Relationship between chemical composition and magnetic susceptibility in sediment cores from Central Indian Ocean Basin

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Three sediment cores in a north–south transect (3°N to 13°S) from different sediment types of the Central Indian Ocean Basin (CIOB) are studied to understand the possible relationship between magnetic susceptibility (χ) and Al, Fe, Ti and Mn concentrations. The calcareous ooze core exhibit lowest χ ($12.32 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$), Al (2.84%), Fe (1.63%) and Ti (0.14%), terrigenous clay core with moderate χ ($29.93 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$) but highest Al (6.84%), Fe (5.20%) and Ti (0.44%), and siliceous ooze core with highest χ ($38.06 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$) but moderate Al (4.49%), Fe (2.80%) and Ti (0.19%) contents. The distribution of χ and detrital proxy elements (Al, Fe, and Ti) are identical in both calcareous and siliceous ooze. Interestingly, in terrigenous core, the behaviour of χ is identical to only Ti content but not with Al and Fe suggesting possibility of Al and Fe having a non-detrital source.

The occurrence of phillipsite in terrigenous clay is evident by the Al-K scatter plot where trend line intersects K axis at more than 50% of total K suggesting excess K in the form of phillipsite. Therefore, the presence of phillipsite might be responsible for negative correlation between χ and Al ($r = -0.52$). In siliceous ooze the strong positive correlations among χ, $\mathrm{Al_{exc}}$ and $\mathrm{Fe_{exc}}$ suggest the presence of authigenic Fe-rich smectite. High Mn content (0.5%) probably in the form of manganese micronodules is also contributing to χ in both calcareous and siliceous ooze but not in the terrigenous core where mean Mn content (0.1%) is similar to crustal abundance. Thus, χ systematically records the terrigenous variation in both the biogenic sediments but in terrigenous clay it indirectly suggests the presence of authigenic minerals.

1. Introduction

Terrigenous material in marine sediments is generally supplied by fluvial and aeolin sources. The variation in the amount and nature of terrigenous material in sediment, through time, can be traced by the simple measurement of χ (Verosub and Roberts 1995). The χ of sediment is largely due to the presence of magnetic minerals (Currie and Bornhold 1983). The spatial and temporal distribution of χ in sediments is not only due to variable abundance of iron-bearing ferri- and anti-ferromagnetic minerals, but also due to the presence of diamagnetic and paramagnetic minerals such as quartz, feldspar, carbonates and clays (Bareille *et al* 1994). Therefore, temporal records of sedimentary χ might indicate changes in relative variations of biogenic, authigenic, and terrigenous components. The χ has been widely used in conjunction with several other palaeoclimate proxies such as calcium carbonate and oxygen isotopes in deep sea sediments as a useful paleoclimate indicator (Kent 1982; Robinson 1986; Mead *et al* 1986; Doh *et al* 1988; Sager and Hall 1990; Bloemendal *et al* 1988, 1992), changing sedimentary environment (Curry *et al* 1995) and

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Table 1. *Details of sediment cores from the Central Indian Ocean Basin.*

Core no.	Latitude	Longitude	Water depth (m)	Core length (cm)	Sediment type
AAS-01/SPC-18	02°59′N	77°10′E	4068	31.5	Calcareous ooze
AAS-40/GC-02	02°59′S	77°10′E	5000	479	Terrigenous sed
AAS-27/GC-01	13°02′S	77°09′E	5400	551	Siliceous ooze

pollution studies (Petrovsky *et al* 1998; Maiti *et al* 2005).

Shankar *et al* (1994) studied a large number of deep Arabian Sea surface sediments and suggested that χ can be used to estimate the iron content of marine sediments. In CIOB long sediment cores were not studied for χ and no effort had been made to correlate χ with detrital and authigenic fractions of individual elements. The χ variability in sediments of the northern Indian Ocean was investigated to understand climate-driven changes during the Quaternary (Bloemendal and de Menocal 1989; Colin *et al* 1998; Sangode *et al* 2001; Anil Kumar *et al* 2005) and weathering history of Himalayas (Chauhan *et al* 2004). As the χ could be a potential indicator of terrigenous material supply to deep ocean floor and, the Himalayan detritus reaching far south in the southern hemisphere of Indian Ocean (Banakar *et al* 2003), it may be possible to obtain records of past-changes in continental supply by monitoring past-variability of χ. Therefore in this study, we investigate the causes of χ variations in different types of sediments, such as calcareous, siliceous ooze and terrigenous clay in the CIOB. Further, we evaluate dominant components responsible for any such variability in the sediment.

2. Materials and methods

Three sediment cores utilized for the present study were collected onboard R. V. *A. A. Siderenko* during cruise nos. 1, 27 and 40. Each of these three sediment cores (table 1) represents different sediment type, viz., calcareous ooze (AAS-01/SPC-18), terrigenous clay (AAS-40/GC-02) and siliceous ooze (AAS-27/GC-01) (figure 1). The calcareous core was 31.5 cm long and sub-sampled at 3 cm intervals, whereas siliceous and terrigenous cores were 5.5 m and 4.8 m long respectively and sub-sampled at 2 cm intervals. Here onwards AAS-01/SPC-01 (calcareous core) is referred to as **CC**, AAS-40/GC-02 (terrigenous core) as **TC** and AAS-27/GC-01 (siliceous core) as **SC** for convenience.

All sub-samples were oven dried at 40°C and powdered in agate mortar. The dried powders were used to measure the χ and analysed for Al, Fe, Ti and Mn concentrations. For χ measurements, accurately weighed aliquots were packed in 8 cm^3 pots and immobilized by covering with plastic films. Volume magnetic susceptibility (κ) was measured on a Barrington Instruments® MS-2 Susceptibility Meter with MS2B dual frequency sensor (460 Hz

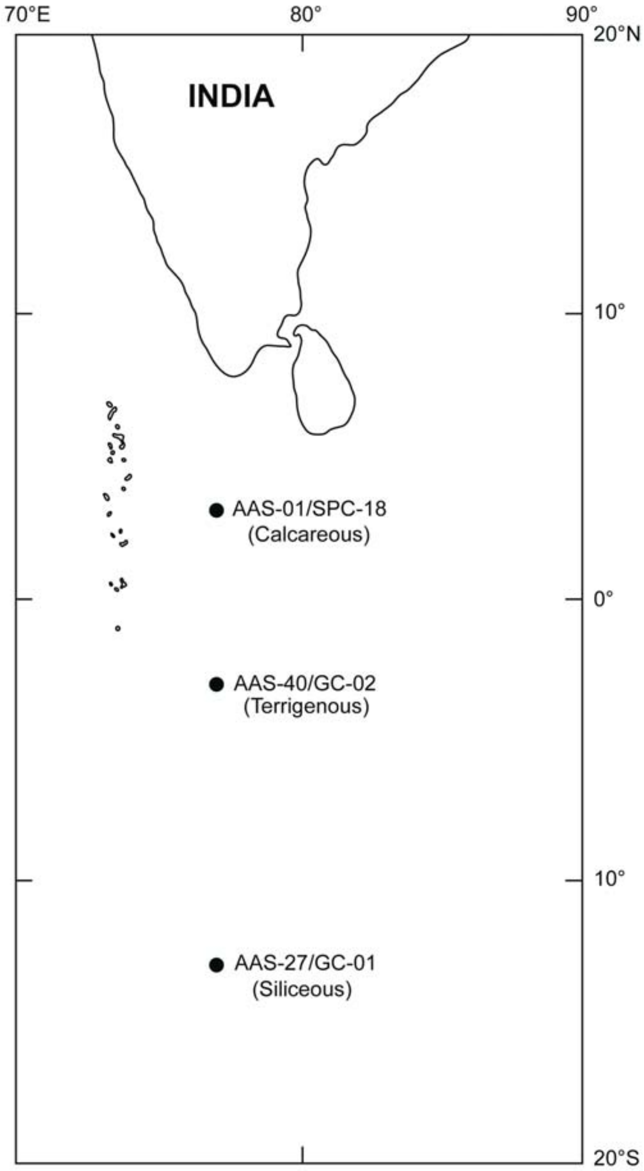

Figure 1. Location map showing three sediment cores from CIOB.

and 4600 Hz). Low frequency, (κ_{lf}, 0.46 kHz) and high frequency (κ_{hf}, 4.6 kHz) were measured twice for each sample on 0.1 range and the average of the two measurements was considered. Mass specific values were calculated and expressed as $\mathrm{m^3 kg^{-1}}$, using $\chi = \kappa/\rho$, where ρ is the dry bulk density and κ is volume-specific. Measurements of frequency-dependent susceptibility ($\chi_{\mathrm{fd}}\%$) is calculated as $\chi_{\mathrm{fd}}\% = (\chi_{\mathrm{lf}} - \chi_{\mathrm{hf}})/\chi_{\mathrm{lf}} \times 100$ (Yamazaki and Ioka 1997). The $\chi_{\mathrm{fd}}\%$ is useful for detecting the presence of super paramagnetic grains (Bloemendal *et al* 1985).

Al, Fe, Ti and Mn concentrations were measured in the aliquots of sub-sections of all three sediment cores ($n = 522$) on a Perkin–Elmer Optima 2000 ICP-OES using solutions prepared in a mixture of HF, $\mathrm{HClO_4}$ and $\mathrm{HNO_3}$ in an open vessel digestion protocol (see Parthiban 2005). International reference standard material MAG-1 was used to check the accuracy and duplicate analysis for precision. The results were accurate and precise to within ±4% for the elements analysed. Structurally unsupported element concentration was estimated as excess element (E_{exc}) content following Murray and Leinen (1996) empirical relationship:

$$E_{\mathrm{exc}} = E_{\mathrm{tot}} X - [\mathrm{Ti}_{\mathrm{Sample}} X (E/\mathrm{Ti}_{\mathrm{Shale}})],$$

where E is element of interest.

The E_{exc} concentration was then subtracted from the total content of respective element to obtain detrital fraction. The other alternative to get the detrital and structurally unsupported fraction in the sediment is by leaching/partition geochemistry, which itself is a separate aspect. However, in calculating the E_{exc} we assumed a uniform element/Ti of shale throughout the core depth. The estimation of E_{exc} using empirical formula is reasonably well accepted (Murray and Leinen 1993; Banakar *et al* 1998; Pattan and Shane 1999).

3. Results and discussion

3.1 *Magnetic susceptibility*

The χ is directly related to magnetic material in the sediment and is the total contribution from all Fe-bearing minerals (Thomson and Oldfield 1986; Verosub and Roberts 1995) and is affected by dia- and para-magnetic minerals resulting in dilution. The χ, Al, Fe, and Ti data of all three sediment cores are plotted against the core depth (figures 2–4). Maximum, minimum and mean values of low-frequency (χ_{lf}), high-frequency (χ_{hf}) and frequency dependence ($\chi_{\mathrm{fd}}\%$) are presented in table 2. In general, the mean χ_{lf} is low in CC ($12.32 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$), moderate in TC ($29.93 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$), and high in SC ($38.06 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$) (table 2). These mean values of χ_{lf} suggest that the magnetic minerals are more abundant in SC compared to the other two sediment types. The χ in CC has nearly 2–3 times lower than SC and TC and shows increasing trend with the core depth (figure 2). The TC is closer to continent compared to SC but the χ values are lower ranging from 9.78 to $83.47 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$ with an average of $29.93 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$ (figure 3). The low values of χ are observed in the top 50 cm, 135 to 155 cm, 225 to 250 cm, and 275 to 460 cm depth-sections in the core, with more or less uniformly low values between 275 cm and 460 cm depth (figure 3). These variations are obviously related to monsoonal intensity on the Indian subcontinent. The SC shows considerable variation in χ ranging from 19.14 to $50.40 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$ with an average of $38.06 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$ (figure 4). The χ is higher in the top 200 cm and below 400 cm and reaches a minimum at ~ 300 cm depth in core. The lowest χ at ~ 300 cm depth in core (figure 4) may be suggestive of significantly reduced sediment input from the Ganges–Brahmaputra river system probably due to arid conditions. The Nd–Sr isotopic studies

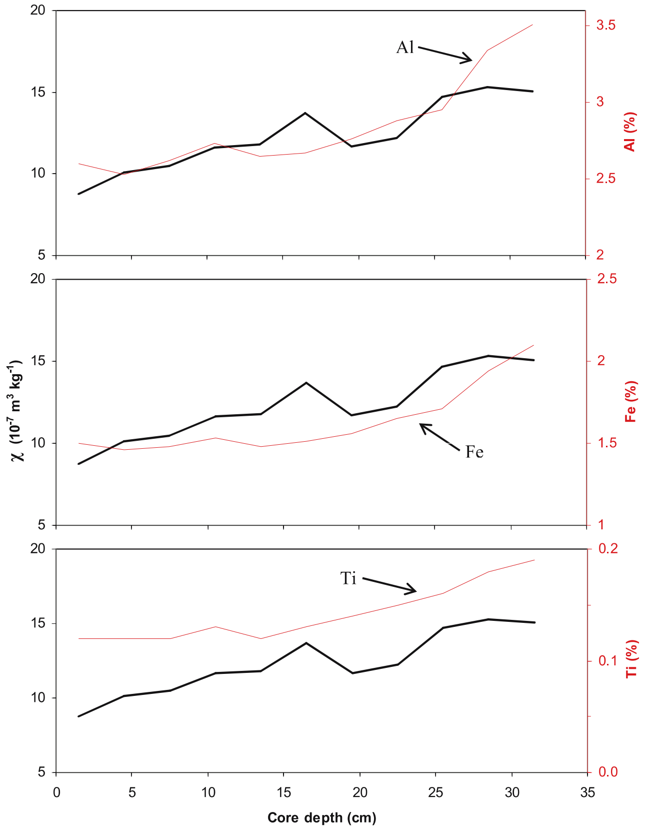

Figure 2. Variation of magnetic susceptibility along with Al (%), Fe (%) and Ti (%) content in a calcareous ooze core (AAS-01/SPC-18) from CIOB.

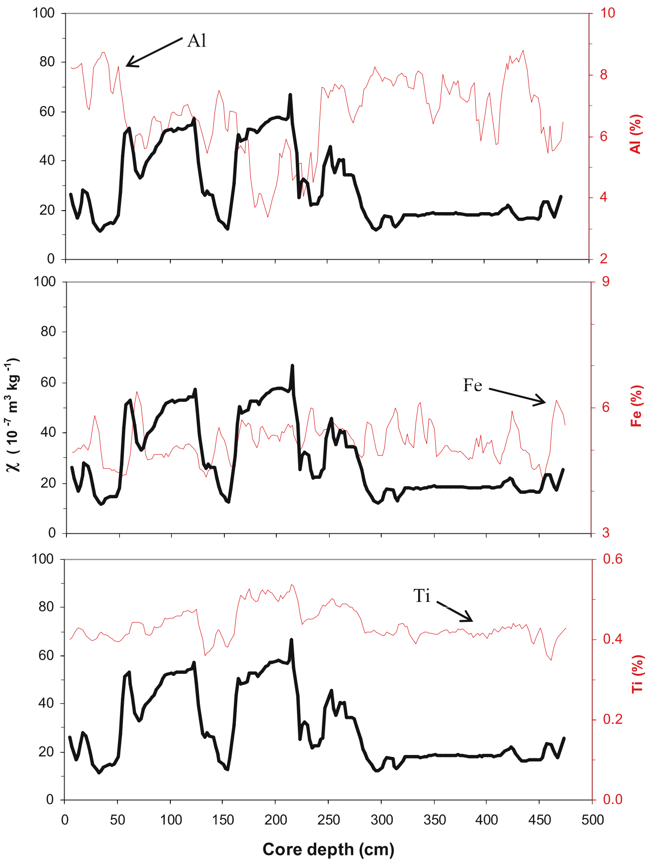

Figure 3. Variation of magnetic susceptibility along with Al (%), Fe (%) and Ti (%) content in a terrigenous core (AAS-40/GC-02) from CIOB.

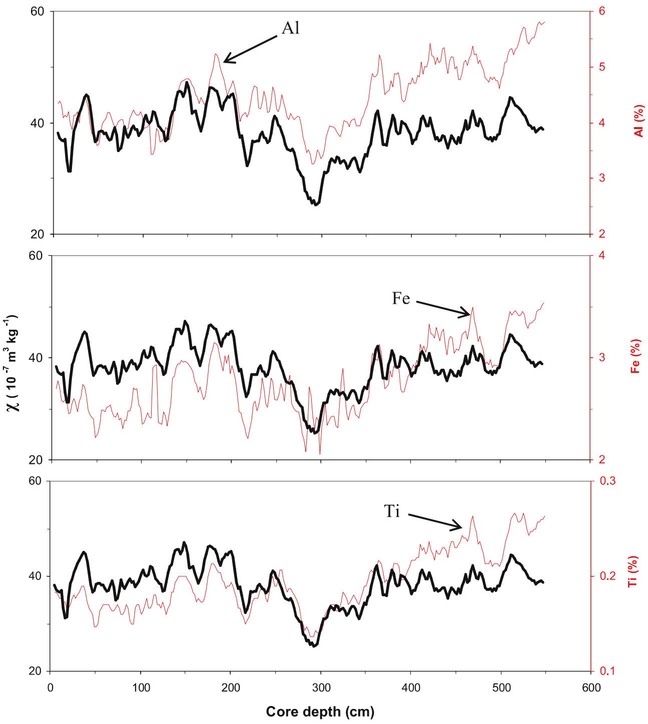

Figure 4. Variation of magnetic susceptibility along with Al (%), Fe (%) and Ti (%) content in a siliceous core (AAS-27/GC-01) from CIOB.

of detrital fractions of the CIOB sediment and Fe–Mn crusts have clearly indicated that most of the terrigenous material has originated from High Himalayan Crystalline Series (Fagel *et al* 1994; Banakar *et al* 2003). There are few significant fluctuations in χ throughout the depth indicative of weak and strong monsoonal rainfall, which brings the detrital fraction into CIOB (figures 3 and 4). The non-availability of a time-scale for the studied sediment cores renders interpretation in terms of past climate changes rather non-feasible.

3.2 *Relationship between elemental concentration and magnetic susceptibility*

Average concentrations of Al, Fe, Ti, Mn, and χ values for all three sediment cores along with inter-elemental correlations are presented in table 3. As expected: (a) in CC, the mean concentrations of Al (2.84%), Fe (1.63%), Ti (0.14%) and χ ($12.32 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$) are low due to dilution by calcium carbonate; (b) the TC record highest content of Al (6.84%), Fe (5.2%) and Ti (0.44%) but associated with moderate χ ($29.93 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$) and (c) SC has moderate content of Al (4.49%), Fe (2.80%), Ti (0.19%) and high χ ($38.06 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$). These chemical data suggest that TC receives nearly 2 and 3-fold increased detrital sediment input compared to CC and SC respectively. But the χ is higher in SC ($38.06 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$) compared to TC ($29.93 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$). In CC and SC, a mutually strong positive correlation ($r > 0.87$: table 3) between Al, Fe, and Ti suggests their common source mainly from terrigenous fraction. Contrastingly, in TC, the Al is negatively correlated with Ti ($r = -0.24$) suggesting that Al is not derived from detrital source, on the other hand, Al and Fe exhibit no mutual

Table 2. *Low frequency, high frequency and frequency dependent parameter for all three sediment cores from CIOB.*

	χ_{lf} ($10^{-7}\,\mathrm{m^3\,kg^{-1}}$)			χ_{hf} ($10^{-7}\,\mathrm{m^3\,kg^{-1}}$)			χ_{fd}%		
Core no.	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.
AAS-01/SPC-18	15.32	8.75	12.32	14.82	8.21	11.29	18.75	00	8.53
AAS-40/GC-02	83.47	9.78	29.93	82.67	8.50	28.58	13.20	00	3.30
AAS-27/GC-01	50.40	19.14	38.06	47.81	20.73	34.07	23.30	4.60	10.75

Table 3. *Some important elemental concentration (average), magnetic susceptibility values and correlation between χ and geochemical elements (bulk, excess and detrital fractions) in three sediment cores from CIOB.*

Core no.	AAS-01/SPC-18	AAS-40/GC-01	AAS-27/GC-02
Sediment type	Calcareous	Terrigenous	Siliceous
No. of sub-samples	$n = 11$	$n = 236$	$n = 275$
χ ($10^{-7}\,\mathrm{m}^3\,\mathrm{kg}^{-1}$)	12.32	29.93	38.06
χfd(%)	8.53	3.30	10.75
Al (mean) (%)	2.84	6.84	4.49
Fe (mean) (%)	1.63	5.20	2.80
Ti (mean) (%)	0.14	0.44	0.19
Mn (mean) (%)	0.46	0.10	0.53
$\mathrm{Al_{exc}}$(%)	16.0	12.0	28.0
$\mathrm{Fe_{exc}}$(%)	31.0	36.0	46.0
$\mathrm{Mn_{exc}}$(%)	84.0	26.0	94.0
Al-Fe (bulk) correlation	$r = +0.99$	$r = +0.06$	$r = +0.87$
Al-Ti	$r = +0.98$	$r = -0.24$	$r = +0.92$
Fe-Ti	$r = +0.98$	$r = +0.35$	$r = +0.88$
Al-Mn	$r = +0.98$	$r = +0.17$	$r = +0.39$
χ-$\mathrm{Al_{exc}}$ correlation	$r = -0.77$	$r = -0.17$	$r = +0.25$
χ-Al detrital	$r = +0.85$	$r = -0.37$	$r = +0.43$
χ-Al bulk	$r = +0.82$	$r = -0.52$	$r = +0.47$
χ-$\mathrm{Fe_{exc}}$ correlation	$r = +0.25$	$r = -0.28$	$r = +0.33$
χ-Fe detrital	$r = +0.86$	$r = +0.69$	$r = +0.43$
χ-Fe bulk	$r = +0.78$	$r = +0.16$	$r = +0.45$
χ-Ti correlation	$r = +0.85$	$r = +0.69$	$r = +0.43$
χ-$\mathrm{Mn_{exc}}$	$r = +0.83$	$r = -0.12$	$r = +0.39$

association ($r = 0.06$) suggesting their independent sources (table 3; also see Parthiban 2005). This type of correlation is rarely observed in the marine sediments.

The positive correlation between Fe and Ti in both CC ($r = 0.98$) and SC ($r = 0.88$) sediments suggests the possible presence of titanomagnetite minerals. In spite of the dominance of biogenic components in both these sediment types, χ follows Al, Fe, and Ti trend within the sediment cores (figures 2 and 4). In TC, Fe and Ti are not strongly correlated ($r = 0.35$) as compared to SC and CC ($r = 0.9$), suggesting that a major portion of Fe may have been associated with authigenic minerals.

In general, χ positively correlates with Ti content in all the three cores, whereas it is positively correlated with Al and Fe content in both CC and SC, but is negatively correlated with Al and no relation with Fe in TC (table 3). To further refine the observed relationships between χ and elemental concentrations, we have portioned the bulk chemical data into detrital and non-detrital ($\mathrm{El_{exc}}$) and is presented in table 3. The $\mathrm{Al_{exc}}$ and $\mathrm{Fe_{exc}}$ are lower in CC and TC compared to SC (table 3). The χ exhibits a negative correlation with $\mathrm{Al_{exc}}$ ($r = -0.77$) in CC because biogenic carbonate is diamagnetic in nature and probably diluting χ. The high calcium carbonate content (55%, Parthiban 2005) in the CC is due to its location (4068 m) above the carbonate compensation depth (Banakar *et al* 1998). The negative correlation between carbonate and χ is similar to the earlier observations (Curry *et al* 1995; Frederichs *et al* 1999). In CC, $\mathrm{Al_{exc}}$ and calcium carbonate show strong positive correlation ($r = 0.86$) (Parthiban 2005). This probably suggests that settling biogenic tests effectively scavenge dissolved Al from the water column (Murray and Leinen 1996; Banakar *et al* 1998).

In both SC and TC, the χ and $\mathrm{Al_{exc}}$ exhibit a weak positive ($r = +0.25$) and negative ($r = -0.17$) correlations respectively. This suggests that $\mathrm{Al_{exc}}$ in both these cores has multiple associations. The $\mathrm{Al_{exc}}$ in marine sediment could also be due to the presence of authigenic Fe-rich smectite (Timothy and Calvert 1998; Pattan *et al* 2005) and volcanic ash of rhyolitic composition (Pattan and Shane 1999). The absence of volcanic ash and no correlation between biogenic opal and $\mathrm{Al_{exc}}$ (Parthiban 2005), and presence of Fe-rich smectite in CIOB sediments (Pattan *et al* 2005) with a positive χ (Frederichs *et al* 1999), might be responsible for the observed positive correlation. The moderate positive correlation between Fe_{exc} and Al_{exc} ($r = 0.35$) further supports the presence of Fe-rich smectite. These types of relationships are not evident in TC. The negative correlation between χ and Fe_{exc} in TC ($r = -0.28$) suggests that Fe possibly has association with very fine biogenic magnetite precipitated by bacteria under suboxic/anoxic conditions (Kirschvink *et al* 1984; Stolz *et al* 1986; Ellwood *et al* 2000). In this core, suboxic conditions are evident by very low Mn content ($< 0.1\%$) which is similar to crustal abundance. The high organic carbon (0.48% to 2.31%) content with very fine grain sediment texture (clay content $> 95\%$) (Parthiban 2005), might have provided favourable conditions for the formation of fine biogenic magnetite. Therefore, we suspect that biogenic magnetite of diamagnetic nature might be responsible for non-association of bulk Al and Fe ($r = 0.01$), and negative correlation between χ and Fe_{exc} ($r = -0.27$) in TC. Further study needs to confirm the presence of biogenic magnetite.

The Fe_{exc} is low in CC (31%) and TC (36%) as compared to SC (46%). The correlation between χ and Fe_{exc} in SC is positive ($r = 0.33$), whereas in TC it is negative ($r = -0.28$) suggesting different phases of Fe_{exc} in these two cores. This is confirmed by our earlier observations that Fe_{exc} in SC and TC is associated with Fe-rich smectite and biogenic magnetite respectively. In TC, Al and K show a strong positive correlation ($r = 0.61$) and the best-fit line intersects the K axis at 1.4% suggesting that nearly 50% of K is of non-detrital nature (Parthiban 2005). This non-detrital or K_{exc} might be in the form of phillipsite, which is diamagnetic in nature and probably responsible for the negative correlation between Al and χ ($r = -0.52$). The manganese content in CC (0.46%) and SC (0.53%) is enriched nearly five times compared to that in TC (0.1%). Similarly as expected, Mn_{exc} is also high (84% to 94%) in both CC and SC compared to TC (26%), suggesting that the former two sediment-types experience higher oxidizing conditions than the latter type. Assuming 0.1% of Mn in TC as silicate structure bound component, the high Mn content in both CC and SC may be authigenic in nature, probably in the form of dispersed particalate Mn–oxide or manganese micronodules. There is a positive correlation between χ and Mn_{exc} in both CC and SC (table 3). In TC, only top 20 cm of the core contains Mn_{exc} resulted by diagenetic remobilization and below 20 cm depth there is no Mn_{exc}. This might have resulted into a no correlation between χ and Mn_{exc} (table 3). Therefore, χ indirectly suggests the presence of authigenic phillipsite, Fe-rich smectite, manganese micronodules and biogenic magnetite in the CIOB sediments.

The frequency dependence of magnetic susceptibility (χ_{fd}) is a diagnostic parameter to understand the magnetic grain variation (Yamazaki and Ioka 1997). The average χ_{fd} of CC and SC is higher (8.53% and 10.75% respectively) compared to that of TC (3.3%). This suggests that TC consists of mainly detrital material which is evident by the textural analysis where clay content is $> 95\%$.

4. Conclusions

We investigated the relationship between magnetic susceptibility and chemical composition (bulk, detrital and non-detrital fractions) of three different sediment types from the CIOB. The results of this study demonstrate the following:

- Low frequency magnetic susceptibility (χ) can be used as an indicator of terrigenous influence in both carbonate and siliceous sediment types, where it behaves identical to that of detrital representing elements such as Al, Fe and Ti. On the other hand, in terrigenous sediment, χ behaves similar to only Ti content, but not with Al and Fe suggesting that both Al and Fe are not derived by the detrital source.
- The correlation between χ and non-silicate element proportions in these studied sediment indirectly suggests the presence of authigenic minerals such as phillipsite, Fe-rich smectite and manganese micronodules. This further indicates active post-depositional diagenetic processes within the sediment.

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