

Geochemical proxies for understanding Paleocyanography

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Last two decades have witnessed an upsurge in the interest to study the subject of paleocyanography. Paleocyanography deals with all the factors that may be physical, geological, chemical or biological that make up the oceans. As the science is all about "paleo", we need good proxies about each variable which control the state of the oceans. As explained in the review by Wefer et al. (1999), a *proxy* is used in its literal sense, which means a stand-by. A proxy is usually a measurable parameter which represents a parameter which cannot be studied at the time of measurement. For example, if one needs to know the sea surface temperature (SST) variation of past ten thousand years, there are no human records. As a proxy, we probably can use oxygen isotopes in the foraminifera. Surface dwelling foraminifera would record the information of the SST prevailing at the time of their calcification. For paleocyanographic studies, various techniques comprising of sediment texture, magnetic properties, micropaleontology, geophysical, geochemical, mineralogical, isotopes etc. are used. Extensive data sets generated are treated statistically, sometimes employing latest techniques such as Neural networks to interpret the data. This field of study is relying more and more on the multi-proxy data. In this talk, emphasis will be on inorganic geochemical tracers, though I would tread on other subjects when necessary.

Provenance changes

Provenance indicates the source terrain composition and it is an important component of paleo-research. Provenance can be determined using mineralogical and geochemical tracers. Among the geochemical tracers, refractory elements such as Ti, Al, Sc, Zr are important in assigning the source candidates. In addition, more and more of radiogenic tracers such as Nd and Pb isotopes are used in interpreting the source composition. Provenance changes can be brought about mainly by terrigenous and submarine volcanic sources.

Terrigenous sedimentation is the most significant process in terms of size and volume. The annual delivery of all types of terrigenous material to the oceans is about 25 to 33 billion tons/yr compared to ~2-3 billion tons/yr of volcanogenic sedimentation and ~1.8 billion tons/yr of

biogenic sedimentation. For discussing the importance of terrigenous sedimentation, data on the sediments influenced by major river systems would be useful. Among many rivers which contribute the continental sediments to the oceans, the Ganges-Brahmaputra system contributes a substantial proportion. The Bengal Fan is built by several cycles of turbiditic sedimentation. Turbidities dissipate the energy built-up in the continental slope area through mass flows. While studying the clay minerals of the deep basins of both sides of the Ninety East Ridge, illite-rich turbiditic sediments derived from the Ganges-Brahmaputra were found in distal areas. Later studies using clay minerals have also shown that the turbiditic sediments were found as south as 8°S. Based on several geochemical tracers, such as the distributional trends of detrital elements, Al, Ti, Fe contents, Al/(Al+Fe+Mn) ratios and the multivariate statistical analyses of geochemical data has shown that the terrigenous flux from the G-B river systems into the northern part of the Central Indian Basin up to 8°S. The argument was further strengthened by rare-earth element geochemistry of the Central Indian Basin sediments. Among the five sediment types studied, the terrigenous sediments from the northern portion has shown flat shale-normalized REE patterns, and Ce/Ce* anomaly values close to unity. In addition, the lanthanum in excess to what can be supplied by the continents was the lowest compared to the other sediments. The absence of Ce fractionation and low L_{excess} values indicate that these sediments are dominated by included terrigenous particulate matter with Ce/Ce* close to 1.

Porewater studies on these sediment cores from north to south have also shown that the northernmost core falling in the zone of terrigenous sediments has no diffusional gradient in porewater nitrate concentrations compared to southern areas probably due to pulses of turbiditic sedimentation. Further geochemical and isotopic investigations clearly pointed out to the Himalayan rocks and the Indo-Gangetic Plain as the chief source area. High Th/Ta ratios were found which are typical of the orogenic calc-alkaline rocks characterizing most Himalayan rocks. Sr-Nd isotope data of sediments scattered between two end-members namely the Himalaya and the seawater.

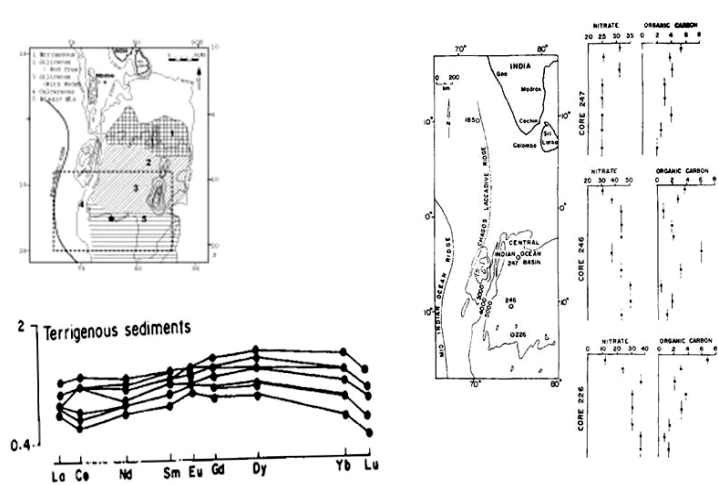


Fig.1. Sediment types are shown in the top left panel. Shale-normalized REE patterns of type 1 sediments representing the terrigenous sediments are nearly flat with a lack of light to heavy REE fractionation (on the bottom left). Porewater nitrate concentrations from the northern portion of the Central Indian Basin with suggested terrigenous influence has no diffusional gradient. Compare it with southern cores from biosiliceous sediments, where the diffusional gradients of nitrate are well defined and show a mirror image relation with sedimentary organic matter.

The contribution of terrigenous component to the marine sediments can be calculated from the concentration of Ti using the equation:

$$\text{Terrigenous \%} = \left(\frac{T_{\text{total}}}{T_{\text{PAAS}}} \right) \times 100 \text{ (Schroeder et al., 1997),}$$

PAAS representing the post-Archaean Australasian shale. Aluminium or titanium are generally used to calculate the terrigenous components. However, Ti is preferred over Al due to the possibility of large scavenged component of Al in the equatorial areas with pelagic sediments.

Titanium in PAAS (0.6%) is close to other shale values and average pelagic clay (0.55% and 0.5% respectively). The formula may not *stricto sensu* represent the entire lithogenic material as the basalts may have larger Ti contents than PAAS and might contribute Ti to the sediments during the weathering.

On the other hand, the nonlithogenic (NL) fraction has been calculated as the difference between the total and lithogenic composition:

$$Me_{\text{NL}} = Me_{\text{total}} - [Al_{\text{total}} (Me/Al)_{\text{crust}}]$$

This calculation assumes that all Al is lithogenic rather than the result of scavenging or biogenic production and is a reliable indicator of aluminosilicate materials. These are reasonable assumptions given the nearshore location of this study area and likelihood of significant terrigenous input.

Chemistry indicating clay-type

Clay minerals can be diagnostic of climatic changes, as chlorite forms in high latitude, physical weathering regime compared to kaolinite which is predominantly a chemical weathering product and typical of tropical, humid climate conditions. Therefore, the clay mineral studies assume importance in interpreting past climatic and weathering regimes in the source areas. It is now proved equivocally that the chemical weathering is an important sink for atmospheric CO₂. Though, the clay minerals can be easily determined using X-ray diffraction techniques, most of the methods are semi-quantitative in nature. Substituting geochemical data as a proxy for clay mineral changes would be useful, as the major elements can be determined precisely with the available geochemical techniques. Changes in clay mineral with time can be deduced from elemental ratios. For example, K/Al can be used to determine the ratio of illite to kaolinite. clay minerals such as illite. The major element chemistry of the clay fraction in sediments is controlled by variation in K, Al, Mg, Si and Fe. The K content of clayey sediments is primarily bound to clay minerals, potassium feldspars and mica and basalts contain less K. No detectable K contents are noticed in biogenic material such as forams and other calcareous biota and negligible quantities in siliceous sponges. Moreover, illite-rich clays are considered as sinks for K.

K₂O/Al₂O₃ ratio, which is used an index of alteration, has been used to decipher episodes of Himalayan orogeny and erosion from the sediment cores from the northern part of the Central Indian Basin. Two layers with micaceous sediments show a ratio around 0.2, which match with those found in the distal Bengal Fan sediments (ODP 116) younger than 1Ma and fall

within the range of Higher Himalayan Crystalline series. Though both illite and kaolinite are aluminosilicates, K is present in illite and not in kaolinite. Therefore, K/Al ratios should reflect the variation of these two minerals. Higher K_2O/Al_2O_3 ratios indicate the dominance of illite and also imply a physical erosion of high-grade metamorphic rocks such as HHC. The ratios also reflect the mixing of

a 'primary' end member composed of illite derived from micas ($K_2O/Al_2O_3=0.33-0.45$) and a secondary end member chlorite ($K_2O/Al_2O_3=0$). In addition, other tracers such as K/Ti and Ca/Ti, along with rare-earth element fractionation indices have been used clearly to distinguish the HHC derived sediments from the normal pelagic clays.

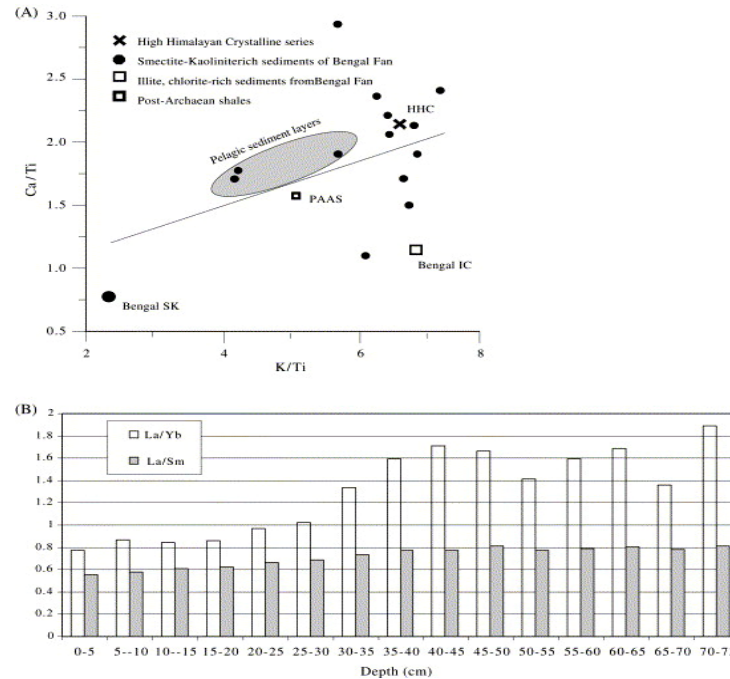


Fig. 2. (A) Plot of Ca/Ti versus K/Ti (bulk analyses of sediments) shows that the sediment sections containing mica fall in an array close to the composition of HHC series and illite+chlorite-rich clays of the Bengal Fan and away from smectite+kaolinite-rich clays. The sediment layers with pelagic signatures plot on the linear regression line, but fall away in a different array. (B) Variation in REE fractionation indices with depth. Changes at 20–25cm and 35–40 cm are drastic. The top four sections have lower La/Yb ratios than the typical ratios for continentally derived material.

K/Al ratios have also been used to determine the long term restoration pattern of an artificially disturbed abyssal seafloor.

Ti/Al ratio as paleostream indicator

The TiO_2/Al_2O_3 ratio in sediments has been tentatively used to deduce past changes in shallow-water stream energies. This approach relies on the fact that in crustal rocks titanium typically exists in insoluble, heavy minerals such as ilmenite, rutile, anatase and sphene. Disaggregation during weathering and subsequent transport with river water leads to hydrodynamic sorting of the crustal matter, and the higher the energies of the suspended matter, the larger will be the fraction of Ti-bearing minerals relative to Al-rich clay minerals. Laboratory experiments confirm that the TiO_2/Al_2O_3 ratio may be a tool as useful as particle size measurements to estimate the energy of a depositional environment. Under controlled conditions the resolution of the indicator is very high, and fractionation is easily recordable, even

in the particle size range 1-4 μm . In natural environments, on the other hand, application of the index may be complex due to differences in the composition of source rocks. In the deep-sea environment the use of the TiO_2/Al_2O_3 stream energy index is complicated by the ubiquitous occurrence of TiO_2 -rich seafloor basaltic matter. For instance, it was shown that the TiO_2/Al_2O_3 ratio in deep-sea sediments decreases with increasing distance from the volcanic islands.

In five Deep Sea Drilling Project cores (213 217), which have been recovered in, and south of, the Bay of Bengal, TiO_2/Al_2O_3 ratios increase linearly with time from the Late Miocene to Recent. The increase reflects fan progradation and intensified bottom current activity on the southern Bengal Fan. These processes are related to the Himalayan elevation by factors such as the maturation of northern India river systems, evolution of orographic monsoon rains and elevation-attributed increases in denudation rates.

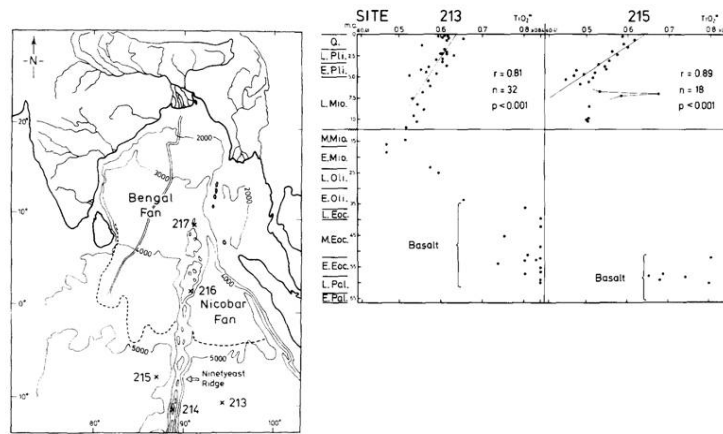


Fig. 3. Map of Bay of Bengal and central-eastern Indian Ocean with DSDP sites marked out. The dotted line shows approximate boundaries of the Bengal and Nicobar Fans. On the right, the distribution of TiO_2^* in DSDP cores drilled on the sea floor adjacent to the Ninetyeast Ridge showing clear variations in the Cenozoic time scales indicating the change in intensity of stream energy index.

From an area with a well constrained source terrain composition, it was shown that Co and Cr are susceptible to secondary alteration. With the support of major and trace element data, it was demonstrated that REEs, high field strength elements, Th and Sc are good indicators of provenance. The ratios and discrimination plots involving REEs and refractory elements such as Ta, Zr, Hf and Th can be used in deciphering provenance from ancient sedimentary sequences, and discriminants involving Co, Cr, and U should be used with caution.

Index of alteration

The chemical index of alteration (CIA = molar ratio of $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)] \times 100$), is calculated from the major element results. This parameter quantifies more precisely the effect of chemical weathering on the rocks by loss of the labile elements Na, Ca and K. CIA for all feldspars is 50, and the mafic minerals biotite, hornblende and pyroxenes have CIA

values of 50–55, 10–30 and 0–10, respectively. The secondary clay minerals and chlorite have CIA values of 100; illite and smectite, 70–85. Consequently, the CIA reflects the proportions of primary and secondary minerals in bulk samples. If the chemical response to climatic changes is rapid enough, then the CIA can be used as a climatic indicator.

Index of alteration has been estimated for the modern sediments from the southwestern coast of India and found that these areas are sinks for atmospheric carbon dioxide. CIA values were also compared with the sediment magnetic properties and the alteration over two cycles of glacial-interglacial time-scales from the Andaman Sea and the Bay of Bengal and it was found that the alteration is more intense during the southwest monsoon periods. Alternate indices of plagioclase feldspar dissolution and index of weathering have also been designed from major element ratios.

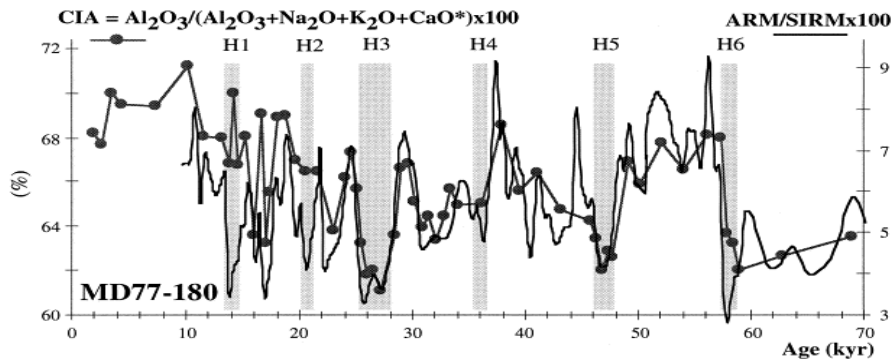


Fig.4. Chemical index of alteration variations and magnetic grain size sensitive ratios ARM/SIRM. Heinrich layers have been underlined. Note the good fit of the CIA values on the ARM/SIRM records in spite of a smaller resolution of the major element measurements.

Past primary productivity

Sedimentary organic matter (C, N and P), calcium carbonate and opal constitute the bulk of the biogenic fraction of the sediments. The sedimentary organic matter is a result of production (through the growth of unicellular phytoplankton and zooplankton) and supply (export flux) from the surface waters. Paleoproductivity studies are intended to document temporal and spatial changes in the production of these biogenic components with time and also to discern the causes and effects of the productivity and its link to the Earth's climate. It is important to study the paleoproductivity because it accounts for the partitioning of carbon dioxide between ocean and atmosphere. Atmospheric CO₂ content in turn would affect the global heat balance and the climate.

Numerous proxies have been used to determine paleoproductivity. Biogenic remnants such as organic carbon, carbonate, opal or biomarkers together with barium, other trace metals such as cadmium and copper, or scavenged radionuclides such as ²³⁰Th have been used flux proxies.

Calcium carbonate is the easiest component to measure as this can react with mild acids such as acetic and HCl, evolving CO₂. About one half of the world's ocean bottom is covered by carbonate sediments (>30%). While the larger benthic organisms such as mollusks, corals and bryozoa constitute the bulk of calcium carbonate in the near shore environs, the carbonate in continental slope and pelagic oceans are almost due to planktic remains of coccolithophores, foraminifera and pteropods. The production of planktic carbon is at maximum between latitudes of 50°N to 50°S coinciding with waters warmer than 10°C. While calcium carbonate is an important tool to decipher the paleoproductivity patterns, its distribution depends on the degree of preservation. Only half of the global export flux of planktic carbonate finally accumulates on continental slopes and the deep sea. The productivity signal is modified because the carbonate tends to dissolve after deposition, increasing dissolution with increasing pressure which is dependent on the water depth. Thus, the elevated areas such ridges and seamounts are carbonate rich in comparison to nearly zero concentrations in the deep abyssal plains. The degree of dissolution/preservation is controlled by: 1) saturation state of seawater with respect to calcite and aragonite; 2) the time of exposure at sediment-sea water interface; 3) organic carbon content or the amount of organic coatings on the planktic carbonate particles. Carbonate dissolution follows a cyclic pattern in the Pacific sediments. However, it would be good to have an index of carbonate dissolution in order to use the carbonate as a proxy. Recently, carbonate dissolution rates were evaluated using Ba(ex) and carbonate MAR during glacial and interglacial periods. The newly developed Ba/Ca ratio is based on the proportional variation of

carbonate and Ba(ex) MARs. However, this has not been tested thoroughly.

Organic carbon (C_{org}) is a good proxy of paleoproductivity since it is the basic element of all the biota. The pattern matching between the C_{org} content of the sediments and the productivity in upper ocean has led to the use of C_{org} as a productivity proxy. However, it was debated in the early nineties whether the organic carbon variation is due to the productivity or preservation. Only a very small part of the organic matter produced in the upper ocean reaches the abyssal sea floor. Throughout its transition through the water column, organic carbon undergoes degradation through microbial and chemical processes. On reaching the seafloor, it is further degraded making only small portion available (labile portion) for the benthic biota for their consumption. Through early diagenetic reactions involving facultative bacteria, organic matter diagenesis takes place at the sediment-water interface. Therefore, the carbon preserved in the geological record is mostly refractory in nature and thus useful as a productivity tracer. Now, it is generally agreed that the organic carbon content is a result of productivity driven bottom water oxygenation conditions. However, factors such as sedimentation rates, local productivity, water depth, sediment mineralogy, texture and surface area, particle winnowing, dilution, biological mixing, and irrigation, local topographic variation, oxygen exposure time are other controlling factors.

Though there are several factors controlling the sedimentary C_{org}, it has been used extensively to estimate the paleoproductivity. At least 3 empirical relations are used to estimate the paleoproductivity, which are as follows:

- 1) PaP = 333.C_{org}.DBD.SR^{-0.3} proposed by Mueller and Suess (1979)
- 2) PaP = 5.31(C_{org}.DBD)^{0.71}.SR^{0.07}.z^{0.45} by Stein (1986)
- 3) PaP = 61.39.(C_{org}.DBD.SR/10)^{0.25}.SR_{cf}^{-0.049}.z^{0.15} by Sarnthein et al., (1992)

where

PaP is paleoproductivity (gCm⁻²a⁻¹), C_{org} is organic carbon (wt.%), DBD is dry bulk density (g cm⁻³), SR is the sedimentation rate in cm ka⁻¹, SR_{cf} is the C_{org}-free sedimentation rate (cm ka⁻¹) calculated with the equation of SR.(1-C_{org}/100) and z is the water depth. The equations include a factor of 10 to convert from [gC cm⁻²ka⁻¹] to [gCm⁻²a⁻¹]. Generally, it is considered that the first equation is more applicable for sediments with a high amount of terrigenous components, and the third equation is more suitable to predominantly biogenic sediments in the pelagic environment.

Organic carbon content can be used as a guide in estimating the biogenic flux of metals to the sediments.

Accumulation rate of nonlithogenic metal in sediment has been used to calculate the biogenic flux of metals to the sediment, F_{NL} , that would be needed to produce the enrichments of Cu, Ba, Cd, Mo, U, and V observed in the sediment cores using the formula

$$F_{NL} = \{[Me]_{NL} \cdot MAR\} / OC \text{ burial efficiency}$$

where MAR is the mass accumulation rate determined from porosity and sedimentation rate. This is suitable for areas where the burial rate of metals at the same rate as particulate organic carbon and that the OC burial efficiency is constant over time. It can be so assumed when it can be ascertained if all the observed fluxes have organic matter as the only source of trace metals to the sediment.

Among the various proxies for determining the paleoproductivity, C_{org} and $CaCO_3$ are plagued by dissolution and sedimentation rate effects and comparatively, opal may be less prone to these effects. Barium content in sediments is being used extensively as a productivity tracer. Barium enrichment in modern deep-sea sediments has been linked to the biogenic productivity by several workers. Although the causal relationship between barium and productivity is not yet understood, the reason for attributing this has been the presence of barium-enriched zones in the upwelling intense equatorial divergence and high productive Indo-Pacific regions.

The amount of biogenic barium (Ba_{bio}) in the sediment can be derived from normative calculations by subtracting the estimated terrigenous barium (Ba_{terr}) from the measured total barium content (Ba_{tot}) as

$$Ba_{bio} = Ba_{tot} - Ba_{terr} \quad (1)$$

where Ba_{terr} is calculated using the measured total Al content (Al_{tot}) and a given value for the terrestrial Ba/Al ratio $(Ba/Al)_{terr}$. Terrestrial values can be used from the known source geochemical data.

$$Ba_{terr} = Al_{tot} \times (Ba/Al)_{terr}$$

To assess past changes in the concentration of barium in seawater, an indirect approach based on the algorithm developed by Dymond et al., (1992) which links the flux of biogenic barium and the concentration of dissolved barium in seawater to (paleo) export productivity:

$$P_{new} = \left(\frac{F_{Ba} \cdot 0.171 \cdot Ba^{22.8} \cdot 0.476 - 0.00478 \cdot Ba}{2056} \right)^{1.504}$$

where P_{new} is the export productivity ($gC \cdot m^{-2} \cdot a^{-1}$), F_{Ba} is the flux of biogenic barium ($mg \cdot cm^{-2} \cdot kyr^{-1}$), which is the accumulation rate of biogenic barium corrected here for a constant preservation rate of 30%, Ba is the concentration of barium in seawater ($nmol \cdot kg^{-1}$), and z is the water depth (m).

The barium distribution in five DSDP drill cores (Sites 213-217) from the eastern Indian Ocean north of and below the present productivity equatorial zone has been studied to trace the plate movement below the equatorial upwelling zone on a time scale of millions of years. Since excess Ba in present day sediments is associated with productive zones and also because Ba is relatively insoluble and barite is thermodynamically stable under deep-sea conditions, it has been assumed that the sediment would record higher Ba contents when passing under the high productivity regions and therefore, gives an idea about the rate of plate movement. Sites 213-217 are particularly suitable for such a study, since they have been drilled in a north-south traverse, along the 90°E ridge, and thus follows the northward passage of the Indian plate beneath the equator.

Barium is not only present as discrete barite particles derived from productivity but also as a trace element in the other sediment constituents contributed by detrital, andesitic, hydrogenous and hydrothermal sources. Therefore, for an effective use of Ba as a proxy for productivity, it is necessary to evaluate the contribution of barium from these sources to the total barium of the sediment. Total Ba content in sediments, removed from high terrigenous sources, itself would be a good proxy.

Though Ba is a potential proxy for the paleoproductivity in deep-sea sediments, Ba deficiency was noted in the near-shore sediments off Namibia, in sediments of Baja California upwelling system, at ODP site 680 off Peru and ODP site 724 off Oman Margin. Sediments from all these locations contain higher organic matter and yet depleted in Ba. This is because, the high sedimentation areas such as the above have shallow sulphate reduction zones and due to the diagenetic processes, the Ba productivity signal is obliterated. In addition, diagenetic barite is a common precipitate (from porewater) in highly anoxic sediments. Ba is also involved in hydrothermal input and removal processes and hydrothermal barite is of quantitative importance in the immediate vicinity of venting sites. Therefore, Ba may not be suitable productivity proxy for both anoxic and hydrothermal sediments.

Other factors which may alter the biological signal of Ba are: (1) diagenetic sequestering of Ba with Mn-oxide phase, (2) fluid expulsion with cold seeps from deeper remobilization or barium in the zone of sulphate

depletion followed by formation of authigenic barite in the near surface sediments. Given these problems and apparent budgetary problems in balancing the Ba accumulation, it was suggested that Ba is unreliable as the sole tool for reconstructing paleoproductivity but may be useful in certain environments in concert with productivity tracers. It was also suggested that the Ba concentrations can be used to qualitatively determine the paleoproductivity, but quantitative estimates of paleoproductivity using equations should be used with caution.

Various paleoproxies were used on a wide range of timescales in varied oceanographic regimes. However, paleoproductivity reconstructions using more than one of the proxies have not been compared at many areas. This can be done by converting geochemical data to C_{export} using published algorithms.

Geochemical tracing of past monsoonal strength

The summer monsoon in the Indian Ocean tropics and adjacent continents is the dominant climatic feature and it is one of the Earth's most dynamic climatic phenomena resulting from ocean-continent-atmosphere interactions. The higher runoff and strong winds during the monsoon season brings enormous loads of clastic sediments to the oceans through rivers or through the atmosphere. The success or failure of the monsoonal rains affects almost every phase of life both in South Asia and North Africa. Good rainfall is necessary for higher food production and water sufficiency in these areas. It is thus necessary to be able to predict the monsoonal variability. For constructing the models to predict the monsoon, it is necessary to understand the past variation of monsoons. Several tools were used to infer the strength of the past monsoons from the sedimentary records.

Accumulation rates of biogenic carbonate, biogenic silica/opal and organic carbon have been linked to the monsoon-induced upwelling, which gets support from the sediment trap results of the western Arabian Sea. The data collected during an Indo-German co-operative project has indicated that about 70% of the annual biogenic flux to the seafloor occurs during the summer monsoon. Since the sediment trap data represents the present day sedimentation patterns, one may consider using these chemically-determined parameters as proxies for monsoon related upwelling. However, as mentioned in the past productivity section, the CaCO_3 and C_{org} concentrations are prone to alteration either due to higher sedimentation rates or due to variations in alkalinity of the seawater on longer time scales. For example, C_{org} invariably degrades to the same low values (0.1 to 0.2%) in most of the deep-sea sediments regardless of delivery rate to the seafloor and hence has limitations. Consequently, studies on high frequency

changes in the major sediment components on the orbital time from the Oman margin reveal that increases in mass accumulation rates (MAR - a function of concentration of component in question, linear sedimentation rate and the dry bulk density of sediments) of CaCO_3 and C_{org} do not coincide with strong monsoons. Unless, we are able to fully remove the effects of sedimentation rate enhanced preservation of C_{org} , organic matter accumulation cannot be used as a reliable index of monsoon variability. Similarly, dissolution features were noticed in carbonate skeletons in sediments even those above the lysocline, which were induced by higher C_{org} contents. Compared to these two proxies, biogenic opal is less sensitive to pH changes, more resistant and little alteration of the opal signal is likely due to post depositional diagenesis. Changes in opal accumulation rates in Oman ridge sediments matched well with other monsoonal indices.

In addition to the carbonate, C_{org} , and opal, foraminiferal assemblages and stable isotopes of C and N were also used. As these proxies will be discussed in specialized talks, these are not repeated here. We will consider the utility of inorganic geochemical tracers for reconstructing the past monsoonal variations and the upwelling intensity. Ti/Al and Ba/Al ratios were been used successfully in interpreting the past variations of monsoonal strength and the upwelling intensity. Downcore records of excess Ba (excess over that can be supplied through terrestrial/lithogenic sources) in the northwestern Indian Ocean sediments to identify the pulses of high paleoproductivity. A striking correspondence between the Ba/Al profile and the planktonic foraminiferal ^{18}O record and the occurrence of Ba peaks deposited during interglacial periods was noticed. Spectral power, coherence and phase from a time-series analyses of Ba/Al content was similar to the proxy-ice volume at both eccentricity (100 kyr) and obliquity (41 kyr) time frequencies of orbital forcing. Considering the refractory and relatively immobile nature of Ti and its concentration in the coarser sediment fractions, Ti/Al ratio in the Arabian Sea sediments has been used to study the wind intensity associated with monsoons following the success of using this ratio to study the fluctuations in the intensity of Aeolian transport associated with glacial/interglacial cycles in the eastern Pacific off Peru. Ti/Al record off Peru was interpreted to be influenced by trade wind velocities modulated by global boundary conditions. The ODP record from the Arabian Sea has shown that the Ti/Al peaks were dominant at the precessional intervals (23 kyr) and matched with other monsoonal indicators such as the maximum abundances of foraminifera *G.bulloides*, MAR of opal, lithogenic grain size and pollen record, and thus have been used as proxy.

Rb/Al and REE abundances were used in addition to Ba, Cd and Mg in linking subtropical monsoon

occurring in the Arabian Sea to the high latitude climate (Greenland and Antarctica). While Ba, Cd and *G.bulloides* abundances were used as proxies for upwelling intensity, Rb/Al was used as an indicator dust flux from the Arabian deserts. Terrigenous content (%) calculated with the help of these parameters has been used as a proxy indicator for aridity and humidity in

Arabia. Based on all these parameters, it was found that the southwest monsoon system has high frequency variability and sub-Milankovitch periodicities of 1785-, 1450- and 1150-years and also found that the southwest monsoon climate shares features with the climatic evolution in both polar hemispheres.

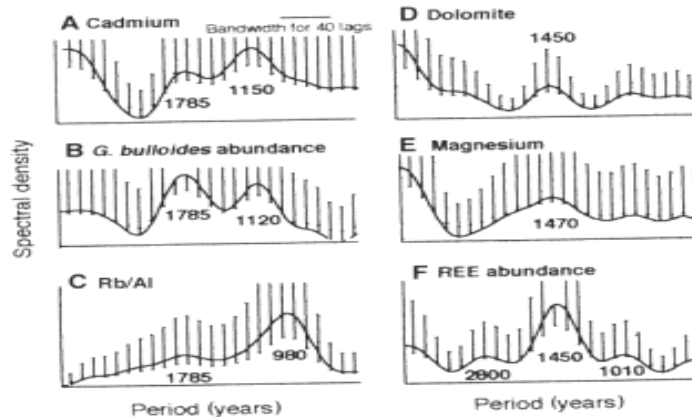


Fig. 5 . Prewhitened spectra of geochemical tracers in a sediment core from the Arabian Sea. Cadmium and *G. bulloides* have been used as tracers of upwelling and the other the remaining four variables have been used to trace the dust discharge tracers; Rb/Al to trace the northeast monsoon winds and Mg content, dolomite and REE abundances as the proxies of Arabian northwesterlies (Source: Sirocko et.al., 1996; Science, 272: 526-529)

Tracing the past oxygenation conditions

An understanding of past oxygenation conditions of the sedimentary environment is important in understanding the genesis of certain ore deposits such as black shales and also the past CO₂ sequestration levels by the oceans. Water column oxygenation exerts a major control on the abundance and type of organic matter preserved and also on many trace and minor elements. This is mainly because some trace metals have multiple valency states on the Earth's surface conditions and these typically have different solubilities in oxygenated or oxygen deficient seawater, or are partitioned between the solid and solution phases to different extent under different redox conditions. In addition to C_{org}, some other elements which undergo changes in response to oxygen levels in water column are Cr, Mn, Mo, Re, U, V, Ce, Cd, Zn, and I. Similarly, these elements also respond to changes in the interstitial water within the sediments. Therefore, it is important to differentiate between the changes undergone within the water column or the sediment column.

Using some of the above tracers, paleoclimatic interpretations such as the 1) expanded oxygen minimum zone in the Indian Ocean during the late Miocene-early Pliocene ; 2) fluctuation in the OMZ in the Arabian Sea; 3) anoxia during the last glacial period were interpreted. However, the timescales of oxidation kinetics may be different and there could be a mismatch

between some of the tracers. In addition, multiple processes control variation in some of the tracers. For example, the magnitude of Ce anomaly (anomaly with respect to its trivalent REE neighbors) would depend on 1) influence of depositional environment, 2) proximity to source areas, 3) redox conditions within the sediments, 4) lithological and diagenetic control, and 5) the carbonate content.

Based on the geochemical behaviour of some redox sensitive elements in modern and ancient sedimentary environments, it has been considered that the occurrence of U enrichments in sediments as a reliable guide for inferring suboxic to anoxic bottom water conditions. Lack of significant reduction of U (VI) to U (IV) has been recorded in the suboxic and anoxic waters of Cariaco Trench and the Black Sea. Nevertheless, a significant increase in porewater and solid phase U concentrations are found at shallow subsurface depths in the Black Sea and off California where the bottom waters are suboxic. Such enrichments have encouraged the sedimentary geochemists to use the ratio of U to Th as a redox indicator (see Nath et.al., 1997 for discussion). Since Th is immobile in low-temperature environments, the ratio is sensitive to changes in U supplied from seawater. In turn, U variation depends on the redox state of seawater, with fixation of low valency U under reducing conditions, U/Th ratios above 1.25 have been used to infer suboxic and anoxic conditions in Upper

Jurassic mudstones from the Norwegian North Sea, and onshore formations of UK such as the Draupus, heather, and Kimmeridge Clay formations. The U/Th ratios in the Arabian sediments also respond similarly to oxygen minimum zone variations (Nath et al., 1997). Another parameter based on U and Th concentrations used is the authigenic uranium calculated as

$$\text{Authigenic U} = (\text{Total U}) - \text{Th}/3,$$

which is used as an index of past oxygenation conditions in ancient sedimentary sequences. An authigenic U content of 2 ppm or 5 ppm is used by two groups of researchers to distinguish oxic from dysoxic sedimentary environments. Authigenic uranium in modern sediments overlain by poorly oxygenated conditions such as those occurring in the Arabian Sea is about 2 ppm (Nath et al., 1997).

In view of varying response of redox sensitive trace elements, we need to assess the depth at which the trace metal is removed. The following is an example of how the removal depth can be calculated. This will help in determining the oxidation states of the sediments and overlying water recorded by the downcore metal profiles in cores were oxic or anoxic.

Re and Mo are important redox-sensitive trace elements responding to water column oxygenation conditions. Removal depths (z) of Re and Mo have been calculated from the eastern tropical North Pacific sediment cores with the following equation assuming that seawater concentrations of these metals did not change appreciably over glacial to interglacial time. Neglecting burial of pore water,

$$Z = \{ \phi \cdot SW \cdot D_{\text{eff}} \} / \{ \text{Me}_{\text{NL}} \cdot S \cdot \rho \cdot (1 - \phi) \}$$

where ϕ is sediment porosity from water content analysis, SW is the metal's seawater concentration, S is the sedimentation rate (cm kyr⁻¹), Me_{NL} is metal in question in the non-lithogenic fraction, ρ is sediment density (2.4 g cm⁻³), and D_{eff} (cm² kyr⁻¹) is the molecular diffusion coefficient.

Diagenetic processes can alter the signal of redox sensitive elements. Therefore, we can indirectly calculate the diagenetically remobilized Mn flux using a diagenetic model. The model assumes that the Mn gradient in the

sediments reflects the loss of Mn in lower reducing zone and subsequent migration to the oxidizing zone and is represented as:

$$\Phi = S \cdot \rho \cdot d\text{Mn}$$

where Φ is the flux of remobilized Mn in gcm⁻²kyr⁻¹, S is sedimentation rate (cm kyr⁻¹), dMn is the difference between top and bottom of Mn (%) in the sediment core, and ρ is the in situ dry bulk density of the sediment (g cm⁻³).

Need for new proxies

The provenance determination of sediments with a single predominant source is not so difficult, but would be difficult in areas with mixed source terrains. A multi-proxy approach would be useful in such areas.

What would be interesting to see is the extent of transport of heavy refractory elements such as Zr, which would help in unscrambling the signals from major terrestrial sources such as the eolian from that of bottom flow. For this, it would be interesting to understand the source to sink patterns of isotopes such as Hf which can fractionate with zircon content.

Further reading

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- M. Kastner (1999) Oceanic minerals: Their origin, nature of their environment, and significance. *Proc. Natl. Acad. Sci. USA*, 96: 3380–3387

Interesting site to visit:<http://www2.ocean.washington.edu/oc540/>