

## Testing the silica leakage hypothesis with sedimentary opal records from the eastern equatorial Pacific over the last 150 kyrs

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[1] We have measured  $^{230}\text{Th}$ -normalized opal fluxes in several cores from the eastern equatorial Pacific (EEP) to test the validity of the “silica leakage” hypothesis, which purports that redistribution of silicic acid from the Southern Ocean to the low latitudes was responsible for a significant portion of the reduction in atmospheric carbon dioxide ( $\text{CO}_2$ ) during the last glacial period. The silica leakage hypothesis predicts higher opal fluxes in the EEP and lower opal fluxes in the Southern Ocean during periods of low atmospheric  $\text{CO}_2$ . These predictions are not borne by the sedimentary record during glacial oxygen isotope stage 2 (OIS 2, 13–27 kyrs B.P.). However, we find a prominent opal flux maximum in the EEP in the middle of OIS 3 (ca. 40–60 kyrs BP) coinciding with low opal fluxes in several cores from the subantarctic zone. This observation is consistent with silica leakage from the Southern Ocean to the equatorial upwelling region during OIS 3, when both low dust flux and extended sea ice could have contributed to limiting diatom productivity in the Southern Ocean. Since this event is not associated with a clear minimum in the Vostok ice record of  $\text{CO}_2$ , its impact on atmospheric  $\text{CO}_2$  appears to be small. **Citation:** Kienast, S. S., M. Kienast, S. Jaccard, S. E. Calvert, and R. François (2006), Testing the silica leakage hypothesis with sedimentary opal records from the eastern equatorial Pacific over the last 150 kyrs, *Geophys. Res. Lett.*, 33, L15607, doi:10.1029/2006GL026651.

### 1. Introduction

[2] Diatom productivity is largely responsible for the settling flux of biogenic silica in the ocean and plays a critical role in the sequestration of  $\text{CO}_2$  from the atmosphere. In contrast to other groups of phytoplankton, diatoms have a requirement for Si in the form of silicic acid ( $\text{Si}(\text{OH})_4$ ) in order to build their opaline frustules. Silicic acid, however, is a scarce commodity over much of the low-latitude ocean [Sarmiento *et al.*, 2004], and particularly in the equatorial Pacific upwelling region [Dugdale and Wilkerson, 1998]. The silica leakage hypothesis explains the drawdown of atmospheric  $p\text{CO}_2$  during the last glacial period by invoking a release of Si-limitation in the low latitude ocean due to advection of excess  $\text{Si}(\text{OH})_4$  generated in the Antarctic Southern Ocean [Matsumoto *et al.*, 2002; Brzezinski *et al.*, 2002]. Relaxation of Fe limitation in this

region by increased dust input during glacial periods would have decreased the silica/nitrate uptake ratio of diatoms allowing the export of  $\text{Si}(\text{OH})_4$  to low latitude upwelling regions fed by Subantarctic Mode Water (SAMW). This is thought to promote an ecosystem shift away from coccolithophorids toward diatoms and consequently a reduction in the rain ratio of carbonate carbon to organic carbon in sinking particulate matter, which would result in higher seawater alkalinity and lower atmospheric  $\text{CO}_2$ .

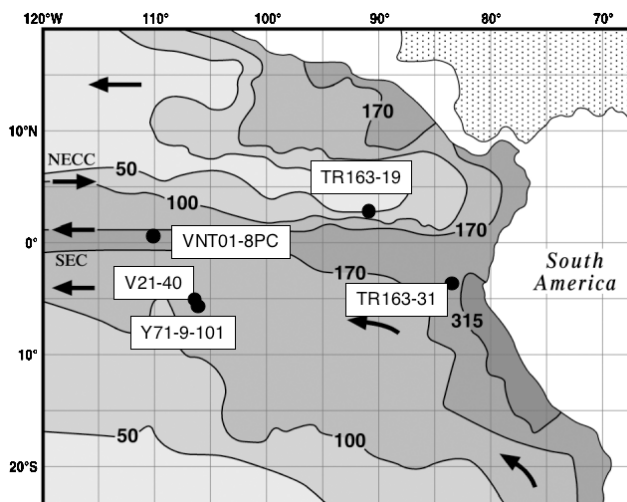
[3] We test this hypothesis by searching the sedimentary record in the EEP for periods of increased opal burial that could be indicative of a large-scale increase in  $\text{Si}(\text{OH})_4$  supply to this region. Indeed, recent results from a one-dimensional ecosystem model of the equatorial Pacific upwelling region suggest that an increase in  $\text{Si}(\text{OH})_4$  source concentration leads to a linear increase in biogenic silica flux from the sea surface [Dugdale *et al.*, 2004]. We assume that opal burial in sediments reflects vertical flux of biogenic silica in this region, as there is no established proxy for opal dissolution yet. Although a simplification, this approach is justified by the positive relationship between vertical opal flux and sedimentary opal burial observed at several sites in the central equatorial Pacific [McManus *et al.*, 1995].

### 2. The EEP and its Connection to the Subantarctic Southern Ocean

[4] From about  $110^\circ\text{W}$  eastward in the EEP, the source of nutrients to the surface is upwelling of the lower branch of the Equatorial Undercurrent (EUC). This water does not upwell along the equator but feeds the coastal upwelling region off Peru and recirculates at the surface into the westward flowing South Equatorial Current [Toggweiler *et al.*, 1991]. The EUC has a northern hemisphere source and a more dominant (50–70%) southern hemisphere source, whose higher density waters are linked to the SAMW production region [Dugdale *et al.*, 2002; Rodgers *et al.*, 2003]. Under modern conditions, waters in the SAMW formation region are characterized by relatively high nitrate but extremely low  $\text{Si}(\text{OH})_4$  concentrations, which are the result of diatom production with an unusually high Si:N uptake ratio (Si:N  $\sim$  4:1 on a molar basis), the latter being a manifestation of iron limitation in this region [Sarmiento *et al.*, 2004 and references therein]. Due to its connection to the Southern Ocean, the EEP is expected to show a close relationship to changes in Southern Ocean chemistry, especially off Peru, where the denser waters of the EUC are upwelled. In contrast to the  $\text{Si}(\text{OH})_4$  poor southern hemisphere source waters in the EUC, northern hemisphere

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**Figure 1.** Core sites used in this study on a map of surface ocean productivity (in  $\text{gC m}^{-2} \text{y}^{-1}$ ) adopted from *Mekik et al.* [2002].

waters contributing to the EUC contain  $\text{Si(OH)}_4$  and nitrate in approximately equal proportions [*Dugdale et al.*, 2002].

### 3. Material and Methods

[5] We present new records of  $^{230}\text{Th}$  normalized opal flux and opal/aluminium ratios of 5 cores from the EEP (Figures 1 and 2) covering the last 150 kyrs. Lateral sediment redistribution can affect the sedimentary record in the EEP and we account for this potential bias by normalizing biogenic opal concentrations to the constant flux of  $^{230}\text{Th}$ . We augmented the  $^{230}\text{Th}$  normalized opal data with opal/Al (wt%/wt%). Normalization of element concentrations of interest to the concentration of a refractory element (such as Al) in the same sample corrects for variable dilution of the bulk sediment by other phases, such as carbonate, which is a major component of EEP sediments. The striking similarity between opal/Al and  $^{230}\text{Th}$ -normalized flux (Figure 2) indicates that the vertical flux of Al to the seafloor is quasi constant at these sites, and therefore variations in opal/Al also reflect variations in preserved opal flux. Core locations, analytical methods and stratigraphies are given in the auxiliary material<sup>1</sup> of this article.

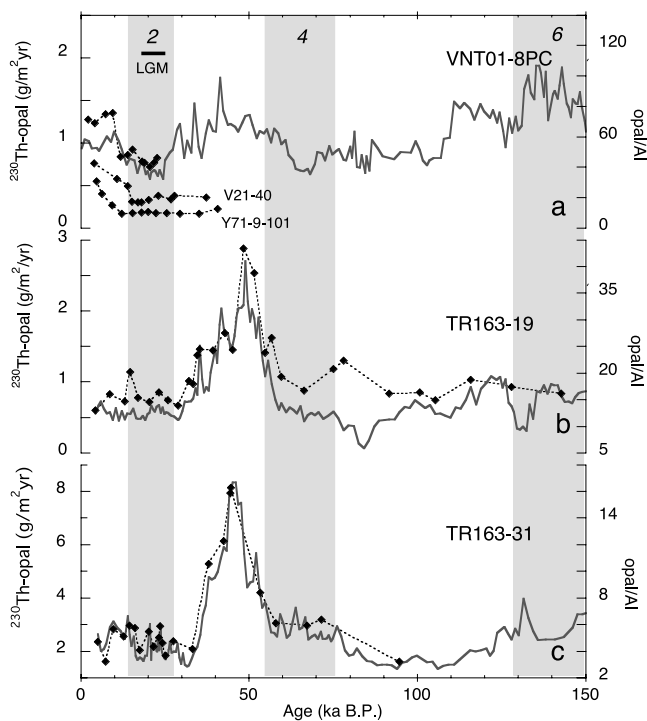
### 4. Results

[6] Th-normalized opal fluxes in all three cores from 105–110°W (Figure 2a) rise from lower values during OIS 2 to values almost twice as high during the Holocene. Over this time span, the eastern more cores TR163-19P and TR163-31P (Figures 2b and 2c) show little systematic variability. However, these latter two sites are characterized by a significant opal flux maximum during OIS 3. Maximal values during this period at TR163-31PC are  $\sim 8 \text{ gm}^{-2}\text{y}^{-1}$ , which is roughly 4 times higher than the modern maximal

opal burial flux measured in the EEP ( $2 \text{ gm}^{-2}\text{y}^{-1}$  or  $3 \mu\text{molcm}^{-2}\text{yr}^{-1}$  [*McManus et al.*, 1995]). TR163-31P is located closest to the Peru upwelling region, and the highest overall values as well as the strong amplitude of the 50 ka event at this site are consistent with the view that the source of  $\text{Si(OH)}_4$  is upwelling off Peru. Farther to the west, site VNT01-8PC also shows a broad period of elevated opal/Al ratios during stage 3, but the relative magnitude of this event is subdued compared to the more eastern sites (Figure 2a).

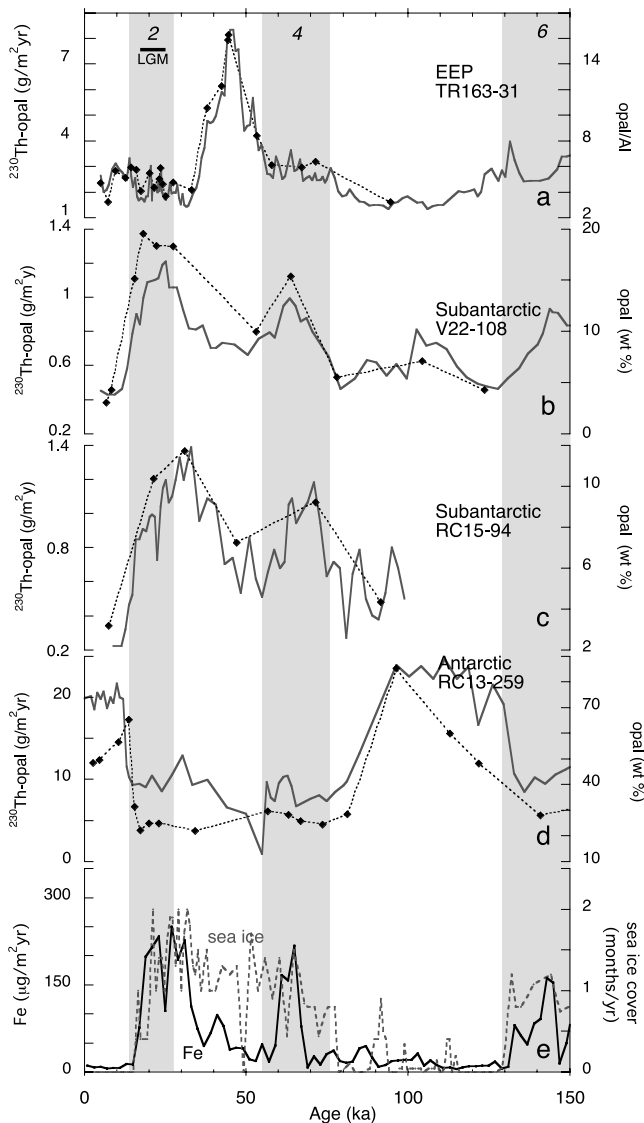
### 5. Discussion

[7] There are two principal ways to change  $\text{Si(OH)}_4$  source concentrations and, by inference, sedimentary opal contents in the EEP. The first one is an increase in the relative contribution of northern hemisphere waters to the EUC, which have significantly higher Si:N ratios than those derived from the southern hemisphere. Model simulations suggest that more northern component water is directed into the EUC relative to southern hemisphere waters when the Indonesian Throughflow, that is, the mean export of water from the Pacific into the Indian Ocean, is reduced [*Rodgers et al.*, 1999]. A  $\sim 1/3$  reduction of Indonesian Throughflow volume was obtained by numerical simulations for the sea level low stand during the last glacial maximum (LGM, from 23–19 kyrs B.P. [*Kuhnt et al.*, 2004]), which could have led to a relative increase in  $\text{Si(OH)}_4$  concentrations in the EEP. Our results do not show an increase in opal deposition during the LGM (Figure 2), however, rendering a change from more southern to more northern hemisphere



**Figure 2.** Biogenic opal/Aluminium ratios (grey lines) and  $^{230}\text{Th}$ -normalized opal fluxes (dashed lines) in the EEP. Note different Y-axes on each panel. Oxygen isotope stages are indicated at the top, LGM stands for last glacial maximum.

<sup>1</sup>Auxiliary material data sets are available at <ftp://ftp.agu.org/apend/gl/2006gl026651>. Other auxiliary material files are in the HTML.



**Figure 3.** (a) Core TR163-31P from the EEP compared to published records of opal flux from the (b, c) subantarctic and (d) antarctic zones of the Atlantic Southern Ocean. (e) Iron (Fe) flux from the EPICA ice core [Wolff *et al.*, 2006] and sea ice cover [Crosta *et al.*, 2004]. Weight % biogenic opal data (grey lines) of cores V22-108, RC15-94 and RC13-259 are from Charles *et al.* [1991] and  $^{230}\text{Th}$  normalized opal flux data (dashed lines) are from Anderson *et al.* [1998] and R. F. Anderson (personal communication, 2005).

source waters unlikely as the main control on opal deposition in the EEP during this time.

[8] The second possibility to change  $\text{Si}(\text{OH})_4$  concentrations in the EEP is through changes in nutrient conditions in the production region of SAMW. Surface nutrients in this region are carried by Ekman transport from the region south of the polar front, where deep water upwelling brings waters with extremely high nutrient concentrations to the surface. Preferential uptake of  $\text{Si}(\text{OH})_4$  over nitrate from these waters as they are advected northward leads to the extremely low Si:N ratios observed in waters of the SAMW production

region today [Sarmiento *et al.*, 2004 and references therein]. Based on the observation that the addition of the micronutrient iron dramatically reduces the Si:N uptake ratio of diatoms, the original silica leakage hypothesis envisioned that higher dust fluxes during peak glacial conditions could have led to an excess pool of silicic acid compared to today in the Southern Ocean [Matsumoto *et al.*, 2002; Brzezinski *et al.*, 2002]. Excess silicic acid could have also been generated by a reduction in diatom abundance due to sea ice cover or due to proliferation of non-diatom phytoplankton such as *Phaeocystis* [Matsumoto *et al.*, 2002]. Paleoreconstructions based on foraminiferal  $\delta^{18}\text{O}$  suggest that the large-scale vertical circulation in the glacial Southern Ocean was similar to today [Matsumoto *et al.*, 2001]. Glacial-age productivity, however, and the degree of Si-utilization were significantly reduced in the sea-ice covered antarctic zone of the Southern Ocean [Anderson *et al.*, 2002 and references therein]. Hence, excess silica generated during glacials would not have been consumed in the antarctic sector. Matsumoto *et al.* [2002] suggested that it could either be consumed in the subantarctic zone (with a negligible effect on  $p\text{CO}_2$ ) and/or be advected into the low latitudes via SAMW. Sedimentary records from the subantarctic zone show little or no change in opal deposition in the Pacific sector, in contrast to increased opal deposition in the Atlantic and Indian sectors during the LGM [Chase *et al.*, 2003]. This contrast has been explained by the closer proximity to dust sources in the Atlantic and Indian sector [Chase *et al.*, 2003]. Based on these findings, one could expect that  $\text{Si}(\text{OH})_4$  not used in the Pacific sector of the glacial Southern Ocean during the LGM would leak into the EEP.

[9] However, the core where we would expect the strongest signal (TR613-31P) does not reveal a clear opal flux maximum during the LGM and no clear trend during the last 30 ka (Figure 2c). Moreover, the records at  $110^\circ\text{W}$  show lower opal fluxes during the LGM and all of OIS 2 (Figure 2a). These observations render silica leakage to the EEP unlikely during stage 2, in good agreement with recent results by Bradtmiller *et al.* [2006]. Consistent with these observations, diatom-bound sedimentary  $^{15}\text{N}/^{14}\text{N}$  ratios from the subantarctic region imply a high degree of nitrate utilization during OIS 2 and suggest that nutrient export, at least that of nitrate, to lower latitudes was limited at that time [Robinson *et al.*, 2005].

[10] The variability in opal deposition between OIS 2 and the Holocene pales in comparison with the opal flux maximum observed during OIS 3 (Figure 2). Coeval with this opal flux maximum in the EEP is an intermittent minimum in opal deposition in records from the subantarctic Southern Ocean (Figures 3b and 3c). During OIS 2 and 4, opal fluxes in the subantarctic region increased, which has previously been explained by a northward shift of the region of diatom production due to more intense sea ice cover around Antarctica during glacial periods [Charles *et al.*, 1991, Chase *et al.*, 2003]. During the full interglacial warm stages OIS 1 and 5, opal is deposited in the antarctic zone. During OIS 3, sea ice cover around Antarctica was still prevalent [Crosta *et al.*, 2004] but atmospheric dust and Fe fluxes were significantly lower compared to OIS 2 and 4 [Wolff *et al.*, 2006; Figure 3e]. We thus suggest that sea ice cover south of the polar front during OIS 3 might have

prevented significant diatom production in this region, causing excess  $\text{Si}(\text{OH})_4$  to be advected into the subantarctic zone. In the subantarctic region diatoms were unable to completely utilize silicic acid due to low Fe availability during OIS 3. This in turn would allow  $\text{Si}(\text{OH})_4$  to be leaked into the EEP, most notably into the upwelling region off Peru, but also into other low latitude areas via the spread of SAMW. Increased opal mass accumulation rates during OIS 3 have indeed been documented off Namibia [Romero *et al.*, 2003]. Note that these low latitude upwelling regions are closer to continental sources of iron than most of the subantarctic Southern Ocean. Based on the records compiled in Figure 3, the pattern of opal accumulation in the Antarctic, Subantarctic and EEP appears to be principally consistent with silica leakage from higher to progressively lower latitudes under conditions which inhibit efficient  $\text{Si}(\text{OH})_4$  uptake further south. Silica leakage from the Southern Ocean as a result of low diatom production in the subantarctic region would presumably be accompanied by low nitrate utilization. This should be reflected in low sedimentary  $\delta^{15}\text{N}$  during OIS 3 in the subantarctic Southern Ocean. However, records to date do not necessarily support this [Robinson *et al.*, 2005], leaving the possibility open that the opal accumulation record in the EEP is not caused by silica leakage, but by another yet to be described mechanism.

## 6. Conclusions

[11] Sedimentary opal records from the EEP covering the last 150 kyrs show no evidence of increased opal burial during glacial OIS 2, but a large opal deposition event close to the Peru upwelling region between 40–60 kyrs BP. The latter event is correlative with a minimum in opal deposition in the subantarctic Southern Ocean. These results do not support silica leakage as originally envisioned during OIS 2 into the EEP. However, the observed oscillatory behavior between opal records from the subantarctic Southern Ocean and the EEP can be explained by silica leakage, and would suggest that silica leakage to lower latitudes only occurs effectively when low dust flux and extended sea ice combine to limit diatom productivity in the Southern Ocean. This event, however, is not associated with a clear minimum in the Vostok ice core record of atmospheric  $\text{CO}_2$ , suggesting that the impact of this mechanism on atmospheric composition might be small.

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