Precession control on sedimentary burial of organic matter and redox sensitive metals in the tropical Indian Ocean

D. Pailler
F. Rostek
E. Bard
CEREGE, Europole de l'Arbois BP80, 13545 Aix-en-Provence cdx 4, France

A. van Geen
R. Mortlock
Y. Zheng
Lamont-Doherty Earth Observatory of Columbia University, Palisades NY 10694, USA

The total organic carbon (TOC) content of oceanic sediments and the total concentrations of several biomarkers are commonly used as qualitative palaeoproductivity proxies. However, fluctuations of these proxies may also be influenced by the variability of secondary processes taking place in the water column and in surface sediments. Past redox conditions of bottom and sediment pore waters are important parameters that can be studied by measuring the concentrations of redox-sensitive trace metals in the authigenic phases of the sediment.

Here, we present a 330 kyr record of organic carbon, total alkenone and authigenic trace metal (U, Cd and Mo) in order to better understand how primary productivity and secondary physico-chemical processes are linked to each other and could explain the TOC variability. Core MD900963 is a 54 m long piston core recovered in the eastern part of the tropical Indian Ocean near the Maldives platform (05°04'N/ 73°53'E; 2450 m water depth). At this location the present day bottom water oxygen is about 130 μmol/l and the primary productivity is about 160 $gCm^{-2}yr^{-1}$ (Antoine *et al.*, 1996). Core MD900963 is well dated by orbital tuning of a high resolution $\delta^{18}O$ record measured on planktonic foraminifera (Bassinot *et al.*, 1994). The studied first 16 meters of the core span the last 330 kyr which translates to an average sedimentation rate of about 5 cm/kyr. Palaeoproductivity was estimated from independent biological indices based on statistical transfer functions using coccoliths or planctonic foraminifera distributions (Beaufort *et al.*, 1997; Cayre *et al.*, 1998). These two records suggest that during a typical 22 kyr cycle the primary productivity varied by roughly a factor of two: between *c.* 200–300 $gCm^{-2}yr^{-1}$ during glacial stages (high $\delta^{18}O$) and *c.* 100–150 $gCm^{-2}yr^{-1}$ warm interstadials (low $\delta^{18}O$).

The bulk sediment concentrations (in ppm) of U, Mo, Cd and Th were measured by isotope dilution ICP-MS following the methods of Zheng *et al.* (1998). During the course of our measurements we estimate the reproducibility to about 3–5% based on replicate analyses of a sediment standard. Authigenic U concentrations were obtained by subtracting a terrigenous component based on the Th concentrations and an aragonitic component based on X-ray analyses of the sediment fine fraction (Haddad, 1994). In general both corrections are small, i.e. less than 10% of the total U concentrations. On the same samples we measured the concentrations of TOC (wt.%) and of C37 alkenones (Tot-C37alk in μg/g), which are synthesized by several species of coccolithophorids. Both proxies were measured by gas chromatographic techniques (see Verardo *et al.*, 1990 for TOC and Sonzogni *et al.*, 1997 for alkenones). By replicating measurements on sediment standards we estimate that reproducibilities for TOC and Tot-C37alk are on the order of 5 and 15%, respectively.

The TOC values are rather low and vary between 0.25 and 0.85% while the Tot-C37alk exhibit larger variations between 0.2 and 7 μg/g. Both records are very well correlated and are dominated by a clear cyclicity on the order of 22 kyr, with high concentrations during glacial stages (high $\delta^{18}O$) and low values during warm interstadials (low $\delta^{18}O$). Authigenic U concentrations range between 0.5 and 5.5 ppm, those of Cd vary between 0.3 and 1.9 ppm and those of Mo between 0.2 and 1.2 ppm which are comparable to the range of values reported by Rosenthal *et al.* (1995) and Crusius *et al.* (1996). Authigenic metals concentrations are also characterized by large and systematic fluctuations with a clear 22 kyr cyclicity and are positively correlated with records of TOC and Tot-C37alk. The clearest correlation with biomarkers and the strongest 22 kyr cyclicity are observed for the U record. This is partly due to its rather high values (about 2.5 ppm on average) when compared to Mo and Cd concentrations which are closer to crustal values. However, it is also clear that the Mo profile does not register all 22 kyr peaks that are so well recorded by other tracers (TOC, Tot-C37alk, U and Cd). These relationships are also valid for records of mass accumulation rates (MAR) of these compounds which take into account the relatively small changes of sedimentation rate.

The cyclic and coherent variations of TOC, Tot-C37alk and authigenic trace metals are highly correlated with palaeoproductivity indices using coccoliths and foraminifera, probably in response to primary productivity variations linked to the insolation precessional cycle (22 kyr). The rather low concentrations of Mo (about 0.5 ppm on average) suggest that at this location oceanic bottom waters did not become anoxic, in contrast with the conclusion by Sarkar *et al.* (1993). The range of metal concentrations in core MD900963 is compatible with removal from sea water by diffusion into pore waters and subsequent precipitation below the sediment-water interface. Part of the U and Cd enrichments in excess of the crustal concentrations may have already originated in the water column in association with plankton matter.

The metal maxima every 22 kyr suggest more reducing conditions in glacial stages sediments in response to the increased primary productivity evidenced by biomarkers and micropalaeontological proxies. During high primary productivity periods, the organic matter burial increased which led to shoaling of the redox front in the sediment interstitial waters. This in turn enhanced the diffusion of dissolved metals from sea water into depleted pore waters. U and Cd were then precipitated in the suboxic zone and Mo in the deeper and anoxic part of the sediment column. A reduction in bottom water oxygen in response to increased productivity could also have resulted in a contribution from a higher flux metal-enriched plankton matter reaching the sediment. Decoupling between U, Cd and Mo concentrations is observed for several palaeoproductivity peaks (e.g. at about 210 kyr BP) which could be due to different behaviours of these metals: for example some Cd and U can also brought directly with organic matter and Mo responds to stronger reducing conditions than the two other metals. A threshold effect could be invoked to explain the observed differences: the primary productivity being high enough to lead to U and Cd enrichments but insufficient for the precipitation of Mo. For this latter metal there may have been an additional effect linked to a reduction of the oxygen content of deep waters.

References

Antoine, D., Andre, J.-M. and Morel, A. (1995) *Global Biogeochem. Cycles*, **10**, 57–67.

Bassinot, F.C., Labeyrie, L.D., Vincent, E., Quidelleur, X., Shackleton, N.J. and Lancelot, Y. (1994) *Earth Planet. Sci. Lett.*, **126**, 91–108.

Beaufort, L., Lancelot, Y., Camberlin, P., Cayre, O., Vincent, E., Bassinot, F. and Labeyrie, L. (1997) *Science*, **278**, 1451–545.

Cayre, O., Beaufort, L. and Vincent, E. (1998) *Quat. Sci. Rev.*, in press.

Crusius, J., Calvert, S., Pedersen, T. and Sage, D. (1996) *Earth Planet. Sci. Lett.*, **145**, 65–78.

Haddad, G. (1994) PhD, Rice University, Houston Texas, 483 pp.