Provenance and supply of Fe-enriched terrigenous sediments in the western equatorial Pacific and their relation to precipitation variations during the late Quaternary

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Iron (Fe) deposition in the equatorial Pacific has important implications for the global carbon cycle, while the provenance of Fe supply and its change remain highly debated. Here, we geochemically characterize the provenance of terrigenous sediments deposited on the pathways of the Equatorial Undercurrent (EUC) and the New Guinea Coastal Undercurrent (NGCUC). The Fe-enriched sediments in the western equatorial Pacific are mostly derived from fluvial inputs of Papua New Guinea (PNG), while nearly negligible impact from eolian dust could be detected. Variability of the terrigenous Fe-enriched deposition (7.4–13.4%) for core KX21-2 in the western equatorial Pacific over the past 380 ka shows dominant precession periods, superimposed on a clear glacial-interglacial trend with higher input during glacial periods. The precession periods are correlated with the precipitation over PNG in response to the local summer insolation (5°S, March) and meridional migration of the Intertropical Convergence Zone (ITCZ). The glacial-interglacial trend is induced by sea level fluctuations that significantly influence the fluvial input from southern PNG. The different expressions of precession periods between glacial and interglacials in core KX21-2 are tightly associated with the undercurrent. The subdued precession periods during interglacials can be attributed to the weakness of the NGCUC, which may link to La Niña-like conditions. The enhanced precession periods during glacial ages should result from increased input from southern PNG on one hand, and an intensified NGCUC on the other hand, due to El Niño-like conditions. Compared to Fe, the proxy ln (Ti/Total) (XRF log-ratio of Ti/Total counts) for core KX21-2 preferentially indicates the northern PNG input, and therefore could be used to reflect the glacial changes in the NGCUC. Our records imply that the NGCUC was particularly stronger in MIS 6 and 10, and weaker in MIS 8.

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1. Introduction

Vast areas of the modern ocean are characterized by excess nutrients yet low concentrations of chlorophyll in the ephorophic zone. Martin (1990) proposed that primary productivity in these high-nutrient low-chlorophyll (HNLC) regions is limited by the availability of iron (Fe). This hypothesis has been demonstrated in the equatorial Pacific, one of the largest HNLC regions (e.g. Behrenfeld et al., 1996; Coale et al., 1996a, 1996b; Gordon et al., 1997). Moreover, deposition of Fe has important implications for the CO2 budget, as Fe addition to

and Ellwood, 2010), a pattern consistent with these interactions has been observed on the glacial-scale (e.g. Martin, 1990; Watson and Lefevre, 1999; Archer et al., 2000), especially the strong link between Fe and opal depositions in the Pleistocene equatorial Pacific (Murray et al., 2012). It is clear that productivity in the modern equatorial Pacific is limited by Fe availability and, this limitation has potential to control the long-term variation in primary production and the subsequent carbon sequestration (e.g. Murray et al., 2012), thereby exerting a significant influence on the global carbon cycle. However, the critical questions in regard to the provenance of Fe supply to this region and its potential changes are still being highly debated.

One prevailing hypothesis is that Fe is transported to the Pacific via eolian dust and this Fe-bearing dust flux may have increased during glacials when global climate was drier and dustier (Lambert et al., 2008; and references therein). Despite higher glacial dust found in ice cores and in some marine sediment cores, records from the equatorial Pacific do not show consistent relationships among climate state and inferred eolian input (e.g. Ollivarez et al., 1991; Krssek and Janecek, 1993; Rea, 1994; Murray et al., 1995; Ziegler et al., 2008). To explain this discrepancy, Rea (1994) proposed that Asian dust can only be
delivered to the equatorial Pacific when the Intertropical Convergence Zone (ITCZ) shifted southward. In contrast to studies relying on stratigraphic accumulation rates, application of the 230Th-normalization technique produces internally consistent results, showing that dust fluxes to the equatorial Pacific are positively related to global ice volume (e.g. Anderson et al., 2006; McGee et al., 2007; Winckler et al., 2008). Yet, there is a considerable controversy concerning the applicability of the 230Th-normalization method (see Lyle et al., 2005, 2007; Francois et al., 2007; Broecker, 2008). At least in the western equatorial Pacific, the excess 230Th deposition seems more likely to be the result of water column scavenging than along-bottom sediment transport (Broecker, 2008).

Direct measurements of Fe-bearing dust are sparse (Duce and Tindale, 1991; Gao et al., 2001; Shank and Johansen, 2008). Nevertheless, their results are within the range of model studies (Ginoux et al., 2001; Gao et al., 2003) and data-model-observation comparisons (Jickells et al., 2005; Mahowald et al., 2005), revealing extremely low eolian Fe supply in the equatorial Pacific. This supply is far from sufficient to explain the high concentrations of Fe in the Equatorial Undercurrent (EUC), which could be the primary fertilizing mechanism. The source of elevated Fe and its associated Al concentrations in equatorial waters at 140°W was shown to be from the EUC, of which upwelling rate and Fe concentration control equatorial primary production (Coale et al., 1996a; Gordon et al., 1997). Gordon et al. (1997) further suggested a lithogenic Fe source from Papua New Guinea (PNG), while a co-existing anomaly of particulate Mn led them to speculate that Fe, Al, and Mn are precipitates derived from shallow hydrothermal vents. It was also suggested that the Fe supply of PNG to the EUC source waters may occur through tectonic and volcanic processes (Wells et al., 1999). Although the western Pacific is tectonically active with hydrothermal vents in the Bismarck Sea and volcanic islands along the north coasts of PNG, several lines of evidence argue against the hydrothermal origin (see Milliman et al., 1999; Mackey et al., 2002).

Instead, because of heavy rainfall, high relief, relatively erodible rocks, small drainage basins, and frequent tectonic activities, PNG contributes a disproportionately huge fluvial input (Milliman, 1995; Milliman et al., 1999). This fluvial input can be transported across the slope over long distances via isopycnal plumes and hyperpycnal flows (Kinke et al., 2000; Kuehl et al., 2004; Renagi et al., 2010), and then entrained in the undercurrents that flow along the PNG coasts and eventually merge into the EUC in the western equatorial Pacific (Lindstrom et al., 1987; Tsuchiya et al., 1989; Fine et al., 1994), constituting the primary provenance of Fe in the EUC. Seawater measurements have showed elevated concentrations of Fe, Al, and Mn along the PNG slope and within the New Guinea Coastal Undercurrent (NGCUC), explicitly indicating that metals to the EUC are supplied by fluvial input and/or sediment resuspension via the NGCUC (Mackey et al., 2002; Slemon et al., 2010). Positive Fe isotopic values suggest that the process releasing dissolved Fe into the NGCUC water is the non-reductive dissolution of Fe-enriched deposition in the western equatorial Pacific (Lindstrom et al., 1987; Tsuchiya et al., 1989; Fine et al., 1994), constituting the primary provenance of Fe in the EUC. Seawater measurements have showed elevated concentrations of Fe, Al, and Mn along the PNG slope and within the New Guinea Coastal Undercurrent (NGCUC), explicitly indicating that metals to the EUC are supplied by fluvial input and/or sediment resuspension via the NGCUC (Mackey et al., 2002; Slemon et al., 2010). Positive Fe isotopic values suggest that the process releasing dissolved Fe into the NGCUC water is the non-reductive dissolution of river sediments (Radic et al., 2011). Sholkovitz et al. (1999) revealed a clear similarity between rare earth element (REE) patterns of the EUC waters, the PNG river waters, and sediments, demonstrating that undercurrents across the PNG slope inherit an island weathering signature (see Milliman et al., 1999; Mackey et al., 2002).

Fig. 1. Geological map and modern oceanography and climatology of the western equatorial Pacific. a) 1, Quaternary sediments; 2, Tertiary sedimentary rocks; 3, Mesozoic sedimentary rocks; 4, Paleozoic sedimentary rocks; 5, Proterozoic sedimentary rocks; 6, intermediate-basic extrusive rocks; 7, acid intrusive rocks; 8, intermediate intrusive rocks; 9, basic intrusive rocks; 10, metamorphic rocks; 11, faults; 12, rivers; 13, surface currents (Fine et al., 1994); New Guinea Coastal Current (NGCC); 14, undercurrents (Fine et al., 1994; Cresswell, 2000; Slemon et al., 2010); South Equatorial Current (SEC), Coral Sea Coastal Current (CSCC) (Wolanski et al., 1995; Harris et al., 1996), Great Barrier Reef Undercurrent (GBRUC), New Guinea Coastal Undercurrent (NGUC), New Ireland Coastal Undercurrent (NIOCUC) and Equatorial Undercurrent (EUC); 15, monsoon systems; 16, location of core KX21-2; 17, locations of major hydrothermal vents in the Bismarck Sea and volcanic islands along the north coasts of PNG, several lines of evidence argue against the hydrothermal origin (see Milliman et al., 1999; Mackey et al., 2002).

For a better understanding of Fe supply to the EUC, we have analyzed the geochemical composition on the sediments of core KX21-2 located in the formation region of the EUC, and of several core-top samples offshore northern PNG. In combination with published clay mineralogical data (Wu et al., 2012), after characterizing the provenance of terrigenous sediments deposited on the pathways of the EUC and NGCUC, we develop geochemical proxies to identify the origin of Fe-enriched deposition in the western equatorial Pacific, particularly to discriminate the fluvial inputs between northern and southern PNG. Furthermore, reconstruction of terrigenous deposition for the sediments in core KX21-2 allows us to constrain the variability of Fe supply to the EUC on orbital-scale for the past 380 ka, with implications for changes in precipitation, sea level, and currents around PNG.

2. Hydrographic and geological settings

Core KX21-2 is situated in the western equatorial Pacific, north of PNG, the opening pathway of the EUC, thereby providing a sensitive monitor of the Fe-enriched sediments supplied to the EUC (Fig. 1a).

The EUC originates at a water mass crossroad where thermocline and intermediate waters formed in both hemispheres meet at 120–320 m depth and flow eastward (Tsuchiya et al., 1989; Fine et al., 1994; Slemon et al., 2010). All the Southern Hemisphere contributions to the EUC are entrained westward in the South Equatorial Current (SEC) and then northward through the PNG region to the equatorial zone by the western boundary undercurrents, which have a common origin in the Coral Sea (Lindstrom et al., 1987; Tsuchiya et al., 1989; Fine et al., 1994; Cresswell, 2000; Slemon et al., 2010) (Fig. 1a). Water circulation in the shallow Gulf of Papua (GOP) basin is controlled by a clockwise gyre generated under the influence of the Coral Sea Coastal Current (CSCC), which
flows along the southern PNG shelf (Wolanski et al., 1995; Harris et al., 1996). The NGCUC is the principal pathway of Southern Hemisphere water into the EUC, including Antarctic Intermediate Water (Tsuchiya, 1991; Fine et al., 1994). The NGCUC (4.8 Sv) provides up to 62% of the EUC (7.8 Sv) at 145°E, and contributes about 50% of the EUC (12.4 Sv) at 156°E, i.e. after the New Ireland Coastal Undercurrent (NICUC, 1.3 Sv) has joined (Slemons et al., 2010).

The climate of PNG is dominated by the Asian–Australian monsoon with marked seasonality in the position of the ITCZ driving local wind and rainfall patterns (Webster et al., 1998; Wang, 2009) (Fig. 1b).
From November to April, the northwest winds (NW monsoon) prevail when the ITCZ shifts southward, resulting in high precipitation over the drainage basin. From May to October, the southeast winds (SE monsoon) dominate when the ITCZ moves northward, reducing rainfall especially in the southern lowlands. Except for deviations caused by the mountainous terrain, the north–south difference in rainfall pattern is primarily due to the position with respect to the ITCZ shifts. The whole of PNG is located under the northern side of the ITCZ during antral summer, while only northern PNG is on the southern limit of the ITCZ during austral winter (Fig. 1b). Consequently, southern PNG has a more pronounced seasonal wet–dry contrast than the northern part, which remains humid throughout the year (Fig. 1c). Meanwhile, precipitation is inter-annually tightly linked to the El Niño Southern Oscillation (ENSO) events (Webster et al., 1998; Wang, 2009). During El Niño events, the center of deep convection moves eastward, reducing rainfall over PNG, whereas rainfall is enhanced during La Niña events. The climate also influences the water circulation. The New Guinea Coastal Current (NGCC) flows northward off the SE monsoon and reverses its direction and weakens during the NW monsoon (Fine et al., 1994) (Fig. 1a). Seasonal variability has little impact on the undercurrents. The NGCCU flows steadily northward along the core slope and outer shelf below 200 m depth (Cresswell, 2000), while it intensifies and shoals during the El Niño events, with its core reaching 0–250 m depth (Ueki et al., 2003).

Northwest–southeast extending mountain ranges with 3–5 km altitude occupy central PNG. Most rivers originate from the central mountains, and form various fluvial plains in their lower reaches. The lithology of PNG is mainly composed of intermediate–basic volcanic rocks and Quaternary sedimentary rocks, accompanied by intermediate–basic intrusive rocks and metamorphic rocks (Fig. 1a). A distinct north–south difference is also observed in the surficial geology of river catchments (Fig. 1a). Rivers flowing to the GOL drain largely (65–95%) carbonate and aluminosilicate terrain, whereas the northward flowing Sepik River drains largely (80%) volcanic and igneous terrain (Brunskill, 2004). Precipitation often reaches > 10,000 mm/ a in mountain areas because of the orographic impacts on atmospheric circulation (Walsh and Nittouer, 2003). Along with relatively erodible rocks and frequent tectonic activity, the PNG mountainous rivers create extremely strong mechanical erosion and thus provide a disproportionately huge fluvial flux (Milliman, 1995; Milliman et al., 1999).

PNG has a significant north–south difference in off-shelf sediment delivery. The sediment load of the Fly River, the largest river in PNG, is largely deposited on the broad ( ~ 150 km) and gentle ( ~ 1:750 gradient) shelf in the GOL, which receives fluvial sediments up to 3.8 × 10^8 t/a (Milliman et al., 1999; Walsh and Nittouer, 2003). This retention of river sediment characterizes southern PNG, but a small portion (~5%) could escape the GOL shelf and then be transported to the Solomon Sea by the CSS (Wolanski et al., 1995; Harris et al., 1996; Walsh and Nittouer, 2003; Keen et al., 2006). By contrast, northern PNG is located at the edge of the Australian Plate and yields a sediment flux of 8.6 × 10^5 t/a (Milliman et al., 1999). The largest river in northern PNG, the Sepik River, has a very narrow ( ~ 10 km), steep ( ~ 1:50 gradient) shelf, and a submarine canyon extends into its estuary (Walsh and Nittouer, 2003). Consequently, over 90% of its fluvial sediments could bypass the shelf to the deep sea via sediment gravity flows and nepheloid layers (Kineke et al., 2000; Walsh and Nittouer, 2003; Kuehl et al., 2004).

3. Materials and methods

Core KX21-2 (1°25.01’S, 157°58.91’E, 1897 m water depth, 6.31 m core length, Fig. 1a) was retrieved by a gravity corer during the KX08-973 cruise onboard R/V Kexue-1 in December 2008. Three core-top (KX15-2, KX13-1, and KX12-1) sediments off the north coast of PNG were collected as well. Core KX21-2 sediments are composed mostly of grayish foraminifera marl ooze without apparent bioturbation. The age model has been established by correlating the planktonic foraminifer (Globigerinoides ruber) oxygen isotope (δ18O) stratigraphy with the LR04 stack (Lisiecki and Raymo, 2005), indicating that the bottom of core KX21-2 is in marine isotope stage (MIS) 10 with an approximate age of 380 ka BP (Zhou et al., 2011). The sedimentation rate of core KX21-2 was higher during interglacial due to enhanced CaCO3 content, and vice versa. Clay mineralogy data for core KX21-2 (425 samples) and the 3 core-top samples have previously been reported (Wu et al., 2012). All the following preparations, measurements, and analyses were performed at the State Key Laboratory of Marine Geology, Tongji University.

A total of 127 samples taken at ~5 cm intervals throughout core KX21-2, together with 3 PNG-offshore core-top samples, were selected for this study. Geochemical analysis was performed on the carbonate-free fine–grained fraction (Liu et al., 2009, 2012). Particles < 63 μm were wet sieved from bulk sediments in deionized water to eliminate coarse grains that may significantly affect the overall geochemical composition. The sieved fraction was decarbonated via reaction with 1% HCl, then centrifuged, oven dried at 60 °C, and ground in an agate mortar. About 30–45 mg powdered samples were heated at 600 °C for 2 h to obtain the loss of ignition, and then digested with a mixture solution of HNO3 + HF on a hot plate. The eluted samples were diluted by 2% HNO3 for major– and trace–element measurements, which were determined by Inductively Coupled Plasma–Optical Emission (ICP-OES) with an IRIS Advantage and by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) with a Thermo VG-X7 mass spectrometer, respectively. Analytical precision and accuracy were monitored by replicate analyses of GSR-5, GSR-6, and GSD-9 standards, showing that the relative deviations between measured and certified values are less than 6% for most elements with the exception of Mn, Sc, Zr, and Er (6–10%).

Grain size measurements were carried out on biogenic carbonate- and silica-free bulk sediments by a Coulter LS230 Laser Particle Size Analyzer (Liu et al., 2005). After processing with 1% HCl, subsamples were treated with 2 N Na2CO3 to remove biogenic silica, which were conducted in an 85 °C heating water bath for 5 h. After that, the Na2CO3 solutions were neutralized by successive rinsing with deionized water. A set of experiments beforehand demonstrated that this pretreatment can effectively remove biogenic silica without apparent alteration of the siliciclastic fraction.

High-resolution, non-destructive, semi-quantitative elemental analyses were performed directly on the surfaces of split cores at 0.5 cm intervals with an Avaatech X-ray fluorescence (XRF) Core Scanner (Zhao et al., 2011, 2012). To avoid contamination of the XRF measurement unit and desiccation of the sediments, the split core surfaces were covered with a 4 μm thick Ultralene® foil. Sediment surfaces were then carefully smoothed to get a maximum quality, with all air bubbles under the foil and all wrinkles in the foil eliminated. Measurements were conducted at setting of 10 kV and 500 mA to obtain intensities of elements from Al to Fe, reported as counts per second (cps), which are proportional to the chemical concentrations. Total counts of elements measured under 10 kV were adopted as a normalizing parameter to eliminate potential dilution from carbonate and organic fractions and to assess relative enrichment/depletion of a specific element (Revel et al., 2010; Zhao et al., 2011; Wu et al., 2012). As it has been suggested that XRF data should be expressed as log-ratios of element intensities (Weltje and Tjallingii, 2008), Fe and Ti are expressed here as ln (Fe/Total) and ln (Ti/Total), respectively.

4. Results and discussions

4.1. Provenance determination of Fe-enriched sediments in core KX21-2

As clay minerals are the primary terrigenous detrital component in marine sediments, clay mineralogy has been widely used to determine
provenance of terrigenous sediments (e.g. Liu et al., 2003, 2008, 2010; Gao et al., 2012). The clay mineral assemblages between KK21-2 core-top sediments and the core-top samples collected offshore PNG are very similar, with the dominance of smectite and minor chlorite, illite, and kaolinite indicating that majority of clay minerals in core KK21-2 are presently derived from the fluvial input of northern PNG (Wu et al., 2012). Specifically, the core-top sediments closer to the north coast of PNG contain higher smectite contents, except that the smectite contents are higher at KK21-2 than KK12-1 and KK13-1. The samples discussed below are given in Table 1 for major-and trace-elements, and Table 2 for REEs.

Major element compositions of the core-top sediments normalized to upper continental crust (UCC) (Taylor and McLennan, 1985, 1995) are very similar, strongly enriched in FeO$_r$ (total Fe), MgO, TiO$_2$, and MnO while depleted in CaO, K$_2$O, Na$_2$O, and P$_2$O$_5$, identical to that of the modern river sediments from northern PNG (Whitmore et al., 2004), thereby corroborating the clay mineralogy results (Fig. 2a). The Australian continent is the largest dust source regionally, but geological records and satellite observations indicate that Australian dust has little effect on core KK21-2 due to its predominantly southeast–northwest pathway (Hesse and McTainsh, 2003; Mackie et al., 2008). Alternatively, it was suggested that Asian dust could provide a small portion of clay minerals for core KK21-2 (Wu et al., 2012). Therefore, we use the Chinese loess composition, the main source of Asian dust (Rea, 1994), for comparison. Relative to the Chinese loess (Jahn et al., 2001), all the PNG-derived sediments are characterized by high concentrations of FeO$_r$, MgO, TiO$_2$, MnO as well as Al$_2$O$_3$ and Na$_2$O, and lower concentrations of CaO and K$_2$O (Fig. 2b), which probably reflects the difference in weathering in addition to provenance.

By contrast, trace element compositions could potentially be more inclusive and robust for provenance determination. Transition elements Sc, V, Co, Cr, and Ni are typically enriched in mafic igneous rocks, whereas Th, Nb, Zr, and Yb are more concentrated in felsic rocks (Taylor and McLennan, 1985; McLennan et al., 1993; Yang et al., 2008). It is therefore expected that a clear distinction will be found characterizing different sediment sources, especially in this study when considering that the lithology of PNG consists mainly of intermediate–basic volcanic rocks, of which the weathering is responsible for the predominance of smectite in the clay mineral assemblage (Liu et al., 2009; Wu et al., 2012). Indeed, very contrasting patterns of trace element compositions are yielded among the PNG-derived sediments and the Chinese loess.
When normalizing to the Chinese loess, KX21-2 core-top sediments are relatively depleted in V, Cr, and Ni, and enriched in Nb and Zr, compared to other PNG-derived sediments (Fig. 3b). This may imply an Asian dust impact. However, the REE fractionation pattern shows no discernible correspondence between sediments in core KX21-2 and the loess-origin Asian dust (Fig. 4). Eolian delivery may fractionate the mafic-mineral elements that are relatively soft and easily ground to finer, transportable particle sizes (Hattori et al., 1996).
However, such remarkable contrasts presented in Fig. 3b lead us to safely conclude that Asian dust may only contribute a small amount, if any, to the terrigenous deposition in the western equatorial Pacific.

REE fractionation parameters give more precise constraints on sediment provenance. Although REEs may be affected by intense chemical weathering (Nesbitt and Markovics, 1997), most studies suggest that sediment provenance plays a dominant role in determining REE compositions (Taylor and McLennan, 1985; Condie, 1991; Yang et al., 2002). REE composition of the Chinese loess (Liu et al., 1993) is flat with respect to UCC (Fig. 4a). Normalized REE patterns of all the PNG-offshore core-top sediments exhibit a well-developed middle REE (MREE) enrichment particularly with a positive Eu anomaly, highly resembling those of KX21-2 core-top sediments as well as the modern Sepik River sediments (Hannigan and Sholkovitz, 2001) (Fig. 4). This
Eu anomaly was also found in the REE patterns of regional Pacific waters (Grenier et al., 2013). The overall pattern is similar while marked negative anomalies of Eu and Lu are present in the modern Fly River sediments (Fig. 4). Likewise, these differences can be clearly observed in the comparisons for river waters and suspended particles (Sholkovitz et al., 1999; Hannigan and Sholkovitz, 2001), indicating that neither sediment grain size, mineral partitioning nor scavenging process exerts a significant control on the anomaly (Fig. 5).

In fact, a strong negative Eu anomaly (δEu) indicates felsic rocks, as does a high ratio of the light to heavy REEs (i.e. LREE/HREE), often approximated by the ratio of La to Yb with normalization to chondrite (i.e. La/Yb) and vice versa (Taylor and McLennan, 1985). This interpretation is supported by the good correlations between δEu and La/Yb (r = −0.87), and LREE/HREE (r = −0.69) (Fig. 6), where r is Pearson’s correlation coefficient, as well as in good agreement with the differences in surficial geology of river catchments over PNG. Intermediate–basic volcanic rocks account for 80% of the area in the catchment of Sepik River, whereas the rivers flowing to the GOP drain largely (65–95%) carbonate and aluminosilicate terrain (Brunskill, 2004) (Fig. 1a). Moreover, mafic-mineral elements show less enrichment in Fly River sediments (Hettler et al., 1997) and GOP sediments (Alongi et al., 1996) than in other PNG-derived sediments (Fig. 3; Table 1). Therefore, the δEu and relevant REE parameters for core KX21-2 are diagnostic of changing sediment sources, and can be employed to differentiate fluvial sediments of southern from northern PNG.

Notably, we do not use Ce and Er to make comparisons since the high error of Er measurements and Ce is generally related to oxidation states of water masses and sediments. In fact, Ce enrichments (contrary to Ce depletion in hydrothermal fluids) in the PNG-derived sediments in our results (Table 2) are in accord with the measurements of subsurface seawater, which suggests that the high-energy sediment remobilization regimes off the PNG rivers are the main sources of the Ce maxima in the EUC (Yang et al., 2007, 2009).

Based on the above results and discussion, we can conclude that the Fe-enriched sediments in core KX21-2 are mostly derived from the PNG fluvial inputs, while a nearly negligible impact from eolian dust could be detected in terms of elemental composition in the sediments, consistent with the clay mineralogy results. After the provenance characterization for core KX21-2 sediments between northern and southern PNG, some critical proxies have been extracted, permitting us to further constrain the temporal variations in Fe-enriched terrigenous supply due to the changing provenance.

4.2. Temporal variability of Fe-enriched sediment supply in core KX21-2

Variability of the Fe-enriched deposition in core KX21-2 for the past 380 ka displays both prominent glacial and precessional periodicity (Fig. 7). Comparisons of the FeO concentrations (carbonate-free basis total Fe concentration, 7.4–13.4%), ln (Fe/Total) (XRF log-ratio of Fe/Total counts), and smectite (Fe-enriched clay mineral) profiles show a strong correspondence, with the dominance of precession periods throughout the records, as well as a distinct glacial–interglacial trend with higher values during glacial periods. Of particular note, a diminished precessional periodicity during interglacials while enhanced during glacial is clearly observed.

4.2.1. Precessional and glacial changes

Poor correlations (r = −0.05–0.19) among the elemental records and mean grain size suggest that sediment grain size has little influence on the elemental concentrations in core KX21-2 (Fig. 7i). Elements Sc, Co, and Ni are primarily enriched in mafic rocks whereas Y, Zr, and Th are more concentrated in felsic rocks, which have been widely used for tracing provenance because they behave conservatively in hypogene environments and are resistant to chemical alteration (Taylor and McLennan, 1985). Accordingly, ratios such as Sc/Th, Co/Th, Ni/Y, etc. allow a distinction to be made between mafic and felsic sources, in addition to offset the grain size effect (McLennan et al., 1993; Yang et al., 2008). Here, we selected Co/Th and Ni/Y for discussion. Both ratios are strongly correlated with FeO (r = 0.71, 0.73), combined with the close relationship between carbonate-free basis Fe concentration (FeO2) and bulk Fe concentration (ln (Fe/Total)) profiles, indicating that the single most important factor determining the Fe-enriched sediments in core KX21-2 is provenance and sediment supply, regardless of dilution effect and Fe biogeochemistry (Fig. 7b–f). This is consistent with previous results, showing that Fe deposition is closely tied to the terrigenous supply (e.g. Ti) in the Pleistocene equatorial Pacific (Murray et al., 1995, 2012). Fe isotopic evidence indicates that dissolved Fe is not produced by dissimilatory iron reduction and redox cycling but is released by the non-reductive dissolution of sediment particles in the PNG region (Radic et al., 2011). In fact, clear resemblances between FeO, ln (Fe/Total), and smectite indicate that Fe deposition is closely tied to the terrigenous supply (e.g. Ti) in the Pleistocene equatorial Pacific (Murray et al., 1995, 2012). Fe isotopic evidence indicates that dissolved Fe is not produced by dissimilatory iron reduction and redox cycling but is released by the non-reductive dissolution of sediment particles in the PNG region (Radic et al., 2011). In fact, clear resemblances between FeO, ln (Fe/Total), and smectite indicate that Fe
mostly resides in the mineral lattices of fine-grained (<2 µm) smectite (Fig. 7b–d).

Moreover, Fe profiles for core KX21-2 exhibit a tight correspondence with the mean insoliation of March (late austral summer, i.e. the edge season of wet–dry) at 5°S (location of PNG) (Laskar et al., 2004) (Figs. 8a, b, 9a), indicating that the precessional variations in the Fe-enriched deposition for core KX21-2 are correlated with the fluvial inputs of PNG, controlled by the precipitation over river catchments, responding to the meridional migration of the ITCZ. The global tropical precipitation can be illustrated by an inter-hemispheric anti-phasing pattern in a precession period on orbital-scale (e.g. Partridge et al., 1997; Wang et al., 2001, 2004; Cruz et al., 2005; Tachikawa et al., 2011; Shiau et al., 2012). Precession forcing regulates the seasonal distribution of incoming solar insolation and exerts an opposite effect on the insolation in the Northern and Southern Hemispheres, which modulates monsoon intensity and, thus the latitudinal position of the ITCZ accompanied by asymmetry in the Hadley circulation (Kutzbach et al., 2008). Our results cannot directly reflect the precipitation changes over PNG due to its location. However, by comparing our data with the terrigenous records offshore PNG that more exclusively preserve precipitation information, an assessment can be made of the changes in the Fe-enriched sediment supply to the western equatorial Pacific and their relation to precessional and glacial variations.

Like Fe, Ti is concentrated in mafic rocks; but they differ in forms of occurrence. Ti is generally used as an indicator of relatively coarse, refractory, and heavy minerals, including rutile and anatase (both as TiO₂), which are expected to be associated with coarse river sediments (Tachikawa et al., 2011). When it comes to terrigenous records offshore PNG, the XRF Fe-bulk and Ti-bulk profiles for the past 400 ka from core MD2920 situated at the mouth of the Sepik River, only show a dominant precessional periodicity without glacial–interglacial change (Tachikawa et al., 2011) (Fig. 8d, e). By contrast, a 180 ka record of terrigenous fluxes from core MD05-2928 off the southeast coast of PNG, estimated by ²⁳⁰Th-normalization method, reveals higher fluvial input during glacial stages, with marked precessional variations superimposing on the glacial changes (Shiau et al., 2012), similar to the Fe records of core KX21-2 (Fig. 8f). The strong positive correlation between Fe-bulk and Ti-bulk for core MD2920 indicates that the Fe and Ti are both derived from Sepik River sediments, which are controlled by precipitation over northern PNG, independent of the sediment dynamic and transport process, and thus represent fluvial input of northern PNG. Although the narrow shelf and small rivers along the southeastern shore of PNG are to the north of core MD2920 (Shiau et al., 2012), this core is situated on the pathway of the CSCC that advects large quantities fluvial sediments from the GOP (Wolanski et al., 1995; Harris et al., 1996; Keen et al., 2006), thereby monitoring the fluvial input of southern PNG (Fig. 1a).

A combination of the absence of glacial cycle in terrigenous proxies for core MD2920 and the glacial–interglacial trend displayed in core MD2928, is interpreted here to indicate that the glacial variability in core KX21-2 primarily results from changes in the fluvial input from southern PNG, responding to sea level fluctuations. The falling sea level during glacial expansion of the continental ice volume caused the exposure of shelves, shortening the distance between river mouth and deep sea. The global sea level has varied significantly during the past 380 ka (Waehlbroek et al., 2002) (Fig. 8g). Given the depth of the GOP shelf, the sediment transport must have been much different in the past (Wolanski et al., 1995). Fluvial input from southern PNG should have substantially increased during low sea level periods, when the GOP shelf became considerably narrower thus allowing the rivers more easily to inject their sediments into the deep sea. Higher ln (Fe/Total) values in core KX21-2 roughly coeval with higher detritus fluxes in core MD2928 during MIS 5 and 3, point to increased supplies of southern PNG at the same time (Fig. 8b, f). As expected from the REE composition of the modern Fly River, variability of εu in core KX21-2 displays a visible glacial–interglacial trend, with more negative values during glacials while being more positive during interglacials (Fig. 7g). This demonstrates that during low sea level periods higher sediment supplies reached core KX21-2 from southern PNG, where rivers drain more felsic rocks. Yet, no expected glacial change in LREE/Yb or LREE/HREE is found (not shown). This is probably because the LREE-enriched heavy minerals (e.g. rutile, anatase) are apt to be deposited on the shelf of the GOP (or close to the base of the slope), and cannot be transported over long distances. By contrast, changes in sea level barely influence the sediment transport in northern PNG due to its active continental margin, resulting in the absence of glacial change in terrigenous records in core MD2920.

4.2.2. Different precession periods in glacial–interglacial cycles

It is interesting to note that the precession periods behave differently in strength for core KX21-2; both Fe and Ti records become stronger during glacials and weaker during interglacials (Fig. 8b, c). Continuous wavelet transform also reveals that statistical power exists for the precessional and glacial bands in ln (Fe/Total) and ln (Ti/Total) of core KX21-2 (Fig. 10). Comparatively, the energy distribution of Fig. 8a) Mean March insolation at 5°S (Laskar et al., 2004), b) and c) ln (Fe/Total) and ln (Ti/Total) for core KX21-2, with a 23 ka band-pass Gaussian filter (bandwidth 0.01), respectively, performed by AnalySeries 2.0.4.2 program (Paillard et al., 1996). d) In (Ti/Total) reported as 5-points running average. d) and e) Fe-bulk and Ti-bulk concentrations for core MD2920 (Tachikawa et al., 2011). f) ²³⁰Th-normalized detritus flux for core MD2920 (Shiau et al., 2012). g) Global mean sea level (Waehlbroek et al., 2002). h) Calculated NINO3 index—a SST anomaly used to measure the strength of modern ENSO events (Clement et al., 1999).
The precessional band ranging 16–32 ka is more coherent and higher for ln (Ti/Total) (Fig. 10), whereas the 100 ka glacial band is more important for ln (Fe/Total) (Figs. 8, 9).

In view of the coherence of precession periods and the consistency between Fe-bulk and Ti-bulk in core MD2920, the difference in the intensity of precession periods for core KX21-2 can be ascribed to variability of the southern PNG input and/or transport process. Since the terrigenous deposition in core KX21-2 is only from northern PNG during interglacials, the subdued precession periods of ln (Fe/Total) in the interglacials can be attributed to the weakness of the NGCUC. During glacials, increased fluvial input from southern PNG should have resulted in higher terrigenous supply to core KX21-2; apart from that, we argue that the enhanced undercurrents should also contribute to the well-developed precession periodicity in those periods. Firstly, considering an over 2/1 ratio of modern fluvial flux between the north coast of PNG and the GOP (Milliman et al., 1999), an increase in fluvial input from the relatively distant southern PNG alone cannot sufficiently account for the nearly doubled precessional increases in Fe supply for core KX21-2 during glacials (Fig. 7b–d). Secondly, given the differences in surficial geology of river catchments over PNG, increased Fe supply and co-varying Co/Th and Ni/Nb ratios in core KX21-2 (Fig. 7d–g) may at least partly result from an increase in fluvial input from a more mafic source, northern PNG rather than southern PNG. This is especially true when taking into account the opposite trend in core MD2920, with stronger precession periods during interglacials, indicative of the fluvial input of northern PNG (Fig. 8d, e).

Modern seasonal variability barely influences the NGCUC, but ENSO does. Observations indicate that as the NGCUC intensifies and shoals during El Niño events, it develops meanders and eddies that augment coupling of the northern PNG shelf to the EUC (Ueki et al., 2003; Ryan et al., 2006). Ample evidence points to reductions in the east–west sea surface temperature (SST) gradient, thermocline slope,
and trade wind strength in the equatorial Pacific during the last glacial, analogous to modern-day El Niño conditions (e.g., Lea et al., 2000; Koutavas et al., 2002; Stott et al., 2002; Koutavas and Lynch-Stieglitz, 2003). Palynological, geochemical, and sedimentological records from northern Australia and Indonesia also indicate an El Niño-like stage during glacial intervals, with drier conditions as a result of weaker monsoons (van der Kaars et al., 2000; Hesse and McIntosh, 2003; Kershaw et al., 2003; Thevenon et al., 2004; Kawamura et al., 2006). Meanwhile, the NGCUC cannot be induced only by wind and thermocline component is probably a key factor in balancing the volume transport between the ocean interior and western boundary (Ueki et al., 2003), just as the North Brazil Current does in the Atlantic (Johns et al., 1998).

The ENSO scenario also has implications for productivity. Modern observations explicitly show that a thermocline shoaling brings increased nutrients to the euphotic zone and, thus an increase in primary production (Li et al., 2011), as determined from boron isotopes (Palmer and Pearson, 2003). Similar to our terrigenous Fe records, paleoproductivity displayed precessional cycles under a glacial–interglacial contrast between the typical precession periods in precipitation records (Murray et al., 2012). Taking together, we deduce that during glacials an intensification of the NGCUC, linked to thermocline deepening associated with the La Niña-like conditions. The enhanced precessional variability during glacials should result from increased input from southern PNG on one hand, and intensified NGCUC on the other hand, because of thermocline shoaling accompanied by the ENSO-like conditions.

5. Conclusions

On the basis of provenance determination and reconstruction of Fe-enriched terrigenous sediments in core KX21-2, we reach the following conclusions for the western equatorial Pacific during the past 380 ka.

1) The fluvial input from PNG is the most important provenance of the Fe-enriched sediments in core KX21-2; eolian dust provides only a negligible contribution.

2) Variability of the Fe-enriched deposition in core KX21-2 displays prominent precession periods throughout the records, as well as a clear glacial–interglacial trend with higher input during glacial intervals. The former is correlated with precipitation over PNG, responding to the local summer insolation (5°S, March) and the meridional shifts of the ITCZ. The latter is induced by sea level changes that substantially influence the fluvial input of southern PNG.

3) The characteristics for precession period are different between glacial and interglacial in core KX21-2. This is closely related to the transport process of the undercurrent. The subdued precession periods during interglacials could be attributed to a weaker NGCUC, which is thought to result from changes in the east–west thermocline slope, related to the influence of tropical insolation on ENSO (Beaufort et al., 2001; Perkins et al., 2002; Li et al., 2011). Seasonal anomalies in insolation driven by precession could have changed ENSO behaviors, as shown by the calculated NINO3 index (Clement et al., 1999) (Fig. 8h). Besides, insolation could affect the thermocline by mediating the evaporation-induced subsidence of surface waters in the subtropical Pacific (Dang et al., 2012). The difference between the typical precession periods in precipitation records from MD2920 (23 ka) and MD2928 (21 ka), and the atypical precession periods in terrigenous Fe record from KX21-2 (~27 ka) (Fig. 9a) as well as tropical Pacific paleoproduction records (~30 ka) was non-linear characteristics of the orbital forcing and considered as a result of the unique ENSO (Beaufort et al., 2001; Thevenon et al., 2004).

Of particular significance, a clear positive relationship between Fe supply and opal accumulation was found in the central equatorial Pacific with higher values during glacial intervals, indicating that terrigenous Fe supply is a first-order control on the biogeochemical response through glacial–interglacial cycles (Murray et al., 2012). Taking together, we thus speculate that the stronger NGCUC during glacial intervals resulted from thermocline shoaling associated with the El Niño-like conditions, which should enhance the supply of Fe-enriched nutrients to the euphotic zone and the primary production; while the weaker NGCUC during interglacial would result from thermocline deepening accompanied by the La Niña-like conditions, leading to a lower productivity due to severe Fe-limitation. If this holds true, it could potentially contribute to the glacial–interglacial difference in the CO2 budget.

Furthermore, we deduce that during glacial an intensified NGCUC could have transported more fluvial inputs from the whole PNG, but southern PNG should only provide a smaller portion of coarse river sediments that are enriched in Ti. This is based on 1) the more coherent precessional variations shown in Fig. 10, as well as the reduced glacial changes in ln (Ti/Total) than in ln (Fe/Total) for core KX21-2 (Fig. 8, 9), 2) the lower Ti concentrations in the fluvial sediments of southern PNG (Fig. 2; Table 1), and 3) the Ti being primarily hosted in coarse, heavy minerals that would be preferentially settled during transport, in conjunction with the longer distance from southern PNG to core KX21-2. This inference is in agreement with our REE results, suggesting that the LREE-enriched minerals (e.g., rutile, anatase) tend to be preferentially deposited on the southern PNG shelf. Therefore, the majority of changes in the ln (Ti/Total) for core KX21-2 represent the input from northern PNG. In turn, it could be used to reconstruct the glacial changes in the NGCUC. The lower coherence between ln (Ti/Total) and 5°S March insolation for precessional band is possibly due to the NGCUC influences (Fig. 9). Our records suggest that the NGCUC was particularly stronger in MIS 6 and 10, and weaker in MIS 8 (Fig. 8c).

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