Supplementary Methods

1. Study area

Core MD012404 (26°38.84′N, 125°48.75′E, water depth: 1397 m) was retrieved from the middle part of Okinawa Trough on WEPAMA Cruise – IMAGES VII, 2001 (Fig. DR1). The Okinawa Trough receives both terrestrial and marine sediment inputs and is thus characterised by moderately high sediment accumulation rates (21.8-80 cm/kyr) (Kao et al., 2008), thereby allowing high resolution paleo-climate and paleoceanography reconstructions. The North Pacific intermediate water (NPIW) forms at high latitudes and flows equatorwards to ~15°N, connecting the subarctic- and subtropical North Pacific (Figs 1A and DR1). NPIW dominates the nutrient supply to the Okinawa Trough euphotic zone (Chen, 1996; Nakamura, 2013; Sarmiento et al., 2004; Zhang et al., 2007). As reported by Chen (1996), Kuroshio intermediate waters contribute more than 90% of euphotic zone nutrients in the East China Sea/Okinawa Trough region.

2. Material and age model

The initial age model of core MD012404 was established using Accelerator Mass
Spectrometry (AMS) $^{14}$C ages (planktonic foraminifers) for the upper 21.745 m, and
by adjusting the benthic foraminiferal $\delta^{18}$O to the benthic $\delta^{18}$O isotope stack curve for
the older part (21.745-43.485 m) (Chang et al., 2009, and references therein). In this
study, we updated the age model framework for the older part (21.745-43.485 m), by
graphically aligning the benthic foraminiferal $\delta^{18}$O from site MD012404 to a more
recent Pacific deep benthic foraminiferal $\delta^{18}$O stack curve (i.e. PD stack, Fig. DR2)
(Lisiecki and Stern, 2016), which has robust age control. Ten age control points were
selected for the older section; considered together with the original 19 AMS $^{14}$C ages,
a new age model for MD012404 was established (Fig. DR2A). The MD012404
benthic foraminiferal $\delta^{18}$O record displays good correlation with the PD stack (Fig.
DR2B).

A 30 kyr-long (0-30 kyr), low resolution (averaged resolution of ca. 375 years per
sample) record of phosphorus from core MD012404 has previously been generated
(Li et al., submitted manuscript, 2016); for the present study, we substantially increase
the temporal resolution of the 0-30 kyr interval and extended the record to 91 kyr,
resulting in an average resolution of 220 years for the entire record. For trace metal
analysis, samples were taken at 20 to 40 cm interval with an average resolution of 607
years.

The MD012404 benthic foraminiferal $\delta^{18}$O is in high resolution (~115 yr on
average), being sufficient to constrain our findings: high (low) $P_{\text{reactive}}$ values occurred
during Greenland interstadials (stadials) during the last glaciation. Besides the
similarity pattern at high frequency, very similar low frequency patterns of reactive P
and Greenland temperature records (Figs 2C and 2D in the main text) can also be
found to support our conclusion above.

3. Analytical Methods

3.1 Phosphorous speciation

The sedimentary phosphorus fractions were analyzed at the National Taiwan Ocean
University, following the protocol described in Fang et al. (2007) modified from
Berner and Rao (1994). Four distinct sedimentary phosphorus reservoirs were
determined basing on their chemical reactivity: (1) ferric iron bound and adsorbed
phosphorus; (2) authigenic calcium phosphate, biogenic hydroxyapatite, plus
CaCO₂-bound phosphorus; (3) detrital apatite and (4) organic phosphorus. Briefly, the
bulk sediment sample was divided into three aliquots. One aliquot was extracted using
a citrate-dithionite-bicarbonate (CDB) mixture at a pH of 7.6 for 0.5 hour, followed
by shaking for another 24 hours at room temperature. This soluble fraction is
operationally defined as ferric iron bound and adsorbed phosphorus and is named as
P_{Fe oxide-associated} in this study. After the CDB extraction, the residue was rinsed with
deionized water, and further extracted with acetate buffer solution (acetic acid/Na
acetate, pH = 4). This fraction is referred to as P_{authigenic}, representing authigenic
calcium phosphate, bone apatite and phosphorus associated with CaCO₃. Another
aliquot was extracted by 1N HCl acid for 24 hours after ashing at 550 °C for 12 hours,
recovering total phosphorus (TP). The last aliquot was extracted by 1N HCl without
ashing to obtain the total inorganic phosphorus (TIP). The organic phosphorus (P_{organic})
was derived from the difference between TP and TIP. The difference between TIP and the sum of $P_{\text{Fe oxide-associated}}$ and $P_{\text{authigenic}}$ is defined as detrital phosphorus. For all the extractants other than the iron bound phosphorus, the ascorbic acid molybdate blue technique was employed to determine soluble reactive phosphorus concentrations on a Perkin-Elmer Lambda Bio 20 spectrophotometer. Before analysis for the CDB extractant, excess sodium dithionate was allowed to oxidize for several days, and ammonium molybdate solution was added to compensate for the interference from citrate. Reproducibility of each extraction was found to be better than 3.5% (triplicate analysis) on average. $P_{\text{reactive}}$ is defined here as the sum of $P_{\text{Fe oxide-associated}}$, $P_{\text{authigenic}}$ and $P_{\text{organic}}$. Results of P speciation are displayed in Fig. DR3.

3.2 Metal analysis

For major and trace element analyses, approximately 0.2 g dry sediment sample was digested using an acid mixture of HF, HNO$_3$ and HClO$_4$ according to the procedure described by Hsu et al. (2003). The digested solution, which contains the dissolved metals was analyzed for Fe and Ti using an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Optima 3200DV, Perkin-Elmer™ Instruments, USA), and for trace metal using an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Elan 6100, Perkin-ElmerTM Instruments, USA).

4. Assessment of reactive P as a proxy for export productivity.

Under anoxic condition, the remobilization of Fe-oxyhydroxides occurs at a narrow redox window where neither oxygen nor sulphide are present (Scholz et al., 2014). We
posit that sedimentary Fe-oxyhydroxides and related $P_{Fe}$ (P bound/absorbed to
Fe-oxyhydroxides) at site MD012404 remained stable and thus effectively fixed in the
sediment for the following reasons: (1) Variability of $P_{Fe}$ did not determine the pattern
of Fe content or Fe/Ti ratio (Fig. DR5) over the last 91 kyr. (2) If low values of
reactive P were due to deletion of $P_{Fe}$ under anoxic conditions, the proportion of $P_{Fe}$ in
reactive P should be very low; however, relatively a high contribution of $P_{Fe}$ to total
reactive P was observed in MD012404 during intervals with lower reactive P content
(Fig. DR6). Furthermore, the fraction of organic P in total reactive P decreased
gradually from $45 \pm 6\%$ in the Holocene to lower than 20% during the 60-91 kyr
interval (Fig. DR6C). This is the classic pattern of reactive P burial with increasing
burial time under oxic bottom water conditions (Schoepfer et al., 2015). (3) Persistent
existence and higher abundance of the benthic foraminifera *Uvigerina spp.* (Fig. DR8),
which favour intermediate to weak hypoxic conditions (Schönfeld and Altenbach,
2005; Praetorius et al., 2015), indicating that bottom water was more oxygen-depleted
compared to the Holocene, but never reached anoxic condition sufficient for
Fe-reducing, which would lead to $P_{Fe}$ escaping from sediment (Praetorius et al., 2015).
In addition, it is reasonable to postulate that the reactive iron oxide in the sediment
was sufficient to form Fe-bound phosphate since the Fe content was substantially
higher than that of total sulfur (Fig. DR5) and organic carbon concentrations were not
particularly high (Fig. DR8).

During the last ice age, both model results and paleo-environmental records suggest
that NPIW dissolved $O_2$ content was reduced during Dansgaard–Oeschger warm
(interstadial) events, and was higher during cold (stadial) events (Behl and Kennett, 1996; Brown and Galbraith, 2016; Cartapanis et al., 2011). This was further supported by redox trace metal records from our core (Fig. DR7). For example, both uranium (U) and molybdenum (Mo) display peak during warm episodes, suggesting reduced bottom water and/or sediment oxygenation. However, we suggest that millennial variability of reactive P from core MD012404 was not primarily controlled by environmental redox, i.e. oxic-suboxic condition favours reactive P burial whereas anoxic not, changes based on the following postulation: If the reactive P were controlled by sedimentary redox conditions, one would expect a proportionally greater loss during warm events at times intermediate water oxygen levels were low and vice versa during cold episodes. Our reactive P consistently displays higher values during warm events and lower values during cold events (Figs DR7 and DR8), suggesting that export productivity rather than environmental redox changes was the dominated driver of reactive P variability. In addition the abundance of planktonic foraminifera fauna assemblages in core MD012404 (Fig. DR8), which is expected to be proportional to euphotic primary productivity, displays a similar pattern to P_{reactive} over the last 40 kyr. Considering the above evidence together, P_{reactive} should effectively reflect changes in export productivity, although one cannot exclude that some alteration might have happened before burial (Schoepfer et al., 2015).
Figure DR1. Core location and the study area. A: Salinity in the upper 2000 m along the western North Pacific (yellow line in the insert panel in A). B: Vertical salinity distribution across the East China Sea continental margin, Okinawa Trough, and western North Pacific (yellow line in the insert panel in B). Salinity data are reported based on WOA2013 (http://www.nodc.noaa.gov/OC5/woa13/woa13data.html). Site MD012404 is labelled as a red star. Salinity contour lines are in black colour. The maps were generated using the Ocean Data View software (R. Schlitzer, 2014, http://odv.awi.de/). NPIW: North Pacific intermediate water.
Figure DR2. Benthic foraminiferal $\delta^{18}O$ records of core MD012404 (red line) and Pacific deep stack (green line). A: Benthic foraminiferal $\delta^{18}O$ records of core MD012404 (red line) plotted versus depth (Chang et al., 2009), and Pacific deep benthic foraminiferal $\delta^{18}O$ stack curve (i.e., PD stack; green line) (Lisiecki and Stern, 2016); Triangles indicate AMS $^{14}C$ dating, and arrows indicate isotope age control points. B: Benthic foraminiferal $\delta^{18}O$ records of core MD012404 plotted on this new age model.
Figure DR3. Phosphorus speciation and contents in core MD012404 over the last 91 kyr.
Figure DR4. Reactive P content (A) and its ratio to Ti (B) in core MD012404 over the past 91 kyr.
Figure DR5. Palaeo-records from core MD012404. A: Total sulphur content (TS) (from Kao et al., 2006). B: Content of Fe-associated P, including ferric iron bound and adsorbed phosphorus (this study). C: Total Fe content (this study). D: Fe/Ti ratio (weight/weight) (this study).
Figure DR6. Fractions of reactive P from core MD012404. A: Percent of $P_{Fe}$ in total reactive P. B: Content of reactive P. C: Fraction of inorganic form (blue) and organic form (green) in total reactive P.
Figure DR7. Redox sensitive metal and reactive P records from core MD012404.

A: U/Ti ratio (this study). B: Mo/Ti ratio (this study). C: Reactive P content (this study). D: Ratio of reactive P to Ti (this study). UCC: Upper continental crust (Taylor and McLennan, 2009).
Figure DR8. Paleo-environmental records from the core MD012404. A: Total organic carbon (TOC) (Chang et al., 2009). B: *Uvigerina* spp. Abundance (this study). C: Reactive P content (this study). D: Total planktonic foraminiferal fauna assemblages (Chang et al., 2008).
Figure DR9. Compilation of reactive P and other paleo-records for the past 91 kyr. A: $\delta^{18}O$ from North Greenland Ice Core Project (NGIRP) (North Greenland Ice Core Project members, 2004). B: $^{231}$Pa/$^{230}$Th records from subtropical northwest Atlantic ODP Site 1063 (15-92 kyr, purple line, 33°41′N, 57°37′W; water depth 4584 m) (Böhm et al., 2015), and OCE326-GGC5 Site (0-19.6 kyr, Violet line, 33°42′N, 57°35′W; water depth 4550 m) (McManus et al., 2004). C: $P_{\text{reactive}}$ content from sediment core MD012404 (this study). D: Biogenic Ba from MR06-04PC-7R
(51°16.87′N, 149°12.57′E; water depth 1256 m) retrieved from the Sea of Okhotsk (Gorbarenko et al., 2012). Biogenic proxies based on original age model indicate that productivity varied in phase with Greenland temperatures; for comparison with this study, the MR06-04PC-7R age model was tuned to the AICC2012 chronology by point-to-point correlating between Greenland ice $\delta^{18}$O and biogenic Ba. E: Bromine to Chlorine ratio (Br/Cl) of site MD02-2508 (23°27.91′N, 110°35.74′W; water depth 606 m) from the Baja California margin (Cartapanis et al., 2014). F: Color b* record from SO201-2-85KL (57°30.30′N, 170°24.77′E; water depth 968 m) retrieved from the Bering Sea (Riethdorf et al., 2013). Sediment color b* generally correlates with biogenic records, e.g. opal, CaCO$_3$ and Bromine (Br) (Riethdorf et al., 2016), and was thus used as export productivity proxy.
Figure DR10. Paleo-records covering the interval from 17 kyr to 71 kyr. 

A: Composite atmospheric CO$_2$ record from Antarctic ice cores (Bereiter et al., 2015). B: Iron flux (dark yellow line) and dust flux (grey line) from Subantarctic zone ODP Site 1090 (Martínez-García et al., 2014) and Antarctic ice core EPICA Dome C (EDC) (Lambert et al., 2012) respectively. C: Opal flux from Subantarctic zone (site PS2498-1) (Anderson et al., 2014). D: P$_{reactive}$ record from sediment core MD012404 (this study).
REFERENCES CITED


Chang, Y.-P., Wu, S.-M., and Wei, K.-Y., 2005, Foraminiferal oxygen isotope stratigraphy and high-resolution organic carbon, carbonate records from the Okinawa Trough (IMAGES MD012404 and ODP Site 1202): Terrestrial, Atmospheric and Oceanic Sciences, v. 16, p. 57-73.


