

## **Fe speciation and Fe/Al ratio in the sediments of southeastern Arabian Sea as an indicator of climate change**

J. N. Pattan<sup>\*</sup>, G. Parthiban, S. M. Gupta and Ishfaq Ahmad Mir  
National Institute of Oceanography (CSIR),  
Dona Paula, 403 004, Goa, India

Correspondence: **Tel**-91-832-2450360, **FAX**: 91-832-2450602,

E-mail: <sup>\*</sup>pattan@nio.org

### **Abstract**

Aluminum, Titanium and Iron are the major lithogeneous contributors to the marine sediment and their abundance varies strikingly with the intensity of monsoonal precipitation. Al and Ti concentration in a sediment core (SK-129/GC-05) from southeastern Arabian Sea exhibit very strong positive correlation ( $r=0.92$ ,  $n=140$ ) suggesting their lithogenous association, whereas, Ti and Fe does not correlate so strongly ( $r=0.44$ ). This suggests that part of Fe is present as structurally unsupported and is evident by two fold increased Fe/Al ratio (0.87 average) compared to upper continental crust (0.44). The presence of structurally unsupported Fe is confirmed by the sequential leaching of Fe which is associated with different fractions such as exchangeable (0.98%), carbonate (1.98%), Fe-Mn oxide (30.8%), organic carbon (4.7%) and biogenic opal (11.4%) which together constitutes nearly 50% of the bulk Fe content. There is a good correlation between time series Fe/Al and differential solar insolation suggesting warmer and humid climatic condition resulting intense weathering of hinterland rocks, associated with increased monsoonal precipitation probably decoupled soluble Fe and its transportation to southeastern Arabian Sea.

**Key words:** Sediment core, SE Arabian Sea, Fe/Al ratio, Fe speciation, sequential leaching, differential solar insolation, monsoonal precipitation, weathering, climate.

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Correspondence: Tel-91-832-2450360, FAX: 91-832-2450602, E-mail: <sup>\*</sup>pattan@nio.org

## Introduction

The abundance and composition of lithogenous fraction within sediments mainly depends on the hinterland geology, weathering and transport pathways, and to some extent altered by the re-sedimentation process (Lamy et al., 2000). Lithogenous fraction introduced by the rivers are the major source of Fe supply to the oceans, with additional contribution from aeolian dust (Duce and Tindale, 1991) which varies with the time scale mainly because of the changes in vegetation cover, wind intensity and direction. However, most of the Fe supplied by the atmosphere appears to be dissolved in the ocean. Lamy et al., (2000) used Fe/Al ratio in northern Chile continental slope sediment core to estimate the past changes in terrigenous sediment provenances. The changes in bulk iron and Fe/Al ratio in the sediments have been related to varying contribution from different source rocks controlled by the rainfall changes (Lamy et al., 2000; Dezileau et al., 2007). Dezileau et al., (2004) observed variations in both Fe/Al and La/Yb ratio in sediment core and successfully used the variability trends to determine the origin of detrital particles. Use of elemental ratios in the sediment to study the monsoonal variability and climate change in the Arabian Sea has not been previously carried out. Sediment core in the present study from the southeastern Arabian Sea showed an average Fe/Al ratio of 0.87, which is nearly two fold enriched as compared to the upper continental crust (0.44) and such a large ratio, needs an explanation. Therefore, in the present study, we have tried to understand the factors responsible for the increased Fe/Al ratio, carried out sequential extraction of iron and made an attempt to demonstrate the usage of Fe/Al ratio as a proxy to understand climate change in the region.

## Materials and Methods

A 5.52 m long gravity sediment core (SK-129/CR-05) was raised from a water depth of 2300 m at 9° 21' N and 71° 59' E from southeastern Arabian Sea during *ORV Sagar Kanya* cruise 129 (Fig.1). The sediment type at the sediment core location is calcareous ooze where calcium carbonate ranges from 30% to 66% (Pattan et al., 2003). The sediment core was sub-sampled at 2 cm intervals onboard, and later dried and powdered in the laboratory. Age model for the core is based on oxygen isotope record of *Globigerinoides Ruber* reported earlier (Pattan et al., 2003; Pattan and Pearce, 2009). Dried and finely powdered sediments were digested in a mixture of HF, HClO<sub>4</sub> and HNO<sub>3</sub> in a PTFE vial and heated in a microwave Owen. After digestion the solutions were evaporated to near dryness under an infrared lamp on a hot plate in a draft chamber. The residue was dissolved into a clear solution using 2M HNO<sub>3</sub>. The aliquots were analysed for Al, Fe and Ti with a Thermo Jarrel Ash IRIS Inductively Coupled Plasma -

Atomic Emission Spectrometer (ICP-AES). An international standard reference material (JB-2) was used to check the accuracy and the values are within the acceptable limit. The precision of measurements based on duplicate analysis was  $\pm 5\%$ . A sequential chemical extraction of Fe involves five fractions such as exchangeable, carbonate, Fe-Mn oxides, organic matter and biogenic opal has been carried out following the procedures of Tessier et al., (1979), Mortlock and Froelich, (1989) and Dezileau et al., (2007). The sequential extraction was conducted in a clean polypropylene 60 mL centrifuge tubes. In brief. Exchangeable. Initially 1g of dried powdered sediment was treated with 8mL of  $MgCl_2$  at room temperature for 1 hour with agitation, centrifuged and filtered to obtain exchangeable fraction. The residue from the step 1 was leached at room temperature with 8mL of 1M NaOAc with Acetic acid, agitated, centrifuged and filtered for carbonate bound metals. For Fe-Mn oxide bound metals the residue from step 2 was treated with 0.04M  $NH_2OH$  HCl in 25% (v/v) HOAC at  $\sim 90^\circ C$  with occasional agitation, centrifuged and filtered. The residue from step 3 was treated with 3mL of 0.02 M  $HNO_3$  and 5 mL of Hydrogen Peroxide at  $\sim 85^\circ C$  for two hours, centrifuged and filtered for organic bound metals. The residue from step 4 was treated with 2M  $Na_2CO_3$  at  $90^\circ C$  for 5 hours, agitated at regular intervals, centrifuged and filtered for biogenic opal bound metals. After every step residue was washed with 18.2 $\Omega$  ohms water and centrifuging was done at 2000 rpm for 30 minutes and supernatant were made to 50 ml of final solution. For each step blank solution were also made. All the five extracted fractions were analysed for Fe on Inductively Coupled Plasma Optical Emission Spectrometer (PE-OPTIMA 2000). To check the precision of the data we have used duplicate samples which was  $\pm 10\%$ . For clay mineralogy,  $<2\mu m$  size sediment was separated and made free from calcium carbonate and organic matter by treating with glacial Acetic Acid and Hydrogen Peroxide respectively. Oriented sections were prepared on glass slides and scanned from  $3^\circ$  to  $30^\circ$   $2\theta$  at  $1.2$   $2\theta$   $min^{-1}$  on a Philips X-Ray Diffractometer (PW-1840) using Nickel filtered Cu- $k\alpha$  radiation. The minerals were identified using procedure of Brindley and Brown (1980). Indian summer monsoon insolation index between  $30^\circ N - 30^\circ S$  (Leuschner and Sirocko, 2003) for the 90 days period between April to July was calculated (Gupta, 2003; 2009) using astronomical formulae of Berger (1978) and ANALYSERIES software (Paillard et al., 1996).

## **Results and discussion**

### **Distribution of La, Sc and Th**

Elements such as La, Sc and Th are well known for their detrital source and used to assess the potential provenance change. Th and Sc content in the sediment core varies from 3ppm to 12ppm (Fig.2), their contents are high during glacial than in the interglacial and reached maximum concentration during MIS-4. La content is comparatively higher than Th and Sc and varies from 14 ppm to 25 ppm (Fig.2). All the three detrital representing elements behave very similarly in the entire last 140 ka suggesting almost uniform supply of terrigenous material. The sharp increase of Th content at ~ 74 ka could be due to high concentration associated with the occurrence of glass shards of YTT origin (avg. 28 ppm, Pattan et al., 2001).

### **Calcium carbonate**

Calcium carbonate content in the marine sediments is mainly controlled by the surface water biological productivity, rate of dissolution during its journey through the water column as well as on the seafloor and dilution by the non-carbonate fraction. The calcium carbonate content in the sediment core varies from 30% to 66 % (Fig. 3) and highest and lowest concentration recorded during the late Holocene and Marine Isotope Stage 4 respectively (Pattan et al., 2003). The low carbonate content at ~ 74 ka was due to dilution by volcanic ash from Youngest Toba Tuff (Pattan et al., 2001). Calcium carbonate content is higher during interglacials than in the glacials (Fig. 3). In general, calcium carbonate shows strong negative correlation with Fe ( $r = -0.66$ ,  $n=140$ ) suggesting dilution by the carbonate.

### **Fe content on carbonate free basis (CFB) and Fe/Al ratio**

The bulk Fe content is recalculated carbonate free basis ( $Fe_{cfb}$ ) to remove the dilution effect caused by the calcium carbonate content. Total  $Fe_{cfb}$  content in the sediment core varies considerably from 2.97% to 11.85%, with an average of  $6.56 \pm 1.2\%$ . During the last ~7 ka,  $Fe_{cfb}$  content was lowest and almost constant (~ 5%) and then from 7 ka to ~ 40 ka it increases to ~ 6%. There is marginal increase of  $Fe_{cfb}$  content during Marine Isotope Stage (MIS) 2, 4 & 6 (5.89%, 6.94% & 7.88%) compared to MIS 1, 3 and 5 (5.77%, 6.29% & 6.45%) respectively (Fig.3) suggesting little increase of  $Fe_{cfb}$  during glacial (6.92%) over interglacial (6.25%) period. However, there is no distinct variation of  $Fe_{cfb}$  with glacial-interglacial time scale. This is similar to the sediments of Cape Basin (Latimer and Filippelli, 2007) and equatorial

Pacific Ocean (Murray et al., 1995). The marginal high  $Fe_{cfb}$  content during glacials could be due to exposure of extended continental shelves by the sea level lowering and thus providing a large source of terrigenous material to the open ocean. During MIS - 5, interstadials and stadials have high and low Fe content. There are two distinct high Fe concentrations at  $\sim 11$  ka and  $\sim 131$  ka which correspond to Glacial Termination (GT) I and II respectively. The lowest Fe concentration at  $\sim 74$  ka could be due to ash layer of YTT origin containing abundant glass shards with low Fe content (0.72%; Pattan et al., 2001).

There exist a very strong positive correlation between Al and Ti ( $r = 0.96$ ,  $n = 140$ ) suggesting a single lithogenous source (Fig.4). Though there is a positive correlation between Ti and Fe ( $r = 0.44$ ), it is not as strong as the correlation that exists between other two lithogenously derived elements (Al and Ti). This indicates that part of the iron is present as structurally unsupported. The marginal high Fe content during glacials compared to interglacials could be due to supply of small quantity of Fe by aeolian dust in addition to the lowering of sea level where terrigenous material is directly delivered. This is similar to North Pacific and SW Pacific Ocean which also received higher aeolian dust during glacial periods than interglacials (Hovan et al., 1991; Oba and Pedersen, 1999).

Iron content is normalized with Al (Fe/Al) to remove the terrigenous effect in the sediments. Fe/Al ratio in the marine sediments depends upon the geochemistry of source rocks and the absolute values of Fe and Al, which are affected by the total amount of terrigenous material relative to the biogenic fraction (Lamy et al., 2000). The Fe/Al ratio in the sediment core varies from 0.44 to 1.61 with an average of 0.87 (Fig. 3) and is two fold higher compared to upper continental crust (0.44) and PAAS (0.455) (Taylor and McLennan, 1985). The highest Fe/Al ratio of 1.61 at  $\sim 131$  ka and 1.21 at  $\sim 11$  ka corresponds to Glacial Termination (GT) - II and I and are higher by nearly four and three times respectively compared to upper continental crust. The lowest Fe/Al ratio (0.44) at  $\sim 74$  ka, indicates its dilution by the presence of Youngest Toba ash.

### **Sequential extraction of Iron**

Sequential leaching of Fe has been carried out on different fractions such as exchangeable, carbonate, Fe-Mn oxide, organic matter and biogenic opal. All the five leachable relative % of Fe fractions with the age are shown in Fig. 5 and their minimum, maximum and average is presented in Table 1. The average leachable Fe% associated with fractions namely exchangeable, carbonate, Fe-Mn oxide, organic matter

and biogenic opal is 0.98%, 1.98%, 30.85%, 4.68% and 11.43 % respectively (Table 1). As expected Fe leachable fraction is lowest with exchangeable followed by carbonate, organic carbon and opal. The highest Fe is associated with Fe-Mn fraction (31%) which is nearly double than the combined remaining four fractions. The total leachable fractions contribute to ~ 50 % of bulk Fe content. In both combined authigenic and Fe-Mn fractions leachable Fe fraction reached maximum during Glacial Termination II and I (Fig.5). It is interesting that even though Fe content is low at ~ 74ka due to dilution caused by the glass shards from ash layer of YTT (Fig.3). Fe associated with Fe-Mn oxide phase at ~74 ka is surprisingly very high. This could be due to adsorption/adhering of Fe-Mn oxyhydroxides on glass shards. Sub stages 5a and 5c have low and 5b have high Fe fraction associated with Fe-Mn oxide. Fe with Fe-Mn oxide phase appears to be associated with Fe phase rather than Mn. This is evident from the low Mn/Al ratio in the sediment (0.004) and this ratio is nearly half compared to that of PAAS (0.009) and upper continental crust (0.007) values (Taylor and McLennan, 1995). Further there is no excess Mn compared to crustal material. Lack of correlation ( $r = -0.01$ ) between Fe/Al and Mn/Al suggest that structurally unsupported Fe in the sediment is not associated with Mn. This probably suggests that structurally unsupported Fe in these sediments appears to be present as Fe-oxyhydroxide phase.

### **Clay mineralogy**

Clay mineral assemblage within sediments is associated with lithology and weathering conditions of source and their formation. The intensity of monsoon and associated climate change influences the formation, liberation and pathways of clay minerals (Weaver, 1989). Smectite, illite, kaolinite and chlorite are the major clay minerals found in the surface sediments of western continental shelf and slope of India with regional variations (Rao and Rao, 1995). In the western Arabian Sea smectite from Deccan trap, illite and chlorite from Himalayas or Iran –Makran region and kaolinite from tropical soils of southern India (Kolla et al., 1981; Debrabant et al., 1993) are reported. The principal clay minerals identified in the present sediments are smectite (18%), illite (38%) and Kaolinite + Chlorite (43%) in the order of their increasing abundance and there is rare occurrence of gibbsite (Andrade. 2006). There is no consistent trend of these clay minerals distribution with respect to glacial and interglacial time scales (Fig.3). Though illite in the northern Arabian Sea derived from Himalayas but its abundance decreases towards central west coast and reaches minimum in the southern end. High illite content in the sediment could be sourced from Western Ghats due to weathering under humid tropical climatic conditions.

Further illite off Cochin is less crystalline than those derived from Indus (Rao and Rao, 1995). The rare occurrence of gibbsite could be derived from laterites under humid climatic conditions. Sediments have higher illite content of 42% and 45% at GT- II (~131 ka) and I (12 ka) respectively and harmonize well with Fe/Al ratio and  $Fe_{cfb}$ . Similarly high illite content (40%) was reported at ~ 12 ka off Cochin at shallow water depth (280m) (Thamban et al., 2002). Here the illite content of 42% is actually measured at ~ 133 ka, as sample at 131 ka was not available for clay mineralogy. We strongly feel illite content at ~ 131 ka would have been more than what has been observed at 133 ka. The highest illite content recorded during GT- II and I suggest comparatively intense physical weathering under warm and humid climatic conditions. Illite chemistry can be assessed by using intensity ratio of  $5A^\circ$  and  $10A^\circ$  reflection peaks and this ratio of  $< 0.5$  suggests the presence of Fe-Mg rich illite which is characteristic of unweathered or weak weathered rocks while,  $> 0.5$  ratio is indicative of Al – rich illite formed by the hydrolysis (Gingele, 1996). In the present sediment core  $5A^\circ/10A^\circ$  ratio varies from 0.6 to 1.38 which suggests that Al-rich illite was formed by the intense chemical weathering under warm and humid climatic conditions (Petschick et al., 1996).

### **Solar insolation**

Indian summer monsoon rainfall is a consequence of upper atmospheric pressure differences between the northern and southern latitudes at ~  $30^\circ$  during Boreal summer, which causes trans-equatorial transport of latent heat in the form of moisture laden clouds resulting into monsoon season over India. Trans-equatorial transport of latent heat and moisture is reported to be related with the solar insolation differences between the Northern and Southern subtropics. Leuschner and Sirocko (2003) opined an Indian Summer Monsoon Index based ( $\delta i$ ) at  $30^\circ$  latitude reported that a high resolution record of upwelling and dust flux from the western Arabian Sea correlates very well. During April to July, the peninsular India witnesses extremely hot and humid climate, and the on-set of Southwest monsoon invariably happens at the end of May or early June every year. Such a prolonged heat (pre-monsoon), climate is ideal for physical weathering of laterites and other iron-bearing country rocks in the peninsular India, and thereafter humid (monsoon rains) climate leaches out iron, draining into the sea as river runoff. A comparison between the Fe/Al ratio and  $\delta i$  ( $30^\circ N$  minus  $30^\circ S$ ) for summer season shows an excellent resemblance at ~ 11 ka, ~ 30-60 ka, ~ 85 ka. ~ 105 ka and ~ 130 ka (Fig.6). This suggests that solar insolation related weathering pattern and intense monsoonal precipitation control the delivery of dissolved Fe into the Arabian Sea. Some part of the dissolved iron in the continental shelf has been

used in the formation of authigenic verdine and glaucony mineral grains (Rao et al., 1993; Thamban and Rao, 2000). The remaining part of dissolved Fe would probably reach deeper part of southeastern Arabian Sea, in the form of Fe-oxyhydroxide. Cross-spectrum analysis by the SPECTRUM program (Schulz and Stattegger, 1997) between Fe/Al ratio and  $\delta_i$  suggests coherency at  $\sim 41$  ka tilt and  $\sim 23$  ka precession cycles, where Fe/Al ratio leads by  $55^\circ$  (6 ka) and  $40^\circ$  (2 ka) radians over the insolation monsoon index, respectively (Fig.7). A Continuous Wavelet Transform power spectrum using Morlet's global window (Torrence and Compo, 1998) in the time series, Fe/Al ratio and  $\delta_i$  exhibits a weakening of precession signal in the sediments of younger than 60 ka along with 23 ka and 41 ka cycles in both time series (Fig.7).

### **Climatic implications**

The mean Fe/Al ratio (0.87) in the sediment core is nearly twice to that of the upper continental crust (0.44) suggesting almost half of the total iron is of authigenic or sedimentary nature. The presence of lowest Fe/Al ratio of 0.44 at  $\sim 74$  ka is due to presence of ash layer of YTT origin. The next lowest Fe/Al ratio in the entire sediment core is 0.6 (where there is no ash layer). The lowest Fe/Al ratio of 0.44 at  $\sim 74$  ka is almost two fold lower than the mean Fe/Al (0.87) ratio in the sediment core. Therefore ash layer of YTT is acting as main dilutant to the sediments. The low and almost uniform Fe/Al ratio between  $\sim 15$  ka to  $\sim 40$  ka (Fig.7 A [a]) coincides well with low and flat  $\delta_i$  (Fig.7 B [a]). This weakening of Fe/Al ratio and  $\delta_i$  are also reflected in wavelet power spectrum (Fig. 7, b). In general, Fe/Al peaks matches well with  $\delta_i$  in the sediment core. This indicates that weathering of the country rocks due to solar insolation on the Indian peninsula. Glacial Termination II and I are strikingly associated with high  $Fe_{cb}$ , Fe/Al ratio, total leachable Fe, illite content and high differential solar insolation. Similar to the present study, Rao et al., (2010) also observed increased Fe/Al ratio in a sediment core at a water depth of 1420 m in southeastern Arabian Sea. Presence of high illite is indicative of physical weathering of source rocks under warm and humid climatic conditions. Periyar and Muvattupuzha rivers mainly flow through four major rock formations such as Precambrian crystalline, Tertiary sedimentary, Pleistocene laterite and Recent to sub Recent sedimentary units (Padmalal et al., 1997). Along the Cochin coastal track rocks have been lateritized extensively and ferruginised sandstones with clay intercalations are exposed at many places (Thamban et al., 2002). Lateritization / bauxitization result from chemical weathering of many rock types under humid tropical climatic conditions involving leaching of Si, Fe, alkalies and alkaline metals. During lateritization,



ordered kaolinite is being replaced by disordered kaolinite during which  $\text{Fe}^{3+}$  is weakly mobile (Balan et al., 2011). Interplay between weathering and monsoonal precipitation the sorbed Fe may be released and transported to southeastern Arabian Sea. Based on clay mineralogy and sediment distribution (Kolla et al., 1981) and sediment trap data (Nair et al., 1989), suggests that lithogenic fraction in the eastern Arabian Sea is largely fluvial in origin. This indicates that eolian input into the present sediment core could be very minimum. Fe rich weathered material from these rocks and strong monsoon might have helped in transporting dissolved Fe to the southeastern Arabian Sea. GT- II and I were associated with a higher degree of warm and humid climate and associated strong monsoonal precipitation compared to rest of the sediment core.

## **Conclusions**

Following conclusions are made based on the present study.

**1.** The mean Fe/Al ratio in the sediment core is increased by two fold compared to upper continental crust suggesting half of the iron is present as structurally unsupported and confirmed by the sequential leaching studies. Fe speciation studies shows that small leachable Fe is associated with exchangeable, carbonate and organic carbon fractions whereas higher fraction with biogenic opal and highest with Fe-Mn oxide phase. High Fe/Al ratio is invariably correlated well with differential solar insolation peaks. Therefore, high solar radiation and intense monsoonal precipitation might have helped in breaking down the source rocks from the Indian peninsular and increased the supply dissolved Fe to the core site respectively. Glacial Termination II and I were associated with comparatively more warm and humid climatic conditions and corroborated with strong monsoonal precipitation.

**2.** A continuous wavelet transform power spectrum of Fe/Al ratio and  $\delta_i$  reveals presence

of 23 ka and 41 ka cycles and weakening of precession signal in the sediments younger than 60 ka.

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## Captions for the figures.

Fig. 1. Location map showing position of the sediment core (SK-129/CR-05) in the southeastern Arabian Sea.

Fig.2. Distribution of Th, Sc and La in a sediment core.

Fig.3 Distribution of  $\delta^{18}\text{O}$ , calcium carbonate, Fe (% cfb), Fe/Al ratio and illite in a sediment core.

Fig.4. Scatter plots of Ti (wt %) vs Al (wt %); Ti (wt%) vs Fe (wt %) for sediments in a core.

Fig.5. Sequential leaching of Fe in a sediment core including, exchangeable, carbonate, Fe-Mn oxide, organic carbon, opal and total authigenic Fe.

Fig.6. Comparison of Fe/Al ratio and solar insolation in a sediment core.

Fig.7. (A). Behavior of Fe/Al ratio and its wavelet power spectrum, (B) Solar insolation and wavelet power spectrum in a sediment core.

Fig.1

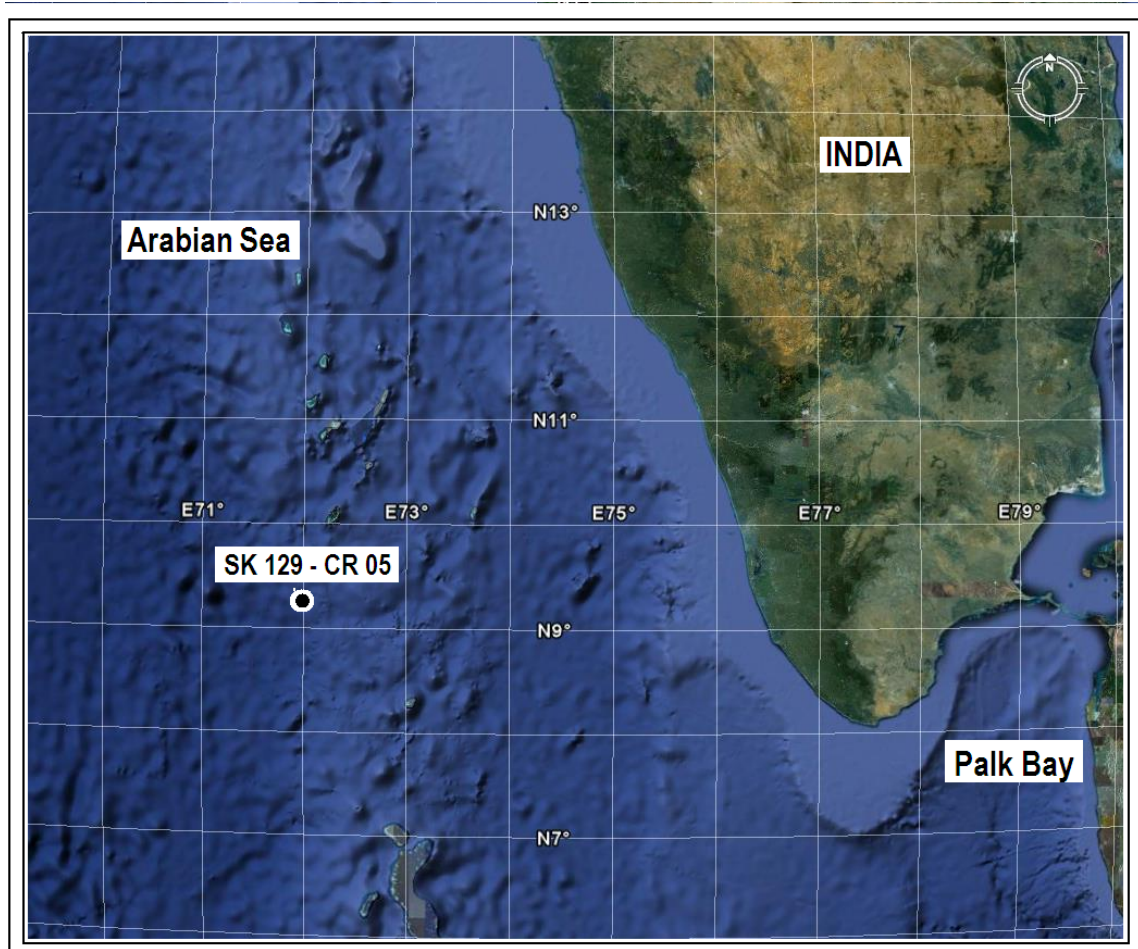


Fig.2

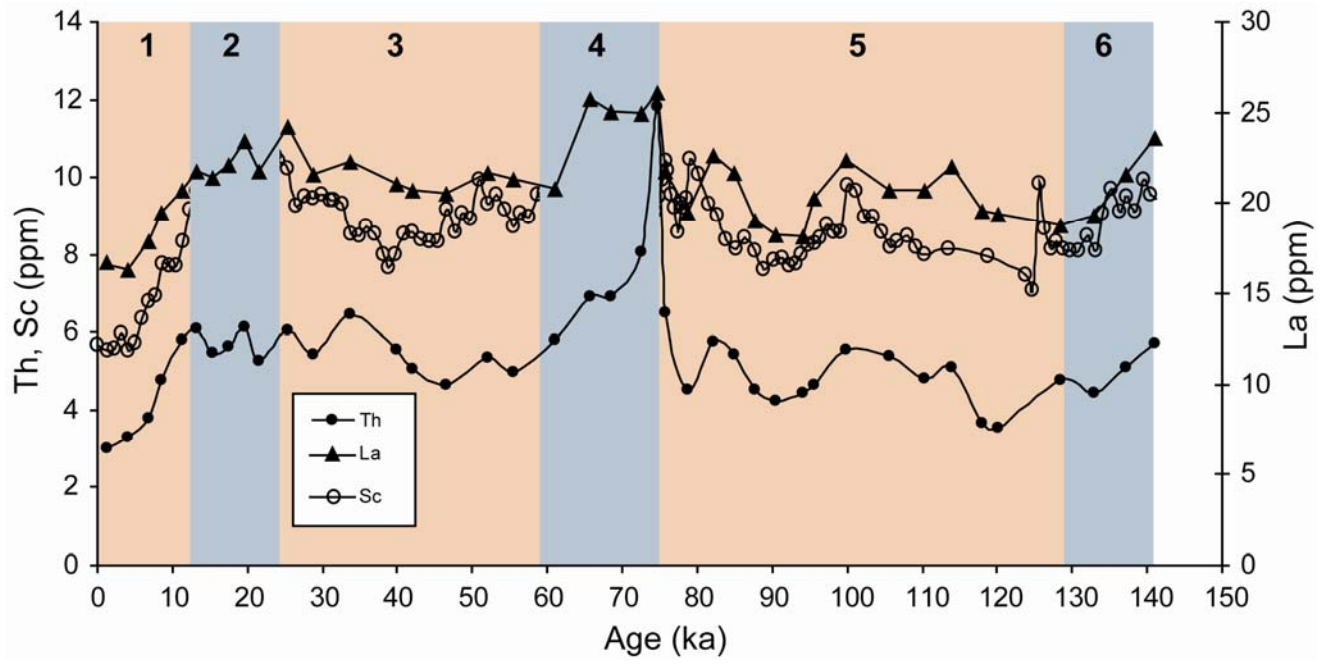


Figure 3

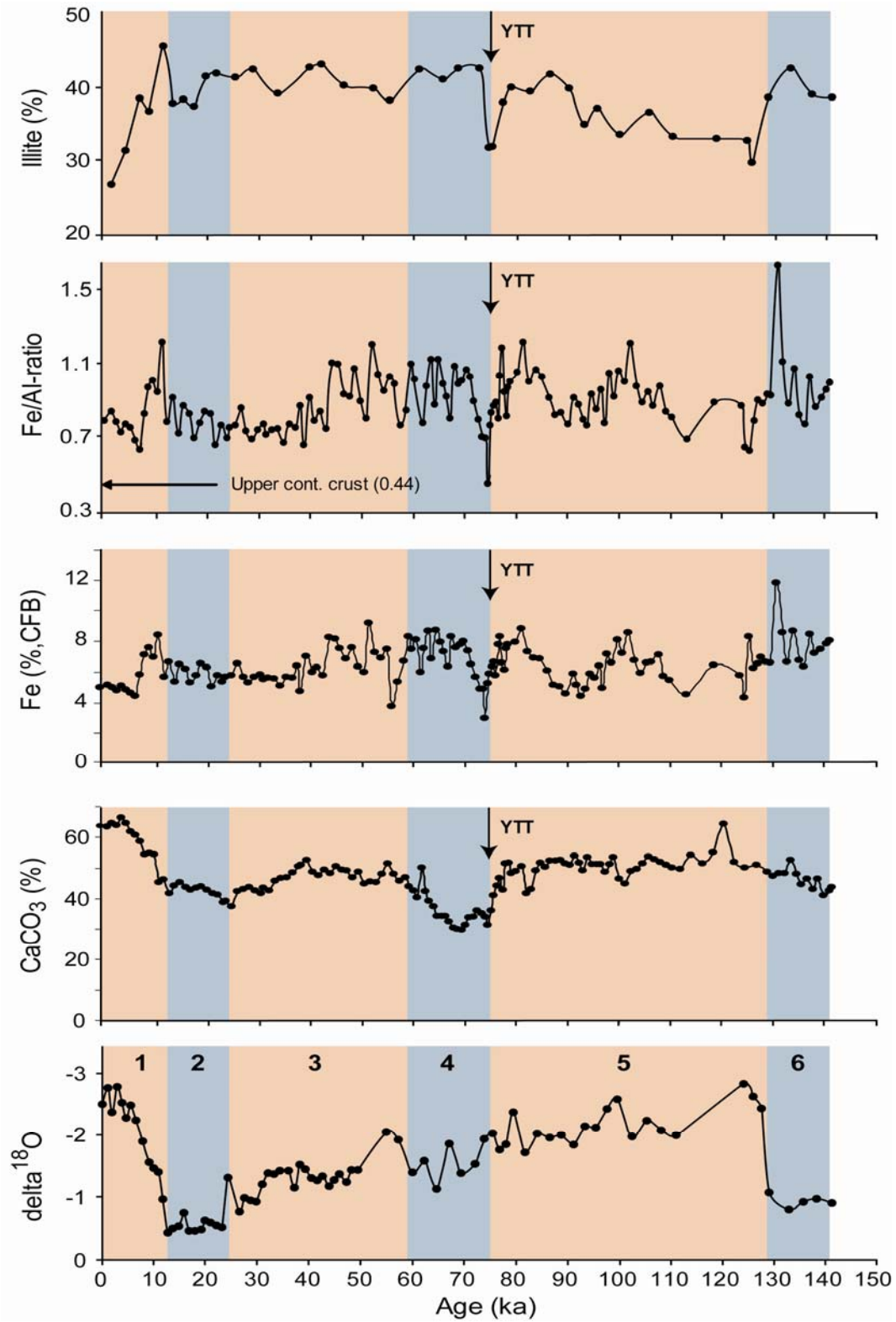




Figure 4

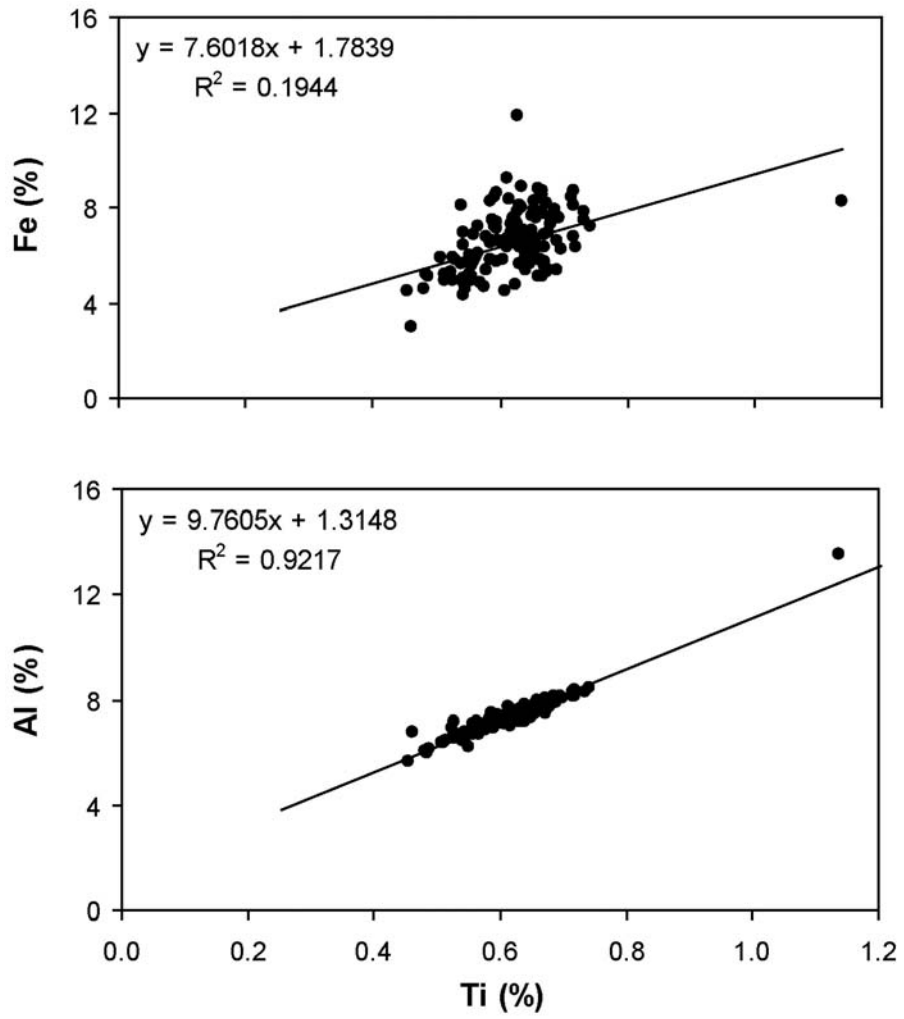


Fig. 5

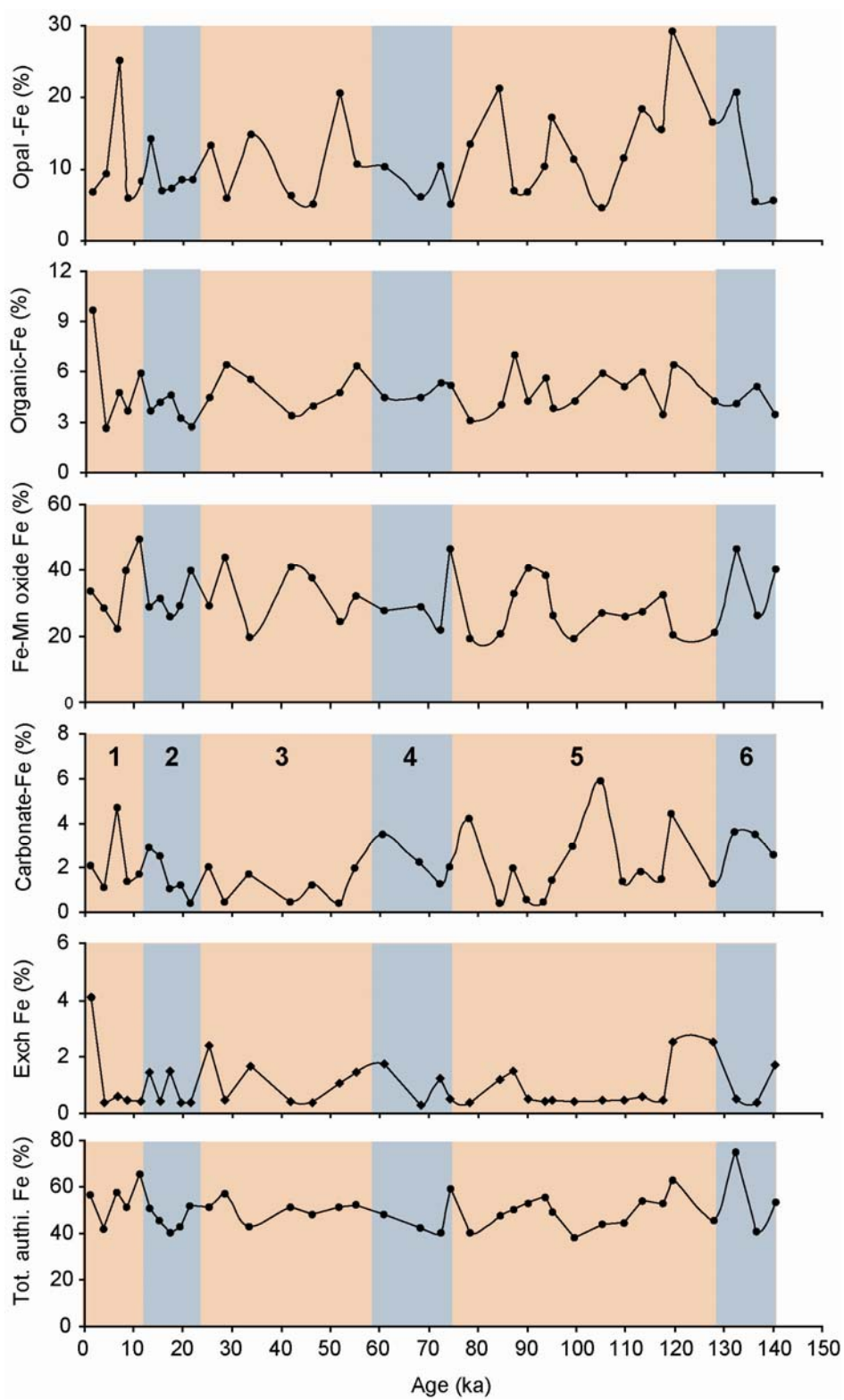


Fig.6

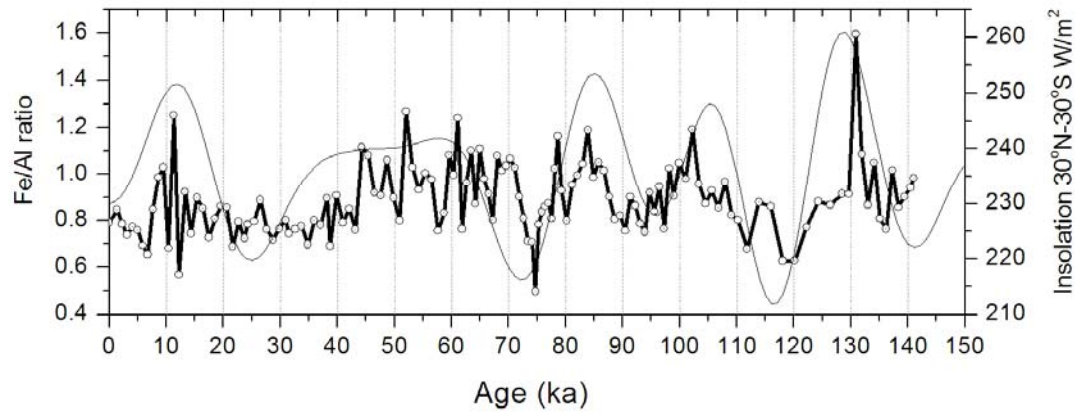


Fig.7

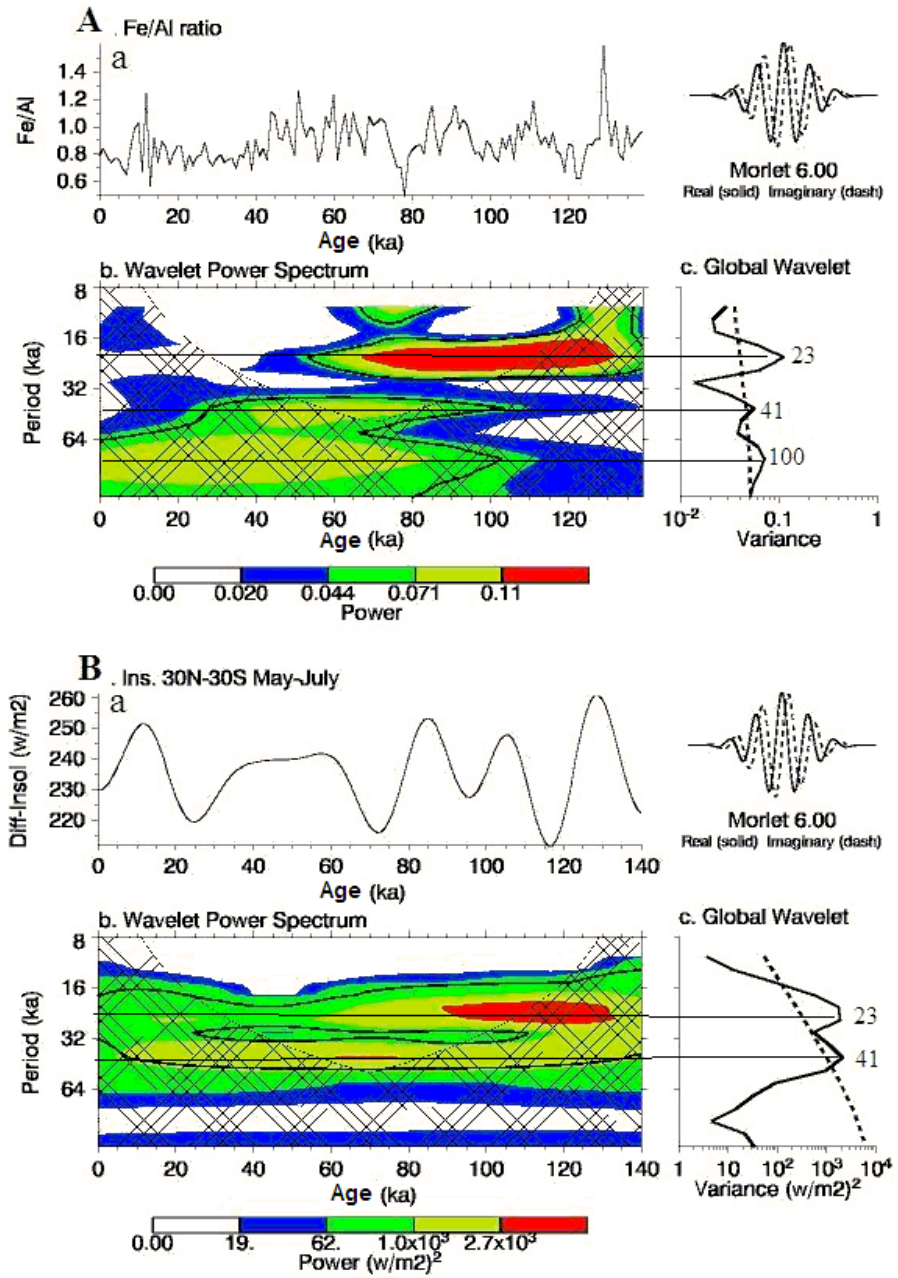


Table 1. Minimum, maximum and average Fe fraction associated with different Phases in a sediment core.

| Fe association                       | Min. (%) | Max. (%) | Avg. (%) |
|--------------------------------------|----------|----------|----------|
| Fraction I: Exchangeable             | 0.20     | 4.10     | 0.98     |
| Fraction II: Carbonate               | 0.40     | 5.88     | 1.98     |
| Fraction III: Fe-Mn oxide            | 19.41    | 49.41    | 30.85    |
| Fraction IV: Organic carbon          | 2.72     | 9.62     | 4.68     |
| Fraction V: Biogenic opal            | 4.58     | 29.20    | 11.43    |
| All fractions (I-V): Total leachable | --       | --       | 49.92    |