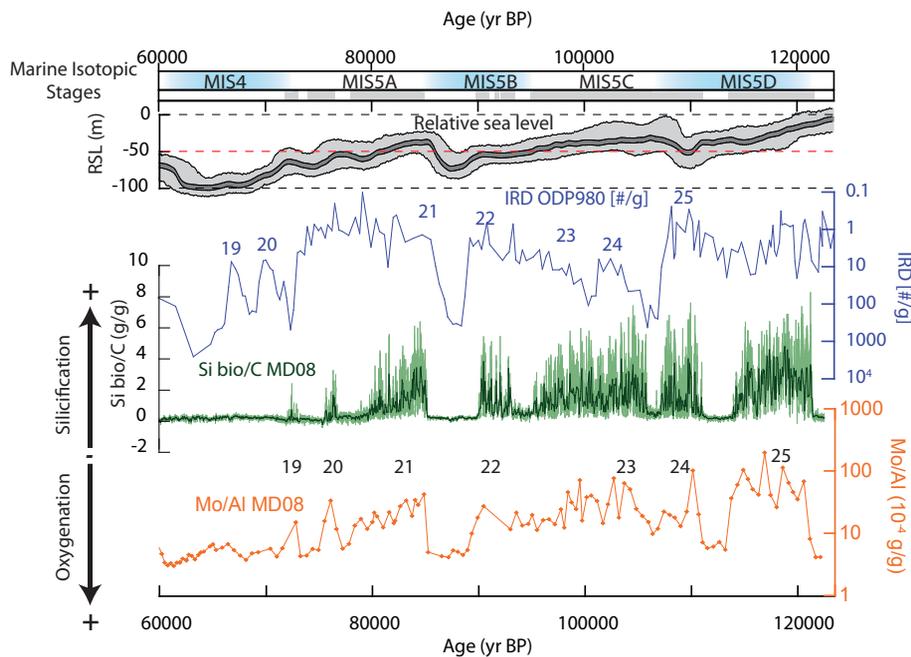




**Fig. 4.** The isotopic composition of NGRIP ice core ( $\delta^{18}\text{O}$  ‰/SMOW) (NGRIP Members, 2004) ; the isotopic composition of Owens Lake sediment ( $\delta^{18}\text{O}$  ‰/PDB) (Li et al., 2004), the isotopic composition of Goshute cave stalagmite ( $\delta^{18}\text{O}$  ‰/PDB) (Denniston et al., 2007); and the opal content, Cd/Al, and Ni/Al in MD02-2508 core.

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**Fig. 5.** The global relative sea level (Grant et al., 2012). Confidence interval of 95% (light grey) and probability maximum (dark grey) are indicated. The 50m depth below modern sea level, corresponding to modern Bering Strait depth is highlighted in red. The Ice Rafted Debris content in north Atlantic ODP site 980 core plotted on an inverse logarithmic scale (Oppo et al., 2006), and the biogenic Si to C ratio (Si bio/C) and Mo/AI in MD02-2508 core.

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