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Radionuclide and biomarker proxies of past ocean circulation and productivity in the Arabian Sea

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[1] We present new excess $^{231}Pa/^{230}Th$ activity ratios and lipid biomarker results from northeastern Arabian Sea sediments (core 93KL) spanning the past 50 ka in an effort to constrain further the relationship between climate at low and high latitudes. $^{231}Pa/^{230}Th$ activity ratios are maintained at values significantly higher than the water-column production ratio of 0.093. Average $^{231}Pa/^{230}Th$ activity ratios are lower during the last glacial period than during the Holocene. The lowest $^{231}Pa/^{230}Th$ activity ratios coincide with the timing of Heinrich Events 1–5. Profiles of lipid biomarker fluxes and $^{231}Pa/^{230}Th$ activity ratios from 32 to 12 ka show similar patterns, suggesting that ^{231}Pa is more efficiently scavenged relative to ^{230}Th at times when diatoms make up a proportionally larger part of the primary biomass signal. In the Holocene, high $^{231}Pa/^{230}Th$ activity ratios may indicate enhanced ^{231}Pa export from the southern to the northern Indian Ocean via intensified thermohaline circulation. **Citation:** Pourmand, A., F. Marcantonio, T. S. Bianchi, E. A. Canuel, and E. J. Waterson (2005), Radionuclide and biomarker proxies of past ocean circulation and productivity in the Arabian Sea, *Geophys. Res. Lett.*, *32*, L10610, doi:10.1029/2005GL022612.

1. Introduction

[2] High-frequency Dansgaard-Oeschger (D-O) cycles first recognized in the Greenland ice cores [*Dansgaard et al.*, 1993; *Grootes et al.*, 1993] represent intense (stadial) and intermediate (interstadial) cold intervals during the last glacial period that vary with 1000-, 1450-, and 3000-year frequencies. These cycles are associated with lower-frequency Heinrich events of massive iceberg discharge into the North Atlantic Ocean [*Bond et al.*, 1993; *Heinrich*, 1988] and are not limited to changes in the climate of the North Atlantic, but have been found to be global in extent [e.g., *Altabet et al.*, 2002; *Behl and Kennett*, 1996; *Peterson et al.*, 2000; *Schulz et al.*, 1998; *Stott et al.*, 2002]. In the Arabian Sea, high-resolution studies of variations in primary productivity proxies (e.g., organic carbon content [*Schulz et al.*, 1998] and $\delta^{15}N$ [*Altabet et al.*, 2002]) have shown an atmospheric linkage between North Atlantic and low-latitude climate change. Periods of a strengthened southwest monsoon, during which upwelling is intensified, are consistent with the timing of D-O interstadials [*Altabet et al.*, 2002; *Pourmand et al.*, 2004]. Here, we employ a multi-proxy approach to constrain the causes of, and responses to, abrupt climatic change in the northeastern Arabian Sea (core 93KL; 23° 35′N, 64° 13′E; water depth of 1,802 m) over the past 50 ka.

[3] ^{231}Pa and ^{230}Th are produced at constant rates throughout the water column from radioactive decay of ^{235}U and ^{234}U, respectively ($^{231}Pa/^{230}Th$ production ratio = 0.093). Unlike U, which behaves conservatively and has an oceanic residence time (τ) of ~400,000 yr [*Palmer and Edmond*, 1993]), both Pa and Th ($\tau_{Pa} \sim 130$ yr, $\tau_{Th} \sim 20$ yr [e.g., *Henderson and Anderson*, 2003]) isotopes are rapidly scavenged by settling particles and accumulate on the seafloor in activities not supported by the amount of parent uranium present in the sediment. Because of their differing geochemistries and, hence, residence times, sedimentary excess $^{231}Pa_o/^{230}Th_o$ activity ratios (excess $^{231}Pa/^{230}Th$ activity ratios corrected for radioactive decay since deposition; hereafter referred to as $^{231}Pa/^{230}Th$) are rarely equal to the production ratio of 0.093 in the oceanic water column. Indeed, changes in these ratios through time, as archived in sediments, yield information on variations in past particle fluxes (i.e., proxy for surface water productivity [*Kumar et al.*, 1995]), particle composition (i.e., proxy for the planktonic community structure [*Chase et al.*, 2002]), or even changes in thermohaline circulation [*McManus et al.*, 2004; *Yu et al.*, 1996].

2. Methods

[4] Sediment was sampled between depths of 5 and 477.5 cm spanning the past 50 ka in core 93KL (see Figure 1 of *Pourmand et al.* [2004] for location). All samples were spiked with ^{233}Pa (half-life of 26.9 days) and digested with concentrated HNO_3, HF, HCl and $HClO_4$ in accordance with the procedure described by *Lao et al.* [1992]. ^{231}Pa was isolated and purified using ion exchange chromatography and analyzed by isotope dilution analysis on an Element 2 Inductively Coupled Mass Spectrometer (ICP-MS) at Tulane University. Replicate analyses indicate an average external reproducibility of less than 3% for ^{231}Pa.

[5] In order to calculate $^{231}Pa/^{230}Th$ ratios, corrections need to be applied for a) the ingrowth of ^{231}Pa and ^{230}Th from authigenic U and b) the supported activities of ^{231}Pa and ^{230}Th in the detrital fraction. ^{230}Th activities for the samples analyzed here for ^{231}Pa are reported by *Pourmand et al.* [2004]. It has been shown that in the majority of the world's oceans the flux of ^{230}Th to the sediments is equal to its production rate in the overlying water column [e.g.,

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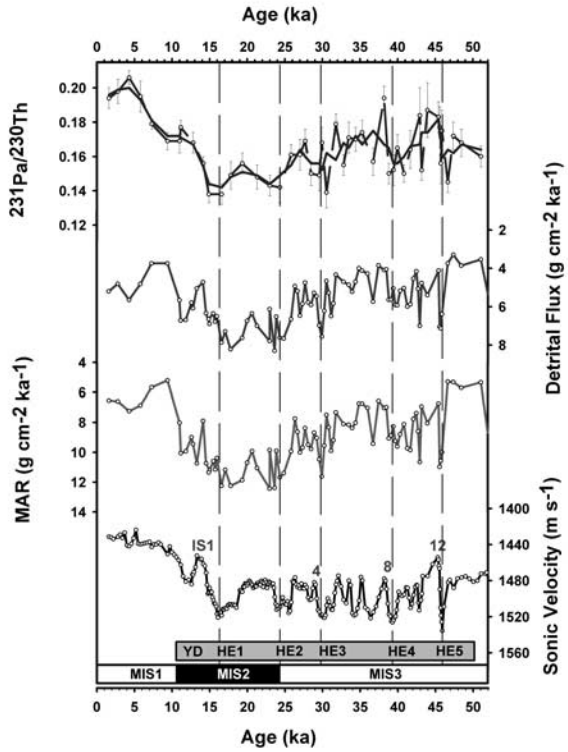

Figure 1. $^{231}Pa/^{230}Th$ activity ratios, detrital fluxes [*Pourmand et al.*, 2004], ^{230}Th-derived MARs [*Pourmand et al.*, 2004], and sonic velocity [*Schulz et al.*, 1998] in core 93KL. In top panel, the dashed line connects individual data points, while the solid line represents a 3-point running mean. Minima in $^{231}Pa/^{230}Th$ ratios correspond to the timing of North Atlantic Heinrich Events (vertical dashed lines). See color version of this figure in the HTML.

Henderson et al., 1999]. This forms the basis for using ^{230}Th measurements in sediments as a constant-flux proxy to calculate sediment mass accumulation rates (MAR) (see review by *Francois et al.* [2004]).

[6] Lipid biomarker compounds were extracted from dried sediment samples using ethylene chloride and methanol (2:1, v:v) and accelerated solvent extraction. The extracts were concentrated by turbo evaporation and saponified using 1N KOH in aqueous CH_3OH (10% H_2O) [*Canuel and Martens*, 1993]. The neutral lipid fraction was separated into its constituent lipid classes using silica gel chromatography. Sterols were converted to their trimethylsilyl (TMS) ether derivatives at 80°C using bis(trimethylsilyl) trifluoroacetamide (BSTFA) and acetonitrile. The sterols were analyzed using a Hewlett-Packard 5890 Series II gas chromatograph (GC) with injections made in the on-column mode. Detection was by flame ionization detection, and compound identifications were confirmed by gas chromatography and mass spectrometry.

3. Discussion

[7] The sonic velocity profile from core 93KL in the northeastern Arabian Sea was originally used by *Schulz et al.* [1998] to correlate the timing of events in this sediment archive with those in the Greenland ice core and, therefore, North Atlantic climate change. In core 93KL, sediment $^{231}Pa/^{230}Th$ ratios are significantly higher than 0.093 over the past 50 ka, with the highest ratios occurring during the Holocene (Figure 1). Similar Holocene and glacial $^{231}Pa/^{230}Th$ ratios have been reported in western Arabian Sea sediments [*Marcantonio et al.*, 2001]. The lowest $^{231}Pa/^{230}Th$ ratios coincide with the timing of Heinrich Events (HE) 1 through 5 (smoothed 3-point running mean; solid line in Figure 1). Although $^{231}Pa/^{230}Th$ ratios during the Younger Dryas (YD) do not reach values as low as those during the HEs, the rate of increase in $^{231}Pa/^{230}Th$ ratios declines significantly during the deglaciation and reaches a plateau at a time consistent with the timing of the YD.

[8] The residence time of ^{231}Pa in the ocean is sufficiently long to allow migration of dissolved ^{231}Pa from oligotrophic regions with low particle fluxes to continental margins, where high rates of primary production and/or high lithogenic fluxes enhance ^{231}Pa removal from the water column [*Anderson et al.*, 1983]. We have previously shown that there is little to no lateral redistribution of sediments at 93KL, and that the vertical flux of particle rain controls the average sediment accumulation rates during the last 110 ka [*Pourmand et al.*, 2004]. If higher particle fluxes were to play a prominent role in controlling the $^{231}Pa/^{230}Th$ ratios at 93KL, one would expect a positive relationship between these ratios and the vertical particle flux, as measured by the ^{230}Th-derived MARs. Instead, the highest MARs, coincident with the timing of the HEs, are associated with the lowest $^{231}Pa/^{230}Th$ ratios (Figure 1). Hence, *changes* in particle flux do not seem to control the *variations* in $^{231}Pa/^{230}Th$ ratios over the past 50 ka in this part of the Arabian Sea.

[9] Another factor that might be called upon to explain variations in the $^{231}Pa/^{230}Th$ ratio is particle composition. Recent studies have shown that particles differ in the efficiency with which they scavenge ^{231}Pa and ^{230}Th [e.g., *Chase et al.*, 2002]. ^{230}Th, for example, may be preferentially scavenged by clay particles, such that decreases in sediment $^{231}Pa/^{230}Th$ ratios may reflect a decrease in the ratio of the fractionation factors of ^{231}Pa and ^{230}Th as lithogenic content increases [*Luo and Ku*, 2004]. Therefore, an increased flux of detrital material in the NE Arabian Sea at times consistent with the timing of HEs [*Pourmand et al.*, 2004] might be invoked to explain the low $^{231}Pa/^{230}Th$ ratios. However, sediment inventories of excess ^{230}Th indicate that the flux of excess ^{230}Th has been equal to its production rate, even given the high lithogenic MARs. Indeed, ^{230}Th-derived MARs are almost identical to those calculated using independently-derived sediment age models, suggesting that high lithogenic clay contents do not bias the measured ^{230}Th concentrations. In addition, we note that there are experimental [*Geibert and Usbeck*, 2004] and world ocean sediment data [*Chase and Anderson*, 2004; *Chase et al.*, 2002] which suggest that preferential adsorption of ^{230}Th by clays is not likely to occur.

[10] ^{231}Pa, in contrast, is believed to be preferentially scavenged by opal, resulting in increased $^{231}Pa/^{230}Th$ ratios in regions that have diatoms as the predominant primary producer. Because opal preservation is low and variable [e.g., *Sayles et al.*, 2001], a proxy for approximating past diatom accumulation rates is needed to test the role that

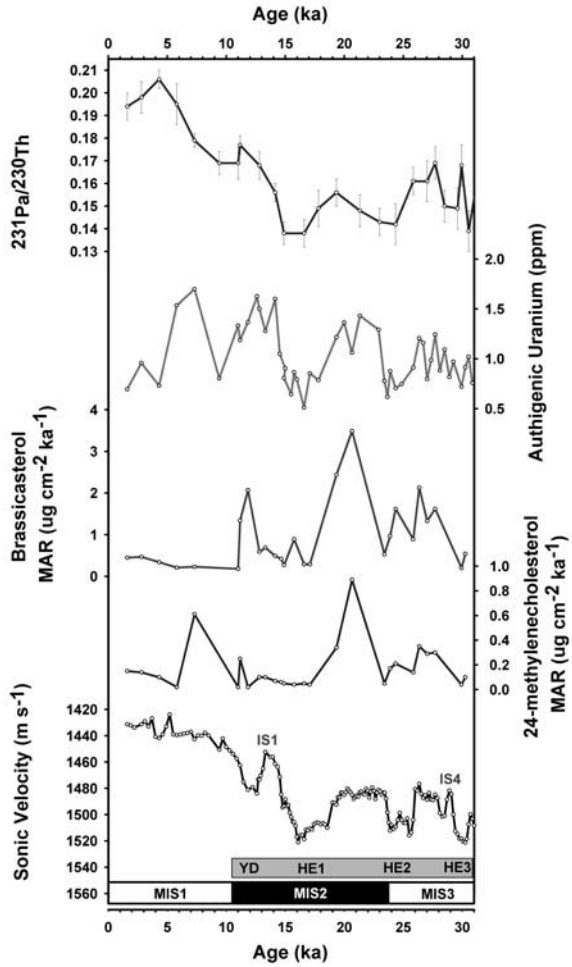

Figure 2. High fluxes of diatom biomarker compounds (brassicasterol and 24-methylenecholesterol) coincide with high authigenic uranium concentrations. Such high biomarker fluxes are likely associated with increased production of diatoms. Except during Holocene time, high $^{231}Pa/^{230}Th$ ratios are coincident with peaks in the fluxes of diatom biomarkers, suggesting an increased scavenging efficiency of ^{231}Pa by diatoms. See color version of this figure in the HTML.

silica plays in controlling $^{231}Pa/^{230}Th$ ratios. Two lipid biomarker compounds, brassicasterol (24-methylcholesta-5,22-dien-3β-ol) and 24-methylenecholesterol (24-methylcholesta-5,24(28)-dien-3β-ol), are abundant in most diatoms species and can be used to trace inputs of diatom phytodetritus to sediments [e.g., *Volkman*, 1986]. Figure 2 shows ^{230}Th-derived lipid biomarker MARs over the past 32 ka. We interpret these biomarker fluxes in a qualitative manner, i.e., the relative changes through time are meaningful whereas changes in the absolute amount are not. During marine oxygen isotope stages (MIS) 2 and 3 the pattern of change of both lipid biomarker MARs is coincident with that of the $^{231}Pa/^{230}Th$ ratios (Figure 2). Minima in both lipid biomarker MARs coincide with lows in $^{231}Pa/^{230}Th$ ratios that are coincident with the timing of North Atlantic HEs 1, 2, and 3. In addition, high brassicasterol and 24-methylenecholesterol fluxes generally correlate with peak authigenic uranium concentrations. This corroborates our suggestion [*Pourmand et al.*, 2004] that authigenic uranium concentrations in the Arabian Sea reflect the export of particulate organic carbon (derived from surface water production) to the underlying sediments.

[11] In the Holocene, however, the relationships between $^{231}Pa/^{230}Th$, the two biomarkers, and authigenic uranium are not as straightforward. The brassicasterol MARs peak during the YD and the 24-methylenecholesterol MARs peak subsequent to the YD in the mid-Holocene. This decoupling of the biomarkers suggests that after the deglaciation a change in planktonic community structure occurs with respect to the diatom speciation. Specifically, the species that produce the brassicasterol are significantly less abundant than those that produce the 24-methylenecholesterol. Although the two biomarker compounds are generally attributed to diatoms, they are not exclusive to diatoms and their abundance varies by diatom species [*Volkman et al.*, 1998]. Importantly, the authigenic uranium concentration does not discriminate between various types of organic particles exported to the sediment.

[12] The lipid biomarkers and the $^{231}Pa/^{230}Th$ ratios record the same pattern of change from 32 to 12 ka, suggesting that ^{231}Pa is more efficiently scavenged relative to ^{230}Th at times when diatoms make up a proportionally larger part of the primary biomass signal. During the Holocene, however, the lipid biomarker data indicate that $^{231}Pa/^{230}Th$ is being controlled by something other than particle composition. One plausible explanation is that enhanced export of ^{231}Pa to this region of the Arabian Sea results from changes in water mass circulation. In the Atlantic Ocean, $^{231}Pa/^{230}Th$ ratios have been shown to be a useful proxy for changes in thermohaline circulation [*McManus et al.*, 2004; *Yu et al.*, 1996]. High ratios, close to the production value of 0.093, during the YD and HE1 have been interpreted as evidence for a slowdown in NADW formation. Lower $^{231}Pa/^{230}Th$ ratios (~0.05–0.06) in the Holocene, on the other hand, suggest higher ventilation rates and strong production of NADW [*McManus et al.*, 2004]. In the Holocene, it is estimated that about 50% of North Atlantic ^{231}Pa is exported to the south via the lower limb of the thermohaline conveyor (i.e., NADW) [*Yu et al.*, 1996, 2001]. Several studies have suggested that most of this Pa is scavenged by the high opal flux in the southern ocean [e.g., *Chase et al.*, 2002]. However, escape and export of Atlantic ^{231}Pa into the Pacific or Indian Ocean basins cannot be ruled out. There are some data from the modern-day southern Indian Ocean suggesting that open-ocean excess ^{231}Pa concentrations are enhanced as a result of transport of NADW into the Indian Ocean [*Thomas et al.*, 2004].

[13] We propose that sedimentary $^{231}Pa/^{230}Th$ ratios in the Indian Ocean may be the complement to those observed in sediments from the Atlantic Ocean [*McManus et al.*, 2004]. Specifically, during the Holocene, Arabian Sea sedimentary $^{231}Pa/^{230}Th$ ratios may be high due to enhanced thermohaline input of excess ^{231}Pa into the Indian Ocean. A decreased input of ^{231}Pa, due to weakened thermohaline circulation, might be the cause of the lower $^{231}Pa/^{230}Th$ ratios observed during MIS 2 and 3. Superimposed on the large glacial-interglacial differences in ^{231}Pa input, it is possible that there are smaller millennial-scale variations

in ^{231}Pa during MIS 3 related to changing patterns of deep-ocean circulation. ^{231}Pa and silica may be supplied to the Indian Ocean during periods of strengthened thermohaline circulation, though this cannot be resolved with the available data. There is Pa/Th evidence for millennial changes in thermohaline circulation during MIS 3 in the North Atlantic [*Major et al.*, 2004]. Radionuclide and biomarker data from additional cores in the Atlantic and the Indian Ocean are needed in order to test this hypothesis more rigorously.

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