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# Environmental magnetism and application in the continental shelf sediments of India

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#### Abstract

Mineral magnetic and geochemical analyses were carried out on surface sediments from the continental shelf of India. The purpose of this study is to examine the environmental assessment of heavy metal concentrations and its impact in the coastal environment using magnetic techniques and to gain an understanding on the factors controlling metal concentrations and distributions in the east and west coast of India. The strong relationships between Anhysteretic Remanent Magnetization ( $\chi_{ARM}$ ) and heavy metals can be explained by the role of iron oxides controlling metal concentrations, though the link is also reinforced by the strong tendency of  $\chi_{ARM}$  to be associated with the finer particle sizes. Higher values of magnetic susceptibility, IRM<sub>20 mT</sub> and SIRM are associated with the east coast shelf sediments suggest the presence of high ferrimagnetic content, which can be derived from the weathering products of the Deccan Basalts.  $\chi_{ARM}$  can be used as a normalizer for particle size effects in the way that Aluminium (Al) is often used. The relationship between magnetic parameters and heavy metal concentrations (Fe, Cu, Cr and Ni) showed a strong positive correlation in the east coast sediments, much less so in the case of the west coast. This finding suggests that the simple, rapid and non-destructive magnetic measurement can be used as an indicator for the heavy metal contamination and proxies for the measurement of heavy metals content in the coastal environment.

Key words: Mineral Magnetic; Heavy metal; Magnetic method; Sediment; Continental shelf; India.

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#### **1. Introduction**

Magnetic measurements are being used as a powerful tool for the assessment of heavy metal contamination in soils and sediments and in the investigation of the compositional properties of rocks, sediments and soils (Thompson and Oldfield, 1986; Walden et al., 1999; Maher and Thompson, 1999). Magnetic minerals in soils are derived either from the parent rocks (lithogenic origin), pedogenesis or as a result of anthropogenic activities. Susceptibility measurements play an important role for monitoring environmental pollution in the case of minor contributions of the first two sources to the magnetic properties of soils. Accumulation of anthropogenic ferrimagnetic particles, originating during high temperature combustion of fossil fuels (e.g. Vassilev 1992; Dekkers and Pietersen 1992), results in significant enhancement of topsoil magnetic susceptibility. Therefore, under favourable circumstances, magnetic properties of soils and sediments can be used for the assessment of imissions, both from local pollution sources and on a wider regional scale. Already a pioneering work of Thompson and Oldfield (1986) reported that soils near urban areas and industrial zones have an increased magnetic susceptibility, due to the deposition of magnetic particles, such as, dusts of the metallurgical industries and fly ashes of the coal combustion. Magnetic measurements are relatively simple and non-destructive and due to high sensitivity and speed are often applied for detecting industrial pollution. Because there is a need for fast and cost effective screening and monitoring tools for industrial pollution, magnetic methods have drawn the attention of modern researchers as an approximate tool, to detect and characterize environmental pollution (e.g., Dearing et al., 1996; Petrovský and Ellwood 1999; Hoffmann et al., 1999; Magiera and Strzyszcz 2000; Petrovský et al., 2001; Hanesch and Scholger 2002; Veneva et al., 2004, and others). This work has been used to identify the sources of industrial pollution (Scoullos et al., 1979; Hunt et al., 1984; Matzka and Maher 1999; Petrovský et al., 2000, 2001; Klose et al., 2001; Knab et al., 2001; Lecoanet et al., 2001; Hanesch and Scholger 2002; Muxworthy et al., 2002; Hanesch et al., 2003; Kapicka et al., 2003; Moreno et al., 2003; Desenfant et al., 2004; Jordanova et al., 2004; Spiteri et al., 2005) and to characterize various depositional environments (e.g. Arkell et al., 1983; Oldfield et al., 1985, 1999; White et al., 1997; Walden et al., 1995, 1997; Schmidt et al., 1999; Wheeler et al., 1999). The relationship between mineral magnetic measurements and chemical/physical properties of sediments and soils have been established in several studies (Oldfield et al., 1985; Oldfield and Yu, 1994; Clifton et al., 1997, 1999; Chan et al., 1998; Petrovský et al., 1998; Xie et al., 1999, 2000; Booth, 2002). Mineral magnetic measurements were used as a tool for determining sediment provenance (Oldfield

and Yu, 1994), transport pathways (Lepland and Stevens, 1996), as a proxy for geochemical, radioactivity, organic matter content and particle size data (Bonnett et al., 1988; Oldfield et al., 1993; Hutchinson and Prandle, 1994; Clifton et al., 1997, 1999; Xie et al., 1999, 2000; Zhang et al., 2001; Booth et al., 2005). Magnetic measurements as a proxy for industrial contamination have also been employed in India (Goddu et al., 2004). Hence, the present study is undertaken in order to examine the environmental assessment of heavy metal concentrations and its impact in the coastal environment using magnetic techniques and to gain an understanding on the factors controlling metal concentrations and distributions along the east and west coast of India.

#### 2. Materials and methods

#### 2.1. Study Area

#### 2.1.1. Geographic setting

The subcontinent of India, geographically covers tropical to subtropical climatic zones and exhibits strong seasonality from warm humid to arid and cold arid conditions. The climate of the subcontinent is dominated by Monsoon systems; this region remains humid during summer and dry during winter. It has basically two main seasons, the wet and dry, instead of four seasons. The gradient of climatic zones is largely affected by the sharp altitudinal changes in the northern half where the Himalaya forms the major relief. The Indian subcontinent experiences mostly a tropical monsoon climate, with significant seasonal variations in rainfall and temperature. The Himalayas, acting as a barrier to the cold northerly winds from Central Asia, maintain the pattern of the Indian Ocean monsoon circulation. The Thar Desert allows oceanic atmospheric circulation and sediment dust-aerosol influx deep into the continent. The southwest (SW) monsoon is divided into Arabian Sea Branch of the SW Monsoon and Bay of Bengal Branch of the SW Monsoon. The Arabian Sea branch extends the low-pressure area over the Thar Desert in Rajasthan whereas the Bay of Bengal branch results in turbulence in the region due to the rapid altitudinal differences and narrowing orography. The Arabian Sea branch is roughly three times stronger than the Bay of Bengal branch. This branch of the monsoon moves northwards along the Western Ghats giving rain to the coastal areas west of the Western Ghats and the eastern parts of the Western Ghats do not receive much rain from this monsoon. The climate-induced sedimentation

processes take place in large-scale during strong monsoons as cyclones occur in the coastal region (Sangode et al., 2007).

#### 2.1.1.2. East Coast-Geology-Climate

The outer limit of the eastern continental shelf of India lies at ~200 m (Fig. 1) and the inner shelf and the continental slope are covered by clastic sediments (Rao, 1985). The outer shelf is covered by calcareous relict sediments and off the river mouths the shelf is covered by fine-grained terrigenous sediments. The shelf at the mouths of the rivers receives a large part of its sediment from the rivers Ganges, Brahmaputra and Mahanadi in the north, Godavari and Krishna in the central region, all forming fertile, heavily populated deltas. Sediment from the rivers has made the bay a shallow sea, and the waters have reduced the salinity of surface waters along the shore. Sediment input and annual discharge is less from the smaller rivers such as Pennar and Cauvery in the south (Rao, 1979; Rao, 1985).

The presence of the Deccan Basalt is observed along the tributaries of the Godavari and discharged into the Bay of Bengal from the east coast of the Peninsular India through the Mahanadi, Godavari and Cauvery river systems (Sangode et al., 2007). Deccan Province also covers the studied stations in the east coast of India (Raman et al., 1995).

#### 2.1.1.3. West Coast-Geology-Climate

The Indus river is the largest source of sediments in the Arabian Sea, which extend outward to a distance of ~1000-1500 km (Rao and Rao, 1995). It predominantly drains the Precambrian metamorphic rocks of Himalayas and to a lesser extent the semi arid and arid soils of West Pakistan and NW India (Krishnan, 1968). Deccan Trap basalts (Fig.1) are the predominant rock types cropping out in the Saurashtra and the drainage basins of the Narmada and Tapti rivers, which annually discharge ~  $60x10^6$  tonnes sediment through the Gulf of Cambay (Rao, 1975) where a semi-arid climate prevails. The Western Ghats are composed of basalts between Mumbai and Goa, and Precambrian granites, gneisses, schists and charnockites between Goa and Cochin (Krishnan, 1968). The Ghats are located on the coast between Goa and Bhatkal but are 50-80 km from the coast south of Bhatkal. The source of sediments in rivers originating in the western part of India is derived the black "cotton soils", covering the Deccan Traps, a large percentage of which is mainly composed of montmorillonite. The drainage area in the upper reaches of these rivers is a

montmorillonite-rich, zone but in the lower reaches, they drain through Precambrian formations that contain kaolinite rich soils that are of secondary significance in the shelf sediments derived from the Godavari and Krishna rivers (Rao, 1991). It is well established that source rock compositions and weathering mechanisms basically control the distinct geochemical compositions of sediments in the east and west coast of India (Alagarsamy and Zhang, 2005).

#### 2.2. Sampling and Analysis

Surface sediments from the east and west coasts of India were collected using a Van Veen Grab/Snapper during several cruises of the R.V. Gaveshani (130, 139 and 143) (Fig. 1; Table 1). Subsamples were collected from the uppermost layer of the sediment taking care to minimize contamination. Samples were frozen after collection and later thawed, dried at 50-60°C in an oven and disaggregated in an agate mortar before chemical treatment for total metal analysis. For element analysis, the known quantity (~0.2 g) of the powdered samples were digested with a mixture of concentrated HF – HNO<sub>3</sub> – HClO<sub>4</sub> for the total metal content (Zhang and Liu, 2002). Solutions were analyzed for Al, Ca, K, Fe, Cr, Cu and Ni using ICP-AES (Model: PE-2000).

Accuracy of the analytical methods was monitored by analysing standard reference materials (GSD-9) with study samples in every batch of analysis. Further checks were made through repeated analyses of the standard reference materials by ICP-AES (Model: PE-2000). Precision of the analyses was checked by triplicate analysis of standard materials. Calculated coefficients of variation were within  $\pm \sim 1-8\%$  for the different elements except K and within  $\pm 4$  for K of the certified ones (NIM-G).

Magnetic susceptibility measurements were carried out on sub samples which were dried at 40 °C and disaggregated. The magnetic susceptibility ( $\chi$ , mass-specific), 'saturation' isothermal remanent magnetization (SIRM) after application of 1T, and then back field remanence measurements at -20 mT, -40 mT, -100 mT and -300 mT were measured on all samples. Both low (0.47 kHz) and high (4.7 kHz) frequency susceptibility ( $\chi_{1f}$  and  $\chi_{hf}$  respectively) were determined using a Bartington MS2 dual frequency susceptibility meter. Frequency dependent susceptibility ( $\chi_{fd}$ ) was calculated from the expression  $\chi_{fd}$  ( $\gamma_{6}$ ) = [( $\chi_{1f} - \chi_{hf}$ )/ $\chi_{1f}$ ] x100. Anhysteretic remanent magnetization (ARM), here expressed as susceptibility of ARM ( $\chi_{ARM}$ ) was measured after demagnetion in an AF field of 100 mT

inducing a DC biasing field of 0.04 mT using a Molspin AF demagnetizer and Minispin pulse magnetizer and measured on the Molspin Minispin magnetometer (Walden et al., 1997). Isothermal Remanent Magnetization (IRM) is the remanent magnetization acquired by a sample after exposure to, and removal from, a steady (DC) magnetic field. IRM depends on the strength of the field applied, which is often denoted by a subscript. It is also a function of the magnetic mineralogy and grain size. The maximum remanence that can be produced in a sample is called Saturation Isothermal Remanent Magnetization (SIRM). IRM is often used as an indicator for the concentration of ferrimagnetic minerals, but antiferromagnetic minerals, such as hematite and goethite also contribute to IRM measurements where fields in excess of 100 mT are used.

After a sample has acquired an IRM it is often possible to (partially) demagnetize the sample by exposing it to a magnetic field of reversed direction. Such a partial demagnetization can yield information about the ease of remanence acquisition, or the coercivity of a sample. The results are expressed as an *S*-ratio, for example,

#### S100=IRM-100/SIRM and S300=IRM-300/SIRM

where  $IRM_{-100, -300}$  denotes an IRM acquired in a reversed field of 100 mT and 300 mT respectively after SIRM acquisition. *S*-ratios can be used to gain information about the magnetic mineralogy (Bloemendal et al., 1992). Hard IRM (HIRM), broadly indicative of antiferromagnetic minerals, mainly hematite, was defined as HIRM = 0.5 x (SIRM+IRM-<sub>300</sub> mT).

#### 3. Results and discussion

The parameters sensitive to fine-grained magnetic minerals ( $\chi_{ARM}$  and  $\chi_{fd}$ ), the ratio of  $\chi_{ARM}$  to  $\chi_{If}$  and  $\chi_{ARM}/\chi_{fd}$  are discussed in this study. The concentration-sensitive magnetic parameters such as magnetic susceptibility (Table 2) and its concentration related parameters (Fig. 2a-c); Magnetic susceptibility vs. IRM<sub>20 mT</sub> (Fig. 3);  $\chi_{ARM}/\chi_{If}$  vs.  $\chi_{ARM}/\chi_{fd}$  (Fig. 4); Fe, Cr, Cu and Ni vs. Al (Fig. 5 a-d); Fe, Cr, Cu; Ni vs.  $\chi_{ARM}$  (Fig. 6a-d); Fe, Cr, Cu and Ni normalized by  $\chi_{ARM}$  vs. Al normalization (Fig. 7) and Magnetic susceptibility vs. EF (metal) (Fig. 8) are presented along the east and west coast of India.

#### 3.1. Variation of heavy metals - influence of particle size

Heavy metals vary significantly in the shelf sediment of east and west coast of India, especially in the case of Cr, Ni and Cu (Table 3). This variability could be due to particle size effects or anthropogenic influences. Finer sediments with abundant clay minerals, iron/manganese oxides as well as organic matter tend to show higher metal concentrations (Rae, 1997). In our study, the heavy metals (Fe, Cr, Cu and Ni) showed a more significant coefficient of determination with magnetic susceptibility in the east coast sediment than the west (Table 4a,b). It is observed that higher concentration of ferrimagnetic minerals are found in the east coast sediments and low concentration in the west coast of India. The comparable or even stronger dependence of heavy metals on Fe (Table 4a,b) is in accordance with the fact that iron and manganese oxides, which are commonly in close association with clay minerals, have strong absorptive capacity for metals (Kersten and Smedes, 2002).

The higher  $\chi_{fd}$  (%) in the east coast showed that the stronger presence of super paramagnetic grains in these samples than in the west. Magnetic quotients are often useful indicators of the properties of certain minerals and domain states (Lu and Bai, 2006). F300 (IRM<sub>300 mT</sub>/SIRM) and S300 (IRM<sub>-300 mT</sub>/SIRM) can be used as approximate indication of relative importance of canted antiferrimagnetic components and to distinguish ferrimagnetic component from antiferrimagnetic components respectively.

#### 3.2. Remanent magnetic parameters

IRM<sub>20 mT</sub> is expected to be approximately proportional to the multidomain (MD) grain content of ferrimagnetic components (magnetite). Hard IRM (SIRM–IRM<sub>300 mT</sub>) can be used as a rough guide to canted antiferrimagnetic (hematite) components in a sample. High values of IRM<sub>20 mT</sub> and SIRM can be sometimes attributed to a greater accumulation of anthropogenic magnetic minerals (Lu and Bai, 2006). There is a highly significant and much stronger correlation between magnetic susceptibility and IRM<sub>20 mT</sub> for east coast shelf sediment of India (Fig. 3; Table 4a) than the west (Table 4b). This suggests that the magnetic susceptibility of east coast sediment contains mainly from MD ferrimagnetic minerals derived from basalts. Magnetic susceptibility and other environmental parameters of the tributaries of the Godavari river sediment revealed the presence of high ferrimagnetic content as it is composed of weathering products of the Deccan Basalt (Sangode et al., 2007).

#### 3.3. Magnetic parameters as proxies of particle size

 $\chi_{ARM}$  is sensitive to single domain (SD, ~0.03–0.07 µm) ferrimagnetic minerals (Maher, 1988), while  $\chi_{fd}$  indicates the presence of fine viscous grains near the SP-SD boundary (Maher, 1988; Oldfield and Yu, 1994). As SP and SD grains are of sub-micrometer size, if they occur as individual particles, it is expected that they would reside mainly in the finest fraction of sediments (e.g. <2 µm). The inter-parameter ratios  $\chi_{ARM}$ /SIRM and  $\chi_{ARM}/\chi$  reflect variations in the ferrimagnetic grain size, with values peaking in the SD range (Maher, 1988) and are used as grain size indicator of magnetic minerals (Banerjee et al., 1981; Maher, 1988). It is shown that similar correlations exist with  $\chi_{ARM}$  as to particle size (Zhang et al., 2007).  $\chi$  is considered as a reflection of magnetic mineral concentration (Thompson and Oldfield, 1986).

The differences in ferrimagnetic grain are explored by using the plot of  $\chi_{ARM/\chi_{lf}}$  vs.  $\chi_{ARM/\chi_{fd}}$  (Fig. 4). It is clearly indicating that finer grains present in the east coast of India showed correlation (R<sup>2</sup>=0.76) than the west. The west coast sediments showed a weaker  $\chi_{fd}$  values and hence the ratio indicated that it contains coarser magnetic grains.

#### 3.4. Variability of heavy metals - Magnetic normalization

A normalizer must covary in proportion with the natural concentration of the metals of interest (Roussiez et al., 2005). A more significant coefficient of determination ( $R^2 =$  0.91-0.98) between  $\chi_{ARM}$  and different heavy metals (Cu, Ni, Cr and Fe) was observed in the east coast sediments than those along the west coast of India (Table 4a,b).  $\chi_{ARM}$ /SIRM demonstrates strong coefficient of determination with heavy metals (Cu, Ni, Cr and Fe) in the east and the same is observed only Cu and Cr in the west coast sediment of India (Table 4a, b).

Compared to the geochemical normalizer Al,  $\chi_{ARM}$  displays equally or even better coefficients of determination with heavy metals (Table 4a,b; Fig. 5a-d; Fig. 6a-d). It is also evident from the previous study that the relationships of heavy metal levels with  $\chi_{ARM}$  are quite similar to those with the <16 µm fractions (Zhang et al., 2007). The preferred association of heavy metals with fine-grained sediments is actually related to sediment mineralogy, since clay minerals and iron oxides, the important carrier phases of heavy metals, are dominantly associated with finer fraction of sediments (Rae, 1997). This relationship may

therefore reflect the important role of iron oxides in controlling heavy metal concentrations in addition to aluminosilicate minerals. This is also reflected in the strong correlations between heavy metals and iron (Table 4a) in the case of east coast sediment samples. Taking into account the high capacity for remanent magnetization of magnetite, magnetic parameters based on remanent value will be dominated by the magnetite signal (Walden et al., 1997). Although magnetite is a minor component in iron oxide assemblages, fine-grained magnetite may be proportional to the major iron oxides (Zhang et al., 2001). These findings reinforce evidence from the study of Irish Sea coastal sediments (Oldfield et al., 1993; Clifton et al., 1999) that  $\chi_{ARM}$  can be used as proxy for finer fraction of sediments and applied to the normalization of heavy metal concentrations for particle size effects.

Currently, Al is the most frequently used geochemical normalizer in estuarine and coastal sediments (Kersten and Smedes, 2002). Fig. 7a-d demonstrates that normalization of heavy metals by  $\chi_{ARM}$  is positively correlated with normalization by means of Al. The weaker relationship for Fe/Al versus Fe/xARM and Ni/Al versus Ni/xARM is evident from the dissimilarity in scatter plots of Ni against these two normalizers (Fig. 7a-d; Table 4a,b). This similar relationship between Ni and  $\chi_{ARM}$  and the <16  $\mu$ m particle size content is observed and suggested that Ni,  $\chi_{ARM}$  may be the preferred normalizer in the study area (Zhang et al., 2007). Overall, in order to compare the degree of pollution at different sites, normalization by  $\chi_{ARM}$  will give comparable results with that by Al, at least for metal Cu. In order to compare the degree of pollution at different sites,  $\chi_{ARM}$  normalization results are comparable with that by Al. Furthermore, analysis of Al requires a total digestion employing HF to destroy silicates within the sediment. As HF digestion would dissolve heavy metals contained in silicates, which are considered to be not related with anthropogenic source (often referred to as the 'residual' phase), a partial digestion with minimal extraction of 'residual' forms is considered to be able to provide more meaningful environmental information in pollution studies (Sutherland et al., 2004). In this case, if Al is to be used as a normalizer, heavy metal and Al determination will require two separate digestion procedures. Compared to geochemical analysis, the measurement of  $\chi_{ARM}$  is relatively straightforward, rapid and therefore cost effective (Walden et al., 1997). There may be a limit to the potential of this method in studies of sediment cores, due to the possibility of reductive diagenetic alteration of fine-grained magnetic minerals under reducing conditions (Walden et al., 1997), and hence the reliability of  $\chi_{ARM}$ . However, it is unlikely that surface sediments under oxidizing conditions would be seriously influenced. Therefore  $\chi_{ARM}$  normalization can play an

important role in similar coastal environments. In the case of the Irish Sea sediments, it is known that the high ARM values linked to the clay fraction are the result of bacterial magnetosomes growing in situ (Oldfield and Yu, 1994), This could be the case here and it is evidenced from the relationship with heavy metals and its enrichment factor in the east coast of India than the west. Hence, there is the possibility that greigite could be present in areas where brackish rather than truly marine salinities prevail. The presence of greigite and biogenic magnetite needs to be confirmed from GRM/RRM and SEM/TEM studies.

#### 3.5. Enrichment Factor-Influence of grain size and mineralogy

Here, as a common practice, Al is used as a normalizer, upon which enrichment factor (EF) were calculated. The following equation was used to estimate the EF of metals from each sediment station using Al as a normalizer to correct for differences in sediments grain size and mineralogy:

#### $EF = (Me/Al)_{sample} / (Me/Al)$ crustal average

where  $(Me/Al)_{sample}$  and  $(Me/Al)_{crustal average value}$  are, respectively, the metal concentration ( $\mu g/g$  dw) in relation to Al levels (% dw) in sediment samples, and crustal average values taken from Taylor and McLennan (1995).

It is observed that there is a good correlation between magnetic properties (e.g. magnetic susceptibility  $\chi$ ) and enrichment factor (EF of metals) in the east coast of India rather than the west suggesting the enrichment of ferrimagnetic mineral (Fig. 8a-d).  $\chi$  is generally regarded as a reflection of magnetic mineral concentration (Thompson and Oldfield, 1986).  $\chi$  vs. EF for metals showed R<sup>2</sup> values of Fe (0.54; 0.14), Cr (0.79; 0.17), Cu (0.76; 0.09) and Ni (0.32; 0.01) for the east coast of India and the west coast respectively.

In the Figs. 5,6,7,8, the four data points of the east coast (Station nos. 3024, 3025, 3026, 3248 and 3249) lie close to the data points of the west coast. The clay mineral smectite mostly derived from the Deccan Trap basalts (Deccan Trap Province), occurs in both the region as this the Deccan Province also covers this stations in the east coast (Raman et al., 1995; Rao and Rao, 1995). One of the end products of chemical weathering of Deccan Traps is smectites, which may be trapping K and thereby contributing to its limited mobility (Das and Krishnaswami, 2006). The major element chemistry of the clay fraction in sediment is controlled by the variation of K, Al, Mg, Si and Fe content. The K content of clayey

sediments is primarily bound to clay minerals, potassium feldspar and mica. K is found to be less in the basalt. K is mainly held in illite and feldspar, therefore the variation in the K/Al ratio may reflect the variations in illite and feldspar present in the sediments. 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 ( $K_2O/Al_2O_3=0$ ). A higher potassium content relative to Al in sediments implies greater feldspar contribution. K/Al values ranged from 0.11 to 0.16 in the above stations compared to the rest in the east coast of India and Ca/Al varied from 2.79 to 11.79 in the above mentioned stations in the east coast compared to the rest of the stations and its similarity with the west coast samples (Alagarsamy and Zhang, 2009).

#### 4. Conclusions

The magnetic properties used in this study for both normalization and for assessment of the degree of contamination from the samples of east and west coast of India showed a distinct variation in this coastal environment. The presence of finer ferrimagnetic grain and enrichment of ferrimagnetic minerals are observed more on the east than the west coast of India. Higher values of magnetic susceptibility, IRM<sub>20 mT</sub> and SIRM are associated with the east coast shelf sediments suggest the presence of high ferrimagnetic content, which can be derived from the weathering products of the Deccan Basalts.

In shelf sediments from the east and west coast of India, the magnetic parameter  $\chi_{ARM}$ , which is sensitive to single domain (SD, ~0.03–0.07 µm) ferrimagnetic minerals, displays more significant relationships with the heavy metals in the east coast sediments than the west. A comparison with Al, which is frequently used to compensate for particle size effects in pollution studies, indicates that in these samples  $\chi_{ARM}$  is an efficient normalizer for comparison of the degree of pollution at different sites. The strong association between  $\chi_{ARM}$  and heavy metals can be explained by the role of particle size and iron oxides in controlling metal concentrations. Furthermore, the rapid and non-destructive nature of mineral magnetic measurements means  $\chi_{ARM}$  can be easily determined, compared to other approaches such as the analysis of Al. When heavy metals are analyzed using a partial digestion method, which can provide more meaningful environmental information related to total pollutant determination, this magnetic approach will prove especially useful for environmental quality assessment. Magnetic parameters,  $\chi$ ,  $\chi_{ARM}$ ,  $IRM_{20 \text{ mT}}$  and SIRM, have shown that more

significant relationship with the concentration of Fe, Cr, Cu and Ni in the east coast of India than the west. Linear relationship between magnetic mineral concentration-related parameters and the concentration of Fe, Cr, Cu and Ni makes it possible to use magnetic technique as a simple, rapid, and non-destructive tool for the assessment of heavy metals contamination in the shelf region. Although the co-variations presented in this study are rather convincing, it is clear that such approach rely on a careful calibration of the proxy i.e. directly comparing heavy metal concentrations and magnetic parameters for a selected set of samples. The calibration will obviously be site specific and must therefore be adapted to each study site.

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#### References

- Alagarsamy, R., Zhang, J., 2005. Comparative studies on trace metal geochemistry in Indian and Chinese rivers. Current Science 89, 299-309.
- Alagarsamy, R., Zhang, J., 2009. Geochemical Characterization of Major and Trace Elements in the Coastal Sediments of India. Environmental Monitoring and Assessment, DOI: 10.1007/s10661-008-0735-2.
- Arkell, B., Leeks, G., Newson, M., Oldfield, F., 1983. Trapping and tracing: some recent observations of supply and transport of coarse sediment from upland Wales, Special Publication of the International Association of Sedimentologist 6, 107–119.
- Banerjee, S.K., King, J., Marvin, J., 1981. A rapid method for magnetic granulometry with applications to environmental studies. Geophysical Research Letters 8, 333–336.
- Bloemendal, J., King, J.W., Hall, F.R., Doh, S.-H., 1992. Rock magnetism of Late Neogene and Pleistocene deep-sea sediments: relationship to sediment source, diagenetic processes, and sediment lithology. Journal of Geophysical Research 97, 4361–4375.
- Bonnett, P.J.P., Appleby, P.G., Oldfield, F., 1988. Radionuclides in coastal and estuarine sediments from Wirral and Lancashire. Science of the Total Environment 70, 215–236.
- Booth, C.A., 2002. Sediment-Source-Linkages in the Gwendraeth Estuary, South Wales, based on mineral magnetic analyses. Unpublished PhD thesis. University of Wolverhampton.
- Booth, C.A., Walden, J., Neal, A., Smith, J.P., 2005. Use of mineral magnetic concentration data as a particle size proxy: A case study using marine, estuarine and fluvial sediments in the Carmarthen Bay area, South Wales, U.K. Science of The Total Environment, 347, 241-253.
- Chan, L.S., Yeung, C.H., Yim, W.W.S., Or, O.L., 1998. Correlation between magnetic susceptibility and distribution of heavy metals in contaminated sea-floor sediments of Hong Kong Harbour. Environmental Geology 36, 77–86.
- Clifton, J., McDonald, P., Plater, A., Oldfield, F., 1997. Relationships between radionuclide content and textural properties in Irish Sea intertidal sediments. Water, Air, & Soil Pollution 99, 209–216.

- Clifton, J., McDonald, P., Plater, A., Oldfield, F., 1999. Derivation of a grain-size proxy to aid the modelling and prediction of radionuclide activity in saltmarshes and mud flats of the Eastern Irish Sea. Estuarine, Coastal and Shelf Science 48, 511–518.
- Das, A., Krishnaswami, S., 2006. Barium in Deccan Basalt Rivers: Its abundance, Relative Mobility and Flux. Aquatic Geochemistry, 12, 221-238. doi 10.1007/s10498-005-5856-4.
- Dearing, J.A., Hay, K.L., Baban, S.M.J., Huddleston, A.S., Wellington, E.M.H., Loveland, P.J., 1996. Magnetic susceptibility of soil: An evaluation of conflicting theories using a national data set. Geophysical Journal International 127, 728–734.
- Dekkers, M.J., Pietersen, H.S., 1992. Magnetic properties of low-Ca fly ash: A rapid tool for Fe-assessment and survey for potentially hazardous elements. In: Glasser, F.P., McCarthy, G.J., Young, J.F., Masson, T.O., and Pratt, P. L. (Eds.), Advanced cementitious systems: Mechanisms and properties. Materials Research Society Symp. Proceedings 245 (pp. 37–47). Pittsburg, PA: Materials Research Society.
- Desenfant, F., Petrovský, E., Rochette, P., 2004. Magnetic signature of industrial pollution of stream sediments and correlation with heavy metals: case study from south France. Water, Air, and Soil Pollution 152, 297–312.
- Goddu, S.R., Appel, E., Jordanova, D., Wehland, F., 2004. Magnetic properties of road dust from Visakhapatnam (India) Relationship to industrial pollution and road traffic. Physics and Chemistry of the Earth 29, 985–995.
- Hanesch, M., Scholger, R., 2002. Monitoring of heavy metal loadings in soils by means of magnetic susceptibility measurements. Environmental Geology 42, 857–870.
- Hanesch, M., Scholger, R., Rey, D., 2003. Mapping dust distribution around an industrial site by measuring magnetic parameters of tree leaves. Atmospheric Environment 37, 5125–5133.
- Hoffmann, V., Knab, M., Appel, E., 1999. Magnetic susceptibility mapping of roadside pollution. Journal of Geochemical Exploration 66, 313–326.
- Hunt, A., Jones, J., Oldfield, F., 1984. Magnetic measurements and heavy metals in atmospheric particulates of anthropogenic origin. Science of the Total Environment 33, 129–139.
- Hutchinson, S.M., Prandle, D., 1994. Siltation in the saltmarsh of the Dee Estuary derived from <sup>137</sup>Cs analysis of shallow cores. Estuarine, Coastal and Shelf Science 38, 471–478.

- Jordanova, D., Hoffmann, V., Fehr, K.T., 2004. Mineral magnetic characterization of anthropogenic magnetic phases in the Danube river sediments (Bulgarian part). Earth and Planetary Science Letters 221, 71–89.
- Kapička, A., Jordanova, N., Petrovský, E., Podrázský, V., 2003. Magnetic study of weakly contaminated forest soils. Water, Air & Soil Pollution 148, 31–44.
- Kersten, M., Smedes, F., 2002. Normalization procedures for sediments contaminants in spatial and temporal trend monitoring. Journal of Environmental Monitoring, 4, 109–115.
- Klose, S., Koch, J., Baucker, E., Makeschin, F., 2001. Indicative properties of fly-ash affected forest soils in Northeastern Germany. Journal of Plant Nutrition and Soil Science 164, 561–568.
- Knab, M., Appel, E., Hoffmann, V., 2001. Separation of the anthropogenic portion of heavy metal contents along a highway by means of magnetic susceptibility and fuzzy c-means cluster analysis. European Journal of Environmental & Engineering Geophysics 6, 125–140.
- Krishnan, M.S., 1968. Geology of India and Burma, Higginbothoms Ltd, Madras, p. 536.
- Lecoanet, H., Leveque, F., Ambrosi, J.P., 2001. Magnetic properties of salt-marsh soils contaminated by iron industry emissions (Southeast France). Journal of Applied Geophysics 48, 67–81.
- Lepland, A., Stevens, R.L., 1996. Mineral magnetic and textural interpretations of sedimentation in the Skagerrak, eastern North Sea. Marine Geology 135, 51–64.
- Lu, S.G., Bai, S.Q., 2006. Study on the correlation of magnetic properties and heavy metals content in urban soils of Hangzhou City, China. Journal of Applied Geophysics 60, 1-12.
- Maher, B.A., 1988. Magnetic properties of some synthetic submicron magnetites. Geophysical Journal 94, 83–96.
- Maher, B.A., Thompson, R., 1999. Quaternary climates, environments and magnetism (pp. 383). Cambridge University Press.
- Magiera, T., Strzyszcz, Z., 2000. Ferrimagnetic minerals of anthropogenic origin in soils of some Polish national parks. Water, Air & Soil Pollution 124, 37–48.

- Matzka, J., Maher, B.A., 1999. Magnetic biomonitoring of roadside tree leaves: Identification of spatial and temporal variations in vehicle derived particulates. Atmospheric Environment 33, 4565–4569.
- Moreno, E., Sagnotti, L., Dinares-Turell, J., Winkler, A., Cascella, A., 2003. Biomonitoring of traffic air pollution in Rome using magnetic properties of tree leaves. Atmospheric Environment 37, 2967–2977.
- Muxworthy, A. R., Schmidbauer, E., Petersen, E., 2002. Magnetic properties and Mössbauer spectra of urban atmospheric particulate matter: a case study from Munich, Germany. Geophysical Journal International 150, 558–570.
- Oldfield, F., Appleby, P.G., van der Post, K.D., 1999. Problems of core correlation, sediment source ascription and yield estimation in Ponsonby Tarn, West Cumbria, UK. Earth Surface Processes Landforms 24, 975–992.
- Oldfield, F., Yu, L., 1994. The influence of particle size variations on the magnetic properties of sediments from the north-eastern Irish Sea. Sedimentology 41,1093–1108.
- Oldfield, F., Maher, B.A., Donoghue, J., Pierce, J., 1985. Particle size related, mineral magnetic source sediment linkages in the Rhode River catchment, Maryland, USA. Journal of the Geological Society (London) 142, 1035–1046.
- Oldfield, F., Richardson, N., Appleby, P.G., Yu, L., 1993. <sup>241</sup>Am and <sup>137</sup>Cs activity in fine grained saltmarsh sediments from parts of the N.E. Irish Sea shoreline. Journal of Environmental Radioactivity 19, 1–24.
- Petrovsky, E., Kapicka, A., Zapletal, K., Sebestova, E., Spanila, T., Dekkers, M.J., Rochette, P., 1998. Correlation between magnetic parameters and chemical composition of lake sediments from Northern Bohemia—Preliminary Study, Physics and Chemistry of the Earth 23, 1123–1126.
- Petrovský, E., Ellwood, B.B., 1999. Magnetic monitoring of pollution of air, land and waters. In: Maher, B.A., Thompson, R. (Eds.), Quaternary climates, environments and magnetism (pp. 279–322). UK: Cambridge University Press.
- Petrovský, E., Kapička, A., Jordanova, N., Boruvka, L., 2001. Magnetic properties of alluvial soils contaminated with lead, zinc and cadmium. Journal of Applied Geophysics 48, 127–136.

- Petrovský, E., Kapička, A., Jordanova, N., Knab, M., Hoffmann, V., 2000. Low-field magnetic susceptibility: A proxy method of estimating increased pollution of different environmental systems. Environmental Geology 39, 312–318.
- Rae, J.E., 1997. Trace metals in deposited intertidal sediments. In: Jickells, T.D., Rae, J.E. (Eds.), *Biogeochemistry of Intertidal Sediments*, Cambridge University Press, Cambridge, pp. 16–31.
- Raman, C.V., Krishna Rao, G., Reddy, K.S.N. and Ramesh, M.V., 1995. Clay mineral distributions in the continental shelf sediments between the Ganges mouths and Madras, east coast of India, Continental Shelf Research, 15, 1773-1793.
- Rao, Ch.M., 1985. Distribution of suspended particulate matter in the waters of eastern continental margin of India. Indian Journal of Marine Sciences 14, 15-19.
- Rao, K. L., 1975. India's water wealth, Orient Longman, New Delhi, 255 pp.
- Rao, K.L., 1979. India's water wealth: its assessment, uses and projections. Orient Longman Ltd., New Delhi, 267.
- Rao, V.P., 1991. Clay mineral distribution in the continental shelf and slope off Saurashtra, west coast of India. Indian Journal of Marine Sciences 20, 1-6.
- Rao, V.P., Rao, B.R., 1995. Provenance and distribution of clay minerals in the sediments of the western continental shelf and slope of India. Continental Shelf Research 15, 1757-1771.
- Roussiez, V.; Ludwig, W., Probst, J., Monac, A., 2005. Background levels of heavy metals in surficial sediments of the Gulf of Lions (NW Mediterranean): an approach based on <sup>133</sup>Cs normalization and lead isotope measurements, Environmental Pollution 138, 167–177
- Sangode, S.J., Sinha, R., Phartiyal, B., Chauhan, O.S., Mazari, R.K., Bagati, T.N., Suresh, N., Mishra, S., Kumar, R., Bhattacharjee, P. 2007. Environmental magnetic studies on some Quaternary sediments of varied depositional settings in the Indian sub-continent. Quaternary International, 159, 102-118.
- Schmidt, A.M., Von Dobeneck, T., Bleil, U., 1999. Magnetic characterisation of Holocene sedimentation in the South Atlantic. Palaeoceanography 14, 465–481.
- Scoullos, M., Oldfield, F., Thompson, R., 1979. Magnetic monitoring of marine particulate pollution in the Elefsis Gulf, Greece. Marine Pollution Bulletin 10, 287–291.

- Spiteri, C., Kalinski, V., Rösler, W., Hoffmann, V., Appel, E., 2005. Magnetic screening of a pollution hotspot in the Lausitz area, Eastern Germany: correlation analysis between magnetic proxies and heavy metal contamination in soils. Environmental Geology 49, 1-9.
- Sutherland, R.A., Tack, F.M.G., Ziegler, A.D., Bussen, J.O., 2004. Metal extraction from road-deposited sediments using nine partial decomposition procedures. Applied Geochemistry 19, 947–955.
- Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental crust. Reviews of Geophysics 33, 241-265.
- Thompson, R., Oldfield, F., 1986. Environmental Magnetism. Allen and Unwin, London
- Veneva, L., Hoffmann, V., Jordanova, D., Jordanova, N., Fehr, T., 2004. Rock magnetic, mineralogical and microstructural characterization of fly ashes from Bulgarian power plants and the nearby anthropogenic soils. Physics and Chemistry of the Earth, 29, 1011–1023.
- Vassilev, S.V. 1992. Phase mineralogy studies of solid waste products from coal burning at some Bulgarian thermoelectric power plants. Fuel, 71, 625–633.
- Walden, J., Smith, J.P., Dackombe, R.V., Rose, J., 1995. Mineral magnetic analyses of glacial diamicts from the Midland Valley of Scotland. Scottish Journal of Geology 31, 79–89.
- Walden, J., Slattery, M.C., Burt, T.P., 1997. Use of mineral magnetic measurements to fingerprint suspended sediment sources: approaches and techniques for data analysis. Journal of Hydrology 202, 353–372.
- Walden, J., Smith, J.P., Oldfield, F., 1999. Environmental magnetism: a practical guide, Quaternary Research Association Technical Guide, vol. 6, 243 pp.
- Wheeler, J., Oldfield, F., Orford, J.D., 1999. Depositional and post-depositional controls on magnetic signals from saltmarshes on the north-west coast of Ireland. Sedimentology 46, 545–558.
- White, K., Walden, J., Drake, N., Eckardt, F., Settle, J., 1997. Mapping the iron oxide content of dune sands, Namib Sand Sea, Namibia, using Landsat Thematic Mapper data, Remote Sensing of Environment 62, 30–39.

- Xie, S., Dearing, J.A., Bloemandal, J., Boyle, J.F., 1999. Association between the organic matter content and magnetic properties in street dust, Liverpool, UK. Science of The Total Environment 205-214.
- Xie, S., Dearing, J.A., Bloemendal, J., 2000. The organic matter content of street dust in Liverpool, UK and its association with dust magnetic properties. Atmospheric Environment 34, 269–275.
- Zhang, J., Liu C.L., 2002. Riverine composition and estuarine chemistry of particulate metals in China – Weathering features, anthropogenic impact and chemical fluxes. Estuarine, Coastal and Shelf Science 54, 1051-1070.
- Zhang, W., Yu, L., Hutchinson, S.M., 2001. Diagenesis of magnetic minerals in the intertidal sediments of the Yangtze Estuary, China, and its environmental significance. Science of the Total Environment 266, 169–175.
- Zhang, W., Yu, L., Lu, M., Hutchinson, S.M., Feng, H., 2007. Magnetic approach to normalizing heavy metal concentrations for particle size effects in intertidal sediments in the Yangtze Estuary, China. Environmental Pollution 147, 238-244.

Table 1. Sample details and locations

Table 2. Magnetic susceptibility in the surface sediments of east and west coast of India Table 3. Metal concentrations (in  $\mu$ g g<sup>-1</sup> except Al and Fe in %) in the surface sediments of east and west coast of India

Table 4a. Coefficient of determination  $(R^2)$  for metals, potential geochemical and magnetic particle size proxies in surface sediments of east coast of India  $(R^2 > 0.28, p < 0.05, n = 12,$ bold figures are significant)

Table 4b. Coefficient of determination  $(R^2)$  for metals, potential geochemical and magnetic particle size proxies in surface sediments of west coast of India  $(R^2 > 0.40, p < 0.05, n = 8,$ bold figures are significant) Legend to Figures.

Fig. 1. Location of sediment sampling stations in the east and west coast of India.

 $\Delta$ -RVG 130;  $\Box$ - RVG 143; o-RVG 139 represent the sampling sites of different cruises.

Fig. 2 (a-c). Plot of magnetic susceptibility and its concentration related parameters along the east and west coast of India.

Fig. 3. Plot of Magnetic susceptibility vs. IRM<sub>20 mT</sub> along the east and west coast of India.

Fig. 4. Plot of  $\chi_{ARM}/\chi_{If}$  vs.  $\chi_{ARM}/\chi_{fd}$  along the east and west coast of India.

Fig. 5 (a-d). Plot of Fe, Cr, Cu and Ni vs. Al along the east and west coast of India.

Fig. 6 (a-d). Plot of Fe, Cr, Cu and Ni vs.  $\chi_{ARM}$  along the east and west coast of India.

Fig. 7 (a-d). Plot of Fe, Cr, Cu, Ni normalized by  $\chi_{ARM}$  vs. Al normalization along the east and west coast of India.

Fig. 8 (a-d). Plot of magnetic susceptibility ( $\chi$ ) vs. EF (metal) along the east and west coast of India.

Table. 1.
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Sr. no.	Station no.	Latitude (N)	Longitude (E)	Depth (m)
East coast	RVG 130 (A)			
1)	XVO 150 (Δ)	16° 26'	81° 31 0'	40
1) 2)	3012	10 20 16° 11'	81 51.0 81° 47 5'	40 55
2)	2014	10 11 15° 54 5'	81 47.5 81° 14 6'	50
<i>3)</i>	3014	15° 30 5'	81° 14.0	30 48
4) 5)	2018	15° 22 8'	81 00 81° 22 1'	48 52
5)	3018	15 22.8	81 55.1 808 16 7	52
0) 7)	3019	13° 0.3	80° 10.7	32
/)	3024	12° 00'	80° 05.6°	49
8)	3025	12° 00'	80° 04.2'	50
9)	3026	11 ° 00'	80° 02.5'	52
	RVG 143 (□)			
10)	3245	14° 54.1'	80° 20.5'	80
11)	3248	13° 30.5'	80° 31.7'	120
12)	3249	13° 7.8'	80° 32.6'	120
West coast				
	RVG 139 (o)			
13)	3164	10° 02.5'	76° 00.0'	35
14)	3165	10° 01.0'	75° 40.1'	90
15)	3170	10° 58.2'	75°18.7'	73
16)	3171	10° 58.2'	75° 39.0'	33
17)	3173	12° 00'	74° 40.0'	75
18)	3180	12° 59'	74° 20.9'	60
19)	3182	$14^{\circ} \ 00^{0}$	74° 19.0'	40
20)	3184	14° 00'	73° 40.0'	78
21)	3191	14° 59.7'	73° 20.0'	75
22)	3192	14° 59.6'	73° 40.0'	49

## Table. 2.

East coast301215901513013463.543630142699.172643017806.67757301817221663019388.53763024239.832343025305.332973026134.83129324514311373248233.8322332495251.1West coast316444.83	6.17 5 9.5 67
301215901513013463.543630142699.172643017806.67757301817221663019388.53763024239.832343025305.332973026134.83129324514311373248233.8322332495251.1West coast316444.8345.1	6.17 .5 9.5 67
3013463.543630142699.172643017806.67757301817221663019388.53763024239.832343025305.332973026134.83129324514311373248233.8322332495251.1West coast316444.8345.1	.5 9.5 .67 5.67
30142699.1726443017806.67757301817221663019388.53763024239.832343025305.332973026134.83129324514311373248233.8322332495251.1West coast5251.1	9.5 .67 5.67
3017806.67757301817221663019388.53763024239.832343025305.332973026134.83129324514311373248233.8322332495251.1West coast316444.83	.67 5.67
301817221663019388.53763024239.832343025305.332973026134.831293245143113793248233.8322332495251.1West coast316444.83	5 67
3019388.53763024239.832343025305.332973026134.83129324514311373248233.8322332495251.1West coast5251.1	5.07
3024239.832343025305.332973026134.83129324514311373248233.8322332495251.1West coast316444.83	
3025   305.33   297     3026   134.83   129     3245   1431   137     3248   233.83   223     3249   52   51.1     West coast   3164   44.83   45.1	.67
3026134.83129324514311373248233.8322332495251.1West coast316444.83	.17
3245   1431   137     3248   233.83   223     3249   52   51.1     West coast   3164   44.83   45.1	.33
3248 233.83 223   3249 52 51.1   West coast 3164 44.83	9.5
3249 52 51.1   West coast 3164 44.83	.67
West coast 3164 44.83 45.1	7
3164 44.83 45.1	
	7
3165 103.5 99.6	7
3170 72.33 72.3	3
3171 20.83 21	
3173 40.83 43.5	
3180 44.17 46.8	3
3182 59.33 61.6	7
3184 33.33 35	
3191 51 51.6	7
3192 127 126	.33

Table. 3.

Metals		East coas	t	West coast							
	Min	Median	Max	Min	Median	Max					
Al	2.25	6.77	11.68	0.7	2.26	4.45					
Fe	1.67 (0.52)	5.27 (0.93)	8.58 (1.20)	1.13 (0.32)	2.20 (1.38)	3.43 (1.92)					
Cr	3.71 (0.04)	70.4 (0.45)	133.22 (0.77)	N.D	5.97 (0.12)	19.39 (0.41)					
Ni	7.8 (0.28)	56.39 (1.19)	81.76 (2.00)	0.32 (0.41)	10.45 (0.74)	16.88 (1.94)					
Cu	10.63 (0.28)	78.27 (0.74)	140.14 (0.85)	3.82 (0.12)	12.89 (0.44)	26.31 (1.22)					

## Table. 4a.

	Fe	Cr	Cu	Ni	χarm	χ <sub>arm</sub> /SIRM	χ <sub>fd</sub> (%)	χ	SIRM	IRM <sub>20mT</sub>	Fe/Al	Cr/Al	Cu/Al	Ni/Al	Fe/X <sub>ARM</sub>	Cr/χ <sub>ARM</sub>	Cu/χ <sub>ARM</sub>	Ni/χ <sub>ARM</sub>
Fe	1.00																	
Cr	0.94																	
Cu	0.94	1.00	1.00															
Ni	0.89	0.92	0.92	1.00														
χarm	0.98	0.94	0.94	0.92	1.00													
χ <sub>arm</sub> /SIRM	0.68	0.81	0.81	0.73	0.72	1.00												
χ <sub>fd</sub> (%)	0.14	0.09	0.09	0.18	0.17	0.00	1.00											
χ	0.76	0.83	0.83	0.64	0.72	0.70	0.00	1.00										
SIRM	0.79	0.89	0.89	0.73	0.76	0.81	0.00	0.93	1.00									
IRM <sub>20mT</sub>	0.79	0.85	0.85	0.64	0.76	0.71	0.01	0.99	0.93	1.00								
Fe/Al	0.41	0.56	0.56	0.42	0.40	0.49	0.02	0.54	0.56	0.53	1.00							
Cr/Al	0.77	0.92	0.92	0.85	0.78	0.83	0.05	0.79	0.86	0.78	0.73	1.00						
Cu/Al	0.75	0.90	0.90	0.79	0.76	0.85	0.04	0.79	0.86	0.79	0.79	0.98	1.00					
Ni/Al	0.33	0.47	0.47	0.56	0.38	0.46	0.14	0.32	0.39	0.29	0.54	0.66	0.64	1.00				
Fe/χ <sub>ARM</sub>	0.31	0.38	0.38	0.45	0.42	0.52	0.09	0.24	0.27	0.25	0.13	0.40	0.40	0.48	1.00			
Cr/χ <sub>ARM</sub>	0.81	0.95	0.95	0.89	0.82	0.87	0.07	0.74	0.83	0.74	0.66	0.98	0.96	0.62	0.42	1.00		
Cu/X <sub>ARM</sub>	0.79	0.91	0.91	0.79	0.78	0.88	0.04	0.73	0.83	0.75	0.72	0.92	0.95	0.50	0.33	0.96	1.00	
Ni/χ <sub>ARM</sub>	0.01	0.00	0.00	0.02	0.01	0.01	0.06	0.02	0.00	0.03	0.02	0.00	0.00	0.19	0.01	0.00	0.02	1.00

### Table. 4b.

	Fe	Cr	Cu	Ni	χarm	χ <sub>arm</sub> /SIRM	χ <sub>fd</sub> (%)	χ	SIRM	IRM <sub>20mT</sub>	Fe/Al	Cr/Al	Cu/Al	Ni/Al	Fe/ <sub>XARM</sub>	Cr/ <sub>2</sub> ARM	Cu/Xarm	Ni/χ <sub>arm</sub>
Fe	1.00						-											
Cr	0.15	1.00					-											
Cu	0.15	1.00	1.00				-											
Ni	0.36	0.28	0.28	1.00			-											
Xarm	0.01	0.14	0.14	0.36	1.00		-											
χ <sub>arm</sub> /SIRM	0.07	0.45	0.45	0.02	0.01	1.00	-											
χ <sub>fd</sub> (%)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
χ	0.20	0.37	0.37	0.05	0.06	0.70	-	1.00										
SIRM	0.07	0.39	0.39	0.02	0.05	0.77	-	0.95	1.00									
IRM <sub>20mT</sub>	0.04	0.47	0.47	0.01	0.00	0.37	-	0.35	0.50	1.00								
Fe/Al	0.00	0.04	0.04	0.01	0.13	0.28	-	0.03	0.08	0.13	1.00							
Cr/Al	0.03	0.53	0.53	0.00	0.01	0.52	-	0.17	0.31	0.69	0.41	1.00						
Cu/Al	0.26	0.14	0.14	0.05	0.00	0.31	-	0.02	0.11	0.47	0.53	0.81	1.00					
Ni/Al	0.26	0.00	0.00	0.02	0.10	0.04	-	0.03	0.00	0.07	0.26	0.16	0.45	1.00				
Fe/χ <sub>ARM</sub>	0.53	0.36	0.36	0.60	0.34	0.02	-	0.02	0.00	0.02	0.06	0.00	0.10	0.07	1.00			
Cr/χ <sub>ARM</sub>	0.16	0.87	0.87	0.44	0.40	0.25	-	0.16	0.15	0.21	0.00	0.31	0.05	0.00	0.62	1.00		
Cu/χ <sub>ARM</sub>	0.12	0.77	0.77	0.46	0.54	0.16	-	0.08	0.08	0.14	0.01	0.24	0.04	0.00	0.66	0.98	1.00	
Ni/χ <sub>ARM</sub>	0.16	0.36	0.36	0.73	0.76	0.01	-	0.00	0.00	0.00	0.06	0.01	0.01	0.01	0.78	0.68	0.78	1.00







Fig. 2.



Fig. 3.



Fig. 4.



Fig. 5



Fig. 6.



Fig. 7.



Magnetic susceptibility  $\chi_{lf}\,(10^{-8}m^3/kg)$ 



Magnetic susceptibility  $\chi_{lf}$  (10<sup>-8</sup>m<sup>3</sup>/kg)

Fig. 8.