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Creators: Pulley, S., Rowntree, K. and Foster, I. D. L.

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Conservatism of mineral magnetic signatures in farm dam sediments in the South African Karoo; the potential effects of particle size and post depositional diagenesis

Simon Pulley • Kate Rowntree • Ian Foster

Abstract

Purpose: A methodology was developed to evaluate and mitigate the impacts of particle size and post-depositional diagenesis when using mineral magnetic signatures to trace the sources of historically deposited sediment in farm dams in the South African Karoo.

Materials and methods: Samples from a range of potential sediment sources were sieved to different particle size fractions and the relationships between pairs of tracer signatures were established for each fraction. Non-conservatism of the magnetic signatures was determined by identifying whether the magnetic signatures of the farm dam sediments were within the range of those of the fractionated source samples. By fractionating the sediment source samples the core samples were able to be traced using appropriately sized sources.

Results and discussion: It was found that strong relationships existed between the pairs of tracer signatures at all particle size fractions. Relationships in the < 32 µm fraction were significantly different to that of coarser fractions. It was also found that particle size had a large effect on all magnetic signatures and would prove to be a large source of uncertainty if not accounted for within any methodology developed for quantitative source discrimination and source apportionment. There was very little non-conservatism caused by diagenetic or biogenic processes in six of the seven dams sampled. In one dam there was evidence to suggest that dissolution had probably caused the loss of almost all small superparamagnetic and stable single domain grains. The other signatures associated with coarser magnetic grains in this dam were generally unaffected by the dissolution processes.

Conclusions: The good preservation of magnetic signatures suggests that they can make reliable tracers over historical timescales (up to 164 years) in the Karoo and similar semi-arid catchments. However, the mitigation of particle size effects and screening for post depositional alteration is an essential part of their use. The methodology presented in this paper is a potential way of recognising tracer non-conservatism and limiting its effects in future studies.

Keywords Historically deposited sediment • Karoo • Mineral magnetic signatures • Non-conservatism • Particle size

1. Introduction

Mineral magnetic signatures have a well-established history of use when reconstructing changing sediment sources (Caitcheon 1993), pollutant dynamics (Lu et al. 2007), and paelaeoclimatic conditions (Peck et al. 1994). The application of magnetic signatures for source tracing is dependent upon their ability to discriminate between sediment sources (Collins and Walling 2002) and the assumption that they are not altered during sediment transport or long-term storage (Foster and Lees 2000; D'Haen et al. 2012; Koiter et al. 2013). Magnetic signatures in soils and subsurface material can be classified as either primary (originating from parent material before weathering) or secondary (formed through chemical processes and biogenic effects) (Thompson 1986). Source discrimination using primary signatures utilises differences in lithology (Shenggao 2000) and anthropogenic inputs of magnetic grains usually deposited on, and incorporated into, topsoil as a result of the fallout of atmospheric pollutants (Zhang et al. 2012). Secondary signatures are formed at different rates in different soil types (Maher 1998) and through diagenetic processes in soils and subsurface material, providing additional potential for the discrimination of sediment sources. Depositional environments such as lakes and floodplain are commonly sampled to reconstruct sediment yield and evaluate past sediment sources (Foster et al. 2007; Foster 2010). Within these depositional environments, magnetic signatures can be classified as being detrital (originating from catchment sources) or as being secondary biogenic and diagenetic signatures (altered within the place of deposition through chemical or biogenic processes) (Wheeler et al. 1999). The accurate use of magnetic signatures for quantitative source tracing is dependent upon distinguishing the detrital primary and secondary signatures from the noise (variability) of secondary magnetic signatures produced in the place of deposition. Pulley et al. (2015) showed that, without a sufficiently strong detrital tracer

signature in the form of large differences in tracer concentrations between sediment sources, uncertainty can significantly alter sediment provenance estimates. An example of the difficulties associated with identifying the detrital signature was shown by Wheeler et al. (1999) who found that biogenic and diagenetic signatures overprinted and degraded the detrital signatures in salt marsh sediments.

The dissolution of magnetic grains under anoxic / reducing conditions has been shown to cause a coarsening of magnetic grain size due to the preferential dissolution of fine-grained magnetite (Anderson and Rippey 1988; Roberts and Turner 1993; Foster et al. 1998). The coarsening grain size results in a higher proportion of high coercivity haematite-type minerals in relation to soft magnetite type grains within the sediment. Under anoxic / reducing conditions, the in-growth of magnetic iron sulphides has also been shown to significantly alter magnetic signatures. Anoxic ingrowth is characterised by the presence of superparamagnetic (SP) Pyrite and ferrimagnetic Greigite (Snowball and Thompson 1988; Liu 2004; Rowan 2009). Greigite can be identified by a high ratio ($\gg 30$) of saturation isothermal remanent magnetisation to low frequency magnetic susceptibility (Roberts 1995). The decomposition of organic matter within sediments has been identified as a causal factor in dissolution and iron sulphide formation processes (Williams 1992). Biogenic alterations to magnetic signatures are often characterised by the in-growth of stable single-domain magnetite formed intracellularly by magnetotactic bacteria in lake sediments (Li et al. 2009). Their presence at significant concentrations can usually be identified when the ratio of susceptibility of anhysteretic remanence magnetisation (χ_{arm}) to saturation isothermal remanence magnetisation (SIRM) $\gg 2$) (Foster et al. 2008).

Magnetic signatures have been shown to be strongly affected by sediment particle size, introducing additional uncertainty to their use (Maher 1998; Blake et al. 2006). Therefore, there is a requirement to separate biogenic, diagenetic and particle size effects for the correct

interpretation of the stability of signatures in deposited sediment. It has proven difficult to mitigate particle size effects on magnetic signatures due to the often non-linear relationships that exist between magnetic properties and particle size (Foster et al. 1998; Oldfield et al. 2009).

The aim of this study was to develop a methodology to identify the particle size dependant, biogenic and diagenetic mineral magnetic signatures and understand their impacts on the interpretation of the detrital (originating from within the catchment) sediment provenance signal present in historically deposited sediment.

2. Site description

The study was undertaken in the central Karoo region of the Eastern Cape of South Africa (Fig. 1). This semi-arid environment has an annual rainfall of 423 mm (1908 – 2002 measured at Gordonville farm, Graaff-Reinet, South Africa) (Grenfell et al. 2014). The lithology of the region is primarily sedimentary deposits of Upper Permian shale in lowland areas, Quaternary colluvium and fluvially deposited sediments in valley bottoms and Triassic sandstones and Jurassic dolerites at high altitude. Soils are generally shallow and poorly developed, often lacking an A and sometimes a B horizon (Boardman 2003). The land in the catchment is primarily utilised for stock grazing, however valley floors have historically been cultivated for wheat and lucerne. The area is characterised by high sediment yields of up to $1096 \text{ t km}^{-2} \text{ y}^{-1}$, which have been attributed to a number of factors including grazing pressures, cultivation and increased connectivity caused by the development of gullies and badlands after European colonisation in the second half of the 18th century (Fox 2000; Foster et al. 2007; 2012). The characteristics of the study catchments are summarised in Table 1 and in greater detail by Foster et al. (2012).

3. Materials and methods

3.1. Field and Laboratory methods

Samples of potential sediment sources were classified as topsoils (the top of the existing soil profile) on different rock types and subsurface material. Nineteen samples were obtained from shale topsoils, 14 from dolerite, 10 from sandstone, and 20 samples were collected from subsurface valley floor colluvium. Each sample was collected using a non-metallic trowel and consisted of an amalgamation of 10 subsamples from within a 10 m radius of the sampling point. Topsoil samples were collected from a depth of 0 to 10 cm which usually represented most of the depth of the upper soil horizon. Subsurface samples were collected from the lower and middle horizons of visibly eroding channel banks, excluding the upper 20 cm which is likely to represent surface material.

A ca. 200 g subsample of each source sample was ultrasonically dispersed using a Labotec (Midrand, South Africa) LC130H unit (35 kHz) for 10 minutes in 400 ml of deionised water before being wet sieved through stainless steel sieves to seven particle size fractions: 2000 – 1000 μ m, 1000 – 500 μ m, 500 – 250 μ m, 250 – 125 μ m, 125 – 63 μ m, 63 – 32 μ m and < 32 μ m. The duration of the ultrasonic treatment was determined to be sufficient to fully disperse the samples through repeat testing.

Sediment cores from seven dams that had been sampled previously provided data that could be compared to the potential source samples. Cranemere Dam, Compassberg Dams 7, and 10 and the Ganora Dam had been previously analysed for magnetism, dated and discussed in detail by Foster et al. (2007; 2012). The analysis of Compassberg dams 37, 53 and 94 used previously unpublished data. The cores were retrieved from dams 37 and 94 using a 50 cm long, 5 cm diameter Russian corer following the methods of Foster et al (2012). Dam 53 was breached by a major flood in 1974 and sediment had been excavated from the dam by a

rapidly down-cutting river. Here, samples were taken from a cleaned exposed section approximately 50 m upstream of the dam wall. Each core was horizontally sliced into 41 – 73 sections with the median section thickness being 3 cm. The sediment core and source samples were oven dried at 40°C and manually disaggregated using a pestle and mortar prior to analysis. The core samples were not sieved prior to analysis due to the limited quantities of material available for analysis.

The organic matter content of the cores was measured using loss on ignition (LOI) at 450 °C following the methods of Grimshaw et al. (1989) and their magnetic signatures were corrected for the effects of organic matter accordingly using the methods of Lees (1999). During the sieving of the source samples organic matter was removed by allowing the minerogenic particles to settle for 24 hours before pouring off excess water and suspended organic matter. Loss on ignition was not analysed on the source samples due to the limited quantities of sample available for analysis. However, the LOI of the unsieved source samples was found to be low (mean 2.7%) and was judged not to represent a significant source of uncertainty. The particle size of the source and sediment samples was measured using a Malvern Instruments (Malvern, UK) Mastersizer 3000 laser granulometer using the methods previously published by Foster et al. (2007; 2012).

The magnetic signatures for all samples were measured following the procedures laid out by Lees (1997) using ~ 10 g of each source and core sample packed tightly into 10 ml polystyrene sample containers. Low Frequency Susceptibility (χ_{lf}) and Frequency Dependant Susceptibility (χ_{fd}) were measured using a Bartington Instruments (Witney, UK) MS2b sensor. Anhyseretic Remanent Magnetisation (ARM(40 μ T)) was measured using a Molspin® anhyseretic remanent magnetiser and Molspin® (Witney, UK) slow-speed spinner magnetometer and was normalised to field strength to produce Susceptibility of ARM (χ_{arm}). Saturation Isothermal Remanent Magnetisation ((SIRM) 1T), Soft Isothermal Remanent

Magnetisation (Soft IRM(-100mT)) and Hard Isothermal Remanent Magnetisation (HIRM) were measured using a Molspin® pulse magnetiser and Molspin® slow-speed spinner magnetometer. Parameter values and ratios were calculated following the procedure detailed by Foster et al. (2008).

3.2. The assessment of conservatism of magnetic tracers

The procedure used to assess the conservatism of the magnetic signatures is summarised in Fig.2. This method was preceded by the use of a linear discriminant analysis in SPSS 20 to determine if the tracers used were able to successfully discriminate between the sediment source groups. The potential sediment sources were analysed to firstly identify the relationships between the different magnetic signatures and secondly to examine the impact of particle size on these relationships. The data from the sediment cores were then examined to determine if these observed relationships were maintained in the sediments of the appropriate particle size or if they had been altered by biogenic and / or diagenetic effects.

Pairs of magnetic signatures were included in bi-plots to identify the potential non-conservatism of the six magnetic signatures measured (χ_{lf} , χ_{fd} , χ_{arm} , SIRM, Soft IRM and HIRM).

The plot of χ_{fd} against χ_{lf} was used to identify the loss or gain of small SP grains (<0.02 μm diameter) in relation to the overall magnetic susceptibility. Dissolution of minerals has been shown to start with smaller grains (Anderson and Rippey 1988) and an increase in χ_{fd} has been shown to indicate an early phase of sulphide formation (Rowan 2009).

χ_{arm} was plotted against SIRM to identify the in-growth or dissolution of χ_{arm} carrying stable single domain grains (SSD) in relation to the total magnetic remanence (SIRM). SSD grains have been shown to be formed by the in-growth of bacterial magnetites and therefore

this process can be identified in this bi-plot (Li et al. 2009). SSD grains are also small (0.02 - 0.4 μm diameter) and therefore would be expected to be dissolved preferentially before other remanence carrying grains (SIRM).

Soft IRM was plotted against SIRM to represent the S – Ratio in order to identify the dissolution or ingrowth of ‘soft’ magnetite type minerals in relation to ‘hard’ haematite type minerals.

Finally SIRM was plotted against χ_{lf} to indicate a gain or loss of remanence carrying minerals in relation to the overall magnetic mineralogy of the sediment. A high χ_{lf} / SIRM ratio is also indicative of the ingrowth of iron sulphides such as greigite (Roberts 1995).

Where potential non-conservatism was identified in the bi-plots down the core profiles of the magnetic signatures were constructed using a regression analysis in SPSS 20. It was then determined if there was down-core loss of the signatures which may indicate the dissolution of minerals over time or at the depth of the local water table.

4. Results

4.1 Potential source samples

Preliminary analysis showed that mineral magnetic signatures were unable to reliably discriminate between sedimentary sources (shale and sandstone topsoils and colluvium). The linear discriminant analysis using all of the magnetic signatures was only able to correctly classify a maximum of 64.6 % of the source samples into their respective groups at any particle size fraction. The signatures were, however, able to discriminate reliably between

almost all dolerite and sedimentary source samples (93.8 %), and for this reason sediment sources were only divided into these two groups for the purposes of this analysis.

Figs 3A and 3C show that in each bi-plot strong relationships exist between the magnetic tracers in the sediment source samples. However, in the χ_{fd} / χ_{lf} and χ_{arm} / SIRM plots the relationships are substantially different for particles smaller than 32 μm and those larger than 32 μm . The Soft IRM and SIRM relationships fall along a single line for all particle size fractions (Fig. 3B). However, smaller particle sizes have greater SIRM and Soft IRM values in dolerite topsoils. A linear relationship is found between SIRM and χ_{lf} in all particle size fractions (Fig. 3D). However, there is a reduction in SIRM in relation to χ_{lf} in the < 32 μm fraction. There appears to be little effect of particle size on the relationships between the tracers in any bi-plot once particle size exceeds 32 μm .

As a result of the different relationships observed between the < 32 μm fraction and all other fractions, the provenance of small particles (< 32 μm) within the cores must be interpreted separately to that of larger particles. The ranges of the < 32 and >32 μm source samples intersect in all graphs when magnetic signatures are low, indicating particle size has less impact on tracing samples with low concentrations of magnetic minerals.

4.2 Core samples

The particle size of the cores was examined initially to determine differences between the cores and to identify which particle size range of the source samples the cores should fall within. The majority of the Cranemere, Dam 7 and Ganora cores have a D50 particle size below 32 μm throughout most of their down-core profiles (Fig. 4). Dam 10 and Dam 37 have coarser particle size distributions and most of the sediment lies between < 32 μm and 220 μm . Dam 53 has a coarse particle size distribution ranging from 200 to 1850 μm . With few exceptions, the LOI of the cores indicate that very little organic matter is present in any of

them. There is some variability in LOI between the cores with Dam 53 having almost no LOI, whereas Dam 37 has a peak LOI of 15% at 130 cm depth (see Electronic Supplementary Material). The following analysis of tracer conservatism is separated into three sections; each discusses cores with different patterns of conservatism and non-conservatism of the magnetic signatures.

4.3 Particle size related non-conservatism

All parts of the Cranemere core have a D50 below 32 μm indicating that all samples should fall within the < 32 μm range of source samples. The majority of samples in the Cranemere core follow the trend of the χ_{fd} / χ_{lf} graph (Fig. 5A) on the < 32 μm line and appear mostly in a tight group. χ_{arm} is higher in relation to SIRM in the core than in the source samples (Fig. 5C), suggesting the possible in-growth of bacterially produced SSD grains. However, Fig. 6 indicates that the relationship between the χ_{arm} / SIRM ratio and particle size is maintained, indicating that this is most likely a particle size effect rather than an in-growth of SSD grains. Soft IRM and χ_{lf} are also elevated in relation to SIRM, which is also likely also to represent a particle size effect.

4.4 Identifying the dissolution of magnetic grains in lake sediments

The D50 particle size of most samples in the dam 7 core (88%) lies below 32 μm , indicating that most of the core should fall within the range of the < 32 μm source samples. However, the majority of samples from the core do not fall within this range in the bi-plots of Fig. 7. There is a reduction of χ_{fd} in relation to χ_{lf} (Fig. 7A) and a reduction in χ_{arm} in relationship to SIRM (Fig. 7C). Soft IRM is not elevated or reduced in relationship to SIRM (Fig. 7B), neither is SIRM in relation to χ_{lf} (Fig. 7D). Therefore, there appears to be some loss of small SP grains (χ_{fd}) and SSD grains (χ_{arm}) within this core.

There are strong down-core trends in χ_{fd} and χ_{arm} , which coupled with their indicated loss in Fig. 7 suggests the dissolution of these grains over time (Fig. 8). Only χ_{fd} and χ_{arm} are significantly correlated with depth in the cores in a logarithmic relationship ($\log_{10} \chi_{fd}$ vs \log_{10} depth $p < 0.001$, $r^2 = 0.771$; $\log_{10} \chi_{arm}$ vs \log_{10} depth $p < 0.001$, $r^2 = 0.80$), indicating that the other signatures are probably resistant to the effects of the dissolution. The total loss of χ_{fd} occurs at 125 cm depth and the loss of χ_{arm} at 120 cm depth. Chronologies previously established for this core by Foster et al. (2007) place these depths at 43 and 38 years before the core was sampled in 2003 suggesting a fast loss of these grains after the sediment is deposited. The rate of loss of χ_{fd} in the core is therefore an average of 2.33% (of the χ_{fd} present at the top of the core) per year and 2.44% of χ_{arm} per year. The almost complete dissolution of χ_{fd} at 125 cm and χ_{arm} at 120 cm may also represent the level of the local water table, with seasonal variability in its level causing varying amounts of dissolution in the upper layers of the core.

4.5 Identifying particle size effects with predominantly stable magnetic signatures

In this section all plots for the cores are provided in the Electronic Supplementary Material.

In the Dam 53 and Ganora cores the sediment falls within one particle size fraction (either $< 32 \mu\text{m}$ or $> 32 \mu\text{m}$) throughout the entire down-core profiles (Fig. 4). The D50 of the sediment within the Dam 10, 37 and 94 cores varied between being coarser or finer than $32 \mu\text{m}$ at different depths (Fig. 4). Laboratory-based particle size information was unavailable for the Dam 94 core, however the texture of the core was described in the field as being composed of organic silty-clay in the top 40 cm of the core before becoming a combination of silts sands and gravels below this depth.

The magnetic signatures of the cores generally fall within the range of the appropriately sized source samples with few exceptions. In Dam 10 at depths of 50, 185, 195 and 225 cm, χ_{arm} ,

χ_{lf} and χ_{fd} appear low (Fig. S2). χ_{fd} also appears slightly elevated in relation to χ_{lf} . However, values are not clearly outside the range of the potential source samples, suggesting that the tracers are conservative.

In Dam 37 four samples at depths of 98, 158, 162 and 262 cm have almost no frequency dependant susceptibility and fall slightly outside of the range of the source samples (Fig. S3). These samples are not associated with a significant increase or decrease of the LOI, or D50 of the sediment and therefore appears to be an unexplained loss of SP grains in parts of this core. This may however represent inputs of sediment from poorly weathered shale bedrock in the region which was found to be low in χ_{fd} . χ_{fd} is slightly elevated in relation to χ_{lf} in the Dam 53 sediment indicating enrichment in SP grains and χ_{arm} is high in 4 samples at depths of 385, 367, 423 and 448 cm (Fig. S4). However, these samples do not clearly fall outside of the range of the source samples.

Despite these small changes to the magnetic signatures in a small number of samples, in three of the cores there was no evidence of large biogenic or diagenetic alterations to the magnetic signatures which would be likely to impact sediment provenance interpretation.

5. Discussion

It has been shown that particle size has significant impacts on all of the magnetic signatures measured as part of this project. However, the use of bi-plots was able to account for these effects and allow for qualitative source apportionment. The very fine particle size in the Cranemere dam fell outside of the range of that measured for source samples suggesting that the χ_{fd} and χ_{arm} signatures would be unsuitable for source tracing, due to their concentration within fine soil particles. Therefore, further fractionation of the $< 32 \mu\text{m}$ particles may be required for future research on source tracing in this catchment. In addition, these results

suggest that the common practice of sieving to $< 63 \mu\text{m}$ is likely to be unsuitable in regions such as the Karoo due to the very different relationships between tracers in the $< 32 \mu\text{m}$ and $32 - 63 \mu\text{m}$ fractions of soils and sediment. These findings support the findings of Maher (1998) and Blake *et al.* (2006) who also showed that the ingrowth of secondary minerals during soil formation occurs primarily in fine soil particle sizes. To date we do not know the rate at which such in-growth occurs and whether significant changes occur over relatively short periods of time. Particle size specific source tracing was also explored by Hatfield and Maher (2009) who demonstrated the ability of specific particle size fractions to achieve good discrimination between sediment sources even in homogeneous catchments.

Dam 7 is the only site in this study of seven Karoo farm dams significantly affected by the dissolution of magnetic signatures. The dissolution affects the parameters χ_{arm} and χ_{fd} , which are controlled by the concentrations of small SP and SSD grains. These grains are commonly formed as secondary minerals during soil formation (Maher 1998) suggesting that much of the discrimination provided by the formation of these secondary minerals could be lost through the dissolution process. Dissolution appears to have little effect on the other magnetic signatures in Dam 7, suggesting that primary magnetic minerals derived from bedrock type are likely to be relatively unaffected. Field based observation of the Dams suggest that Cranemere, Dam 37 and Ganora are almost always flooded or wet, whereas Dam 10 is almost full of sediment and is now dry for the majority of the time. Even though the main dam wall is now breached, Dam 7 has been observed to have a highly variable and fluctuating water table providing a potential explanation for the dissolution of magnetic signatures in the core. χ_{fd} and χ_{arm} were most significantly affected by dissolution, while other signatures were not. This suggests that future research could focus upon searching for down-core reductions in these signatures that might be indicative of post-depositional dissolution. The results also suggest that using χ_{lf} , SIRM, Soft IRM and HIRM in cores may

produce a result less susceptible to the effects of dissolution. The coarser multidomain grains (MD) which contribute to these signatures have previously been shown to be less susceptible to dissolution than smaller SP and SSD grains (Anderson and Rippey 1988). However, their use may lose the added discrimination provided by secondary minerals produced during soil formation.

The χ_{arm} / SIRM plots did not show any evidence of the ingrowth of bacterially produced stable single domain grains in any core. This finding suggests that the ingrowth shown in other published studies e.g. (Snowball 1994; Li et al. 2009) was not taking place in the Dams of the Karoo.

The ingrowth of iron sulphides has been shown to begin with an increase in SP grains (χ_{fd}) through pyrite formation (Rowan et al. 2009). χ_{fd} was observed to be slightly increased in relation to χ_{lf} in Dams 10 and 53 suggesting some slight in-growth of SP grains in the cores. However, there is no clear increase in χ_{lf} in relation to SIRM in any of the cores, which would be indicative of the in-growth of Greigite (Snowball and Thompson 1988; Roberts 1995; Foster et al. 2008). The small increase in χ_{fd} is unlikely to significantly alter qualitative interpretations of sediment provenance. An approach to remove the effects of the ingrowth and dissolution of magnetic grains was presented by Maher et al. (2009), who used hydrochloric acid to remove all discrete magnetic particles and magnetic coatings, leaving only magnetic inclusions protected within silicate grains. Such approaches would allow for the reliable tracing of sediments such as in Dam 7 with heavily altered magnetic signatures.

The lack of significant alterations to the magnetic signatures in six of the seven cores through biogenic and diagenetic processes are in contrast to the findings of many previously published studies (e.g. Karlin and Levi 1983; Anderson and Rippey 1988; Snowball 1994; Oldfield and Wu 2000; Rowan et al. 2009). The low LOI of the cores sampled (< 5% in most samples) is a potential explanation for the stability of tracer signatures, due to the fact that the

decomposition of organic matter is often a causal factor in dissolution processes and iron sulphide formation (Williams 1992). Cores sampled elsewhere in the world typically have far higher LOIs, for example, lake Qarun Egypt 9.09% (Foster et al. 2008), Aqualate Mere, Central England up to 60% (Pittam et al. 2009) and between 20 and 28% in a lake core from Pajep Njakajaure in northern Sweden (Snowball 1994). The particle size of the sediment appears to have little impact on dissolution as the very fine sediment in Cranemere and Ganora and the coarse sediment in Dam 37 and Dam 53 all appear to be unaltered.

6. Conclusions

The results presented here demonstrate the need to refine tracing methods to account for particle size and diagenetic effects on magnetic signatures, and show the potential for the methodology presented in this paper to achieve this refinement. The previous interpretation of sediment provenance in one of the sediment cores by Foster et al. (2012) was confounded by the apparent dissolution of fine grained magnetite but the methodology presented in this paper enables identification of those signature that are most likely affected by this process. Similarly, traditional tracing methods are unlikely to account for the concentration of secondary magnetic grains in the $< 32 \mu\text{m}$ fraction of the source samples and the methodology presented here overcomes this limitation by tracing different sized particles in a single core using appropriately size-fractionated source samples.

The methodology presented in this paper could potentially be a precursor to un-mixing modelling, such as that used by Collins et al. (1997), for quantitative source apportionment. Using this methodology signatures that are non-conservative will fall above or below the range of the source samples and changes in sediment provenance will be represented by changes to the signatures within the range of the source samples. The signatures determined

to be affected by post-depositional alteration should be removed prior to modelling, and the different particle size ranges of cores should be fingerprinted separately. Using this method much of the potential uncertainty associated with the use of historically deposited sediment discussed by D'Haen et al. (2012) can potentially be removed. The good preservation of magnetic signatures in six of the seven dams suggests that mineral magnetic signatures make reliable tracers over historical timescales in the Karoo and as is likely to be the case, in similar semi-arid catchments.

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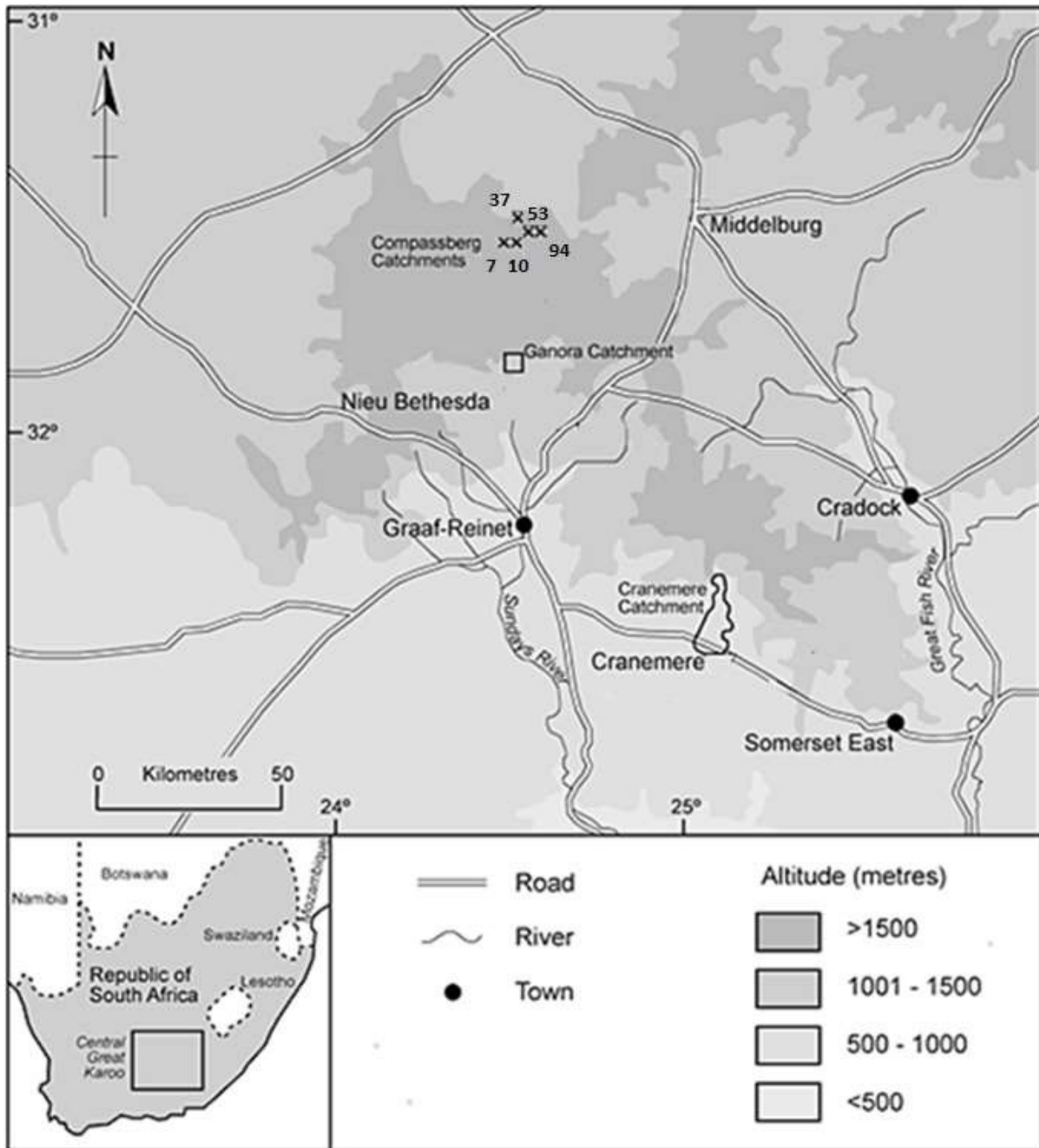


Figure 1: The location of the study region and sediment core sampling sites (After Foster *et al.* 2012).

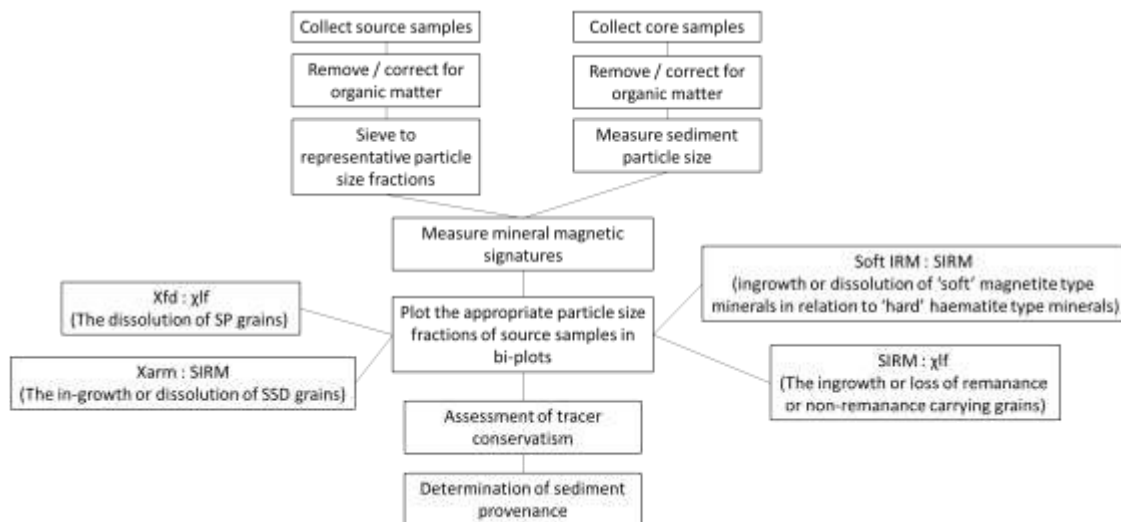


Figure 2: Flow diagram of the analysis procedure.

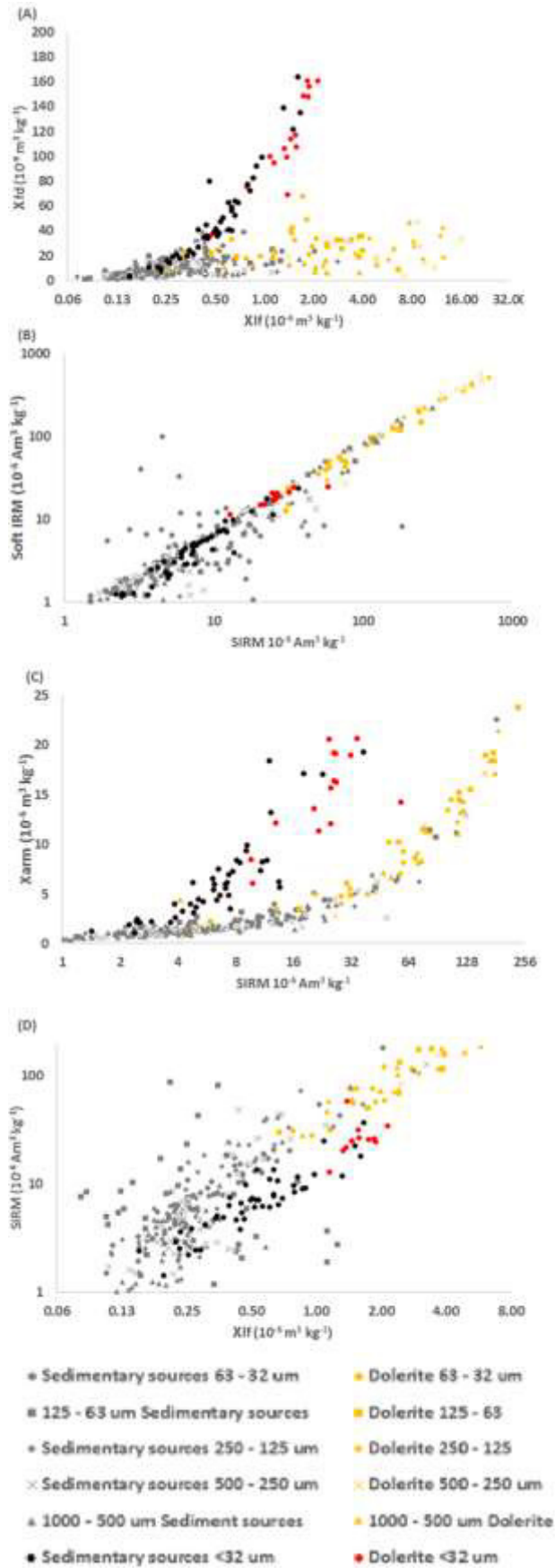


Figure 3: The relationship between different pairs of magnetic signatures in sedimentary and dolerite source samples of different particle size fractions.

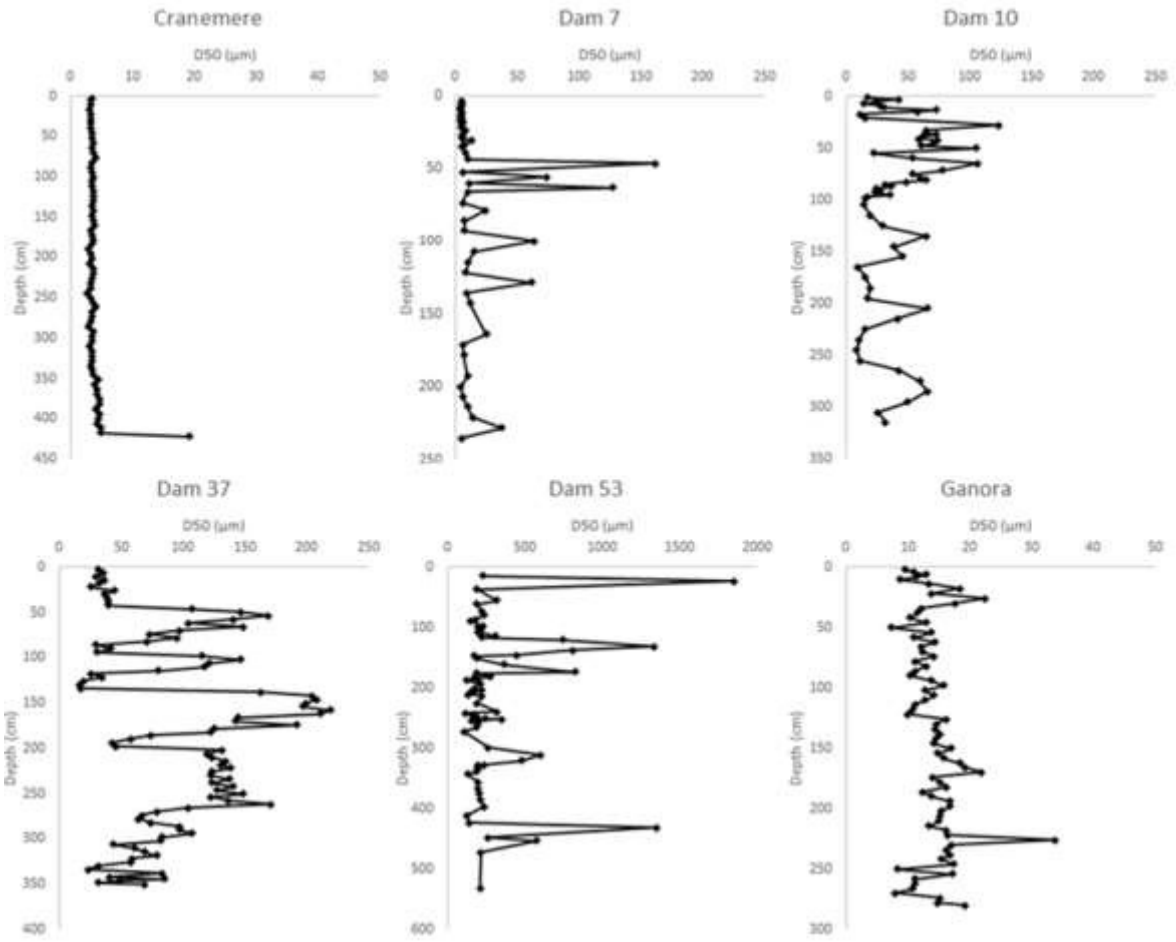


Figure 4: Down-core trends in D50 particle size.

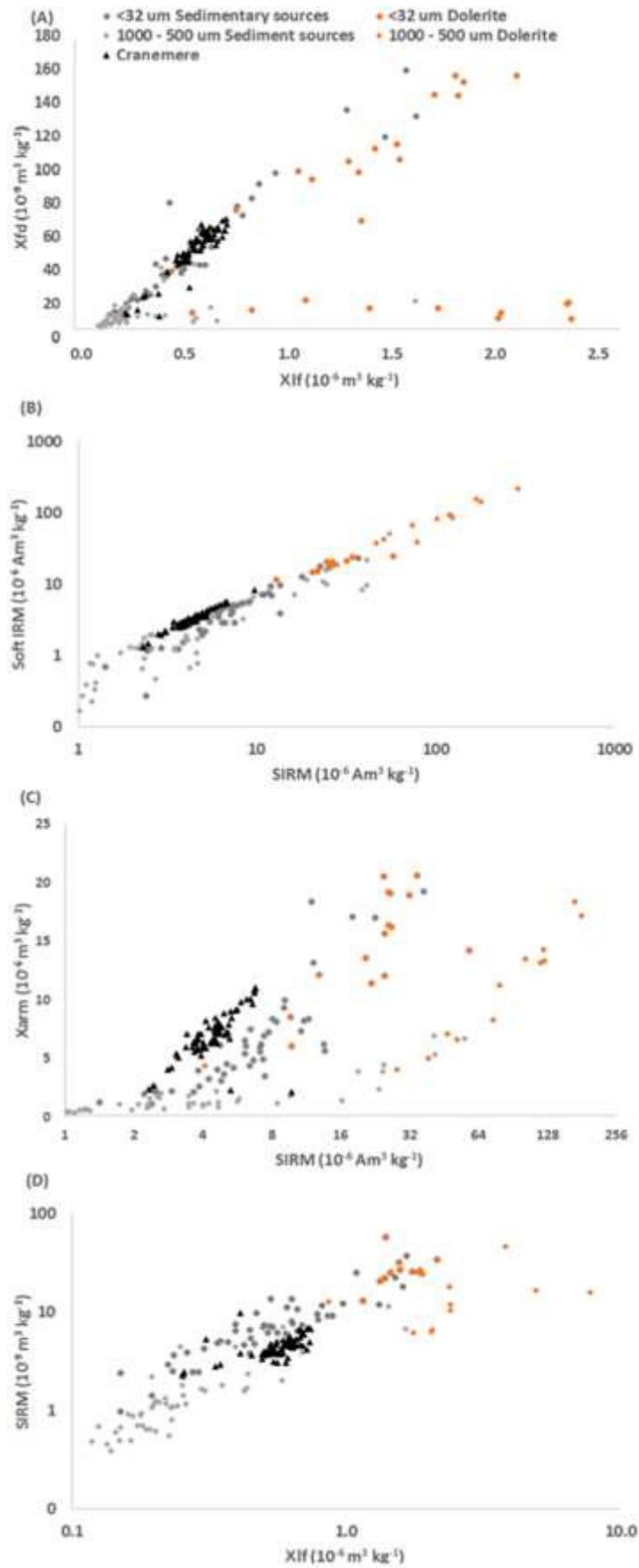


Figure 5: A comparison between source samples and the Cranemere sediment core using bi-plots of magnetic signatures.

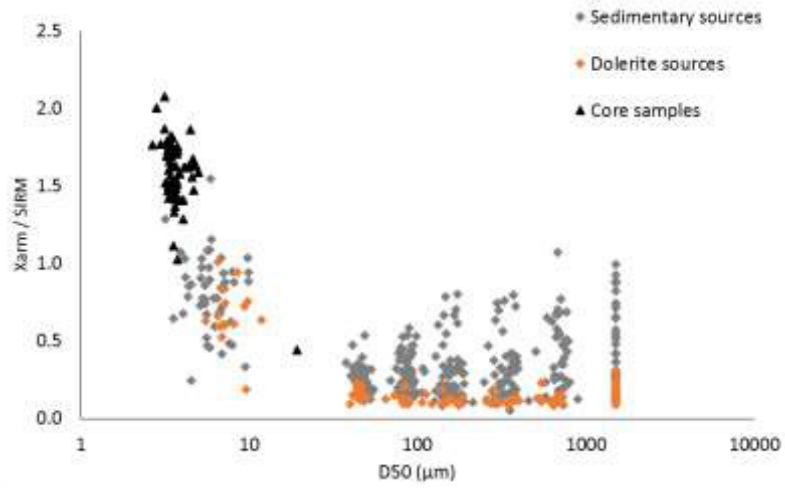


Figure 6: The relationship between the $\chi_{ARM} / SIRM$ ratio and D50 particle size in the sediment source and Cranemere core samples.

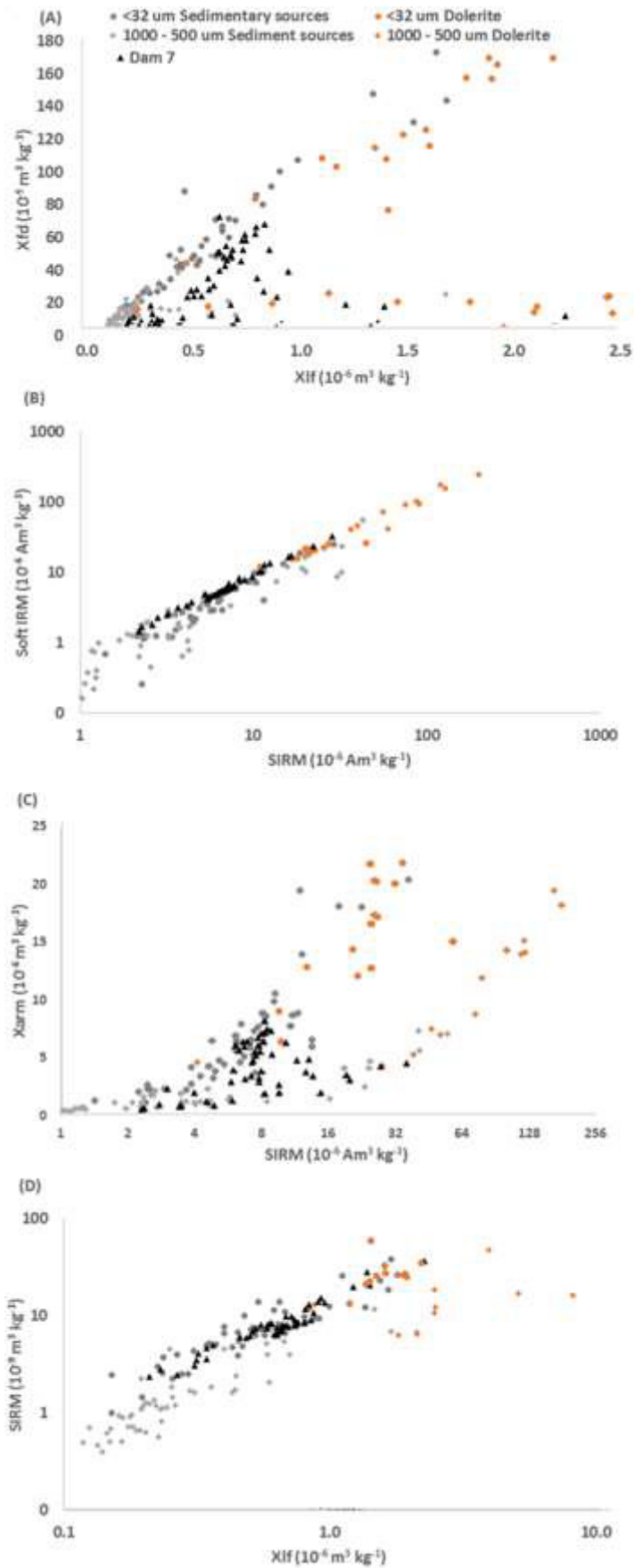


Figure 7: A comparison between source samples and the Dam 7 sediment core using bi-plots of magnetic signatures.

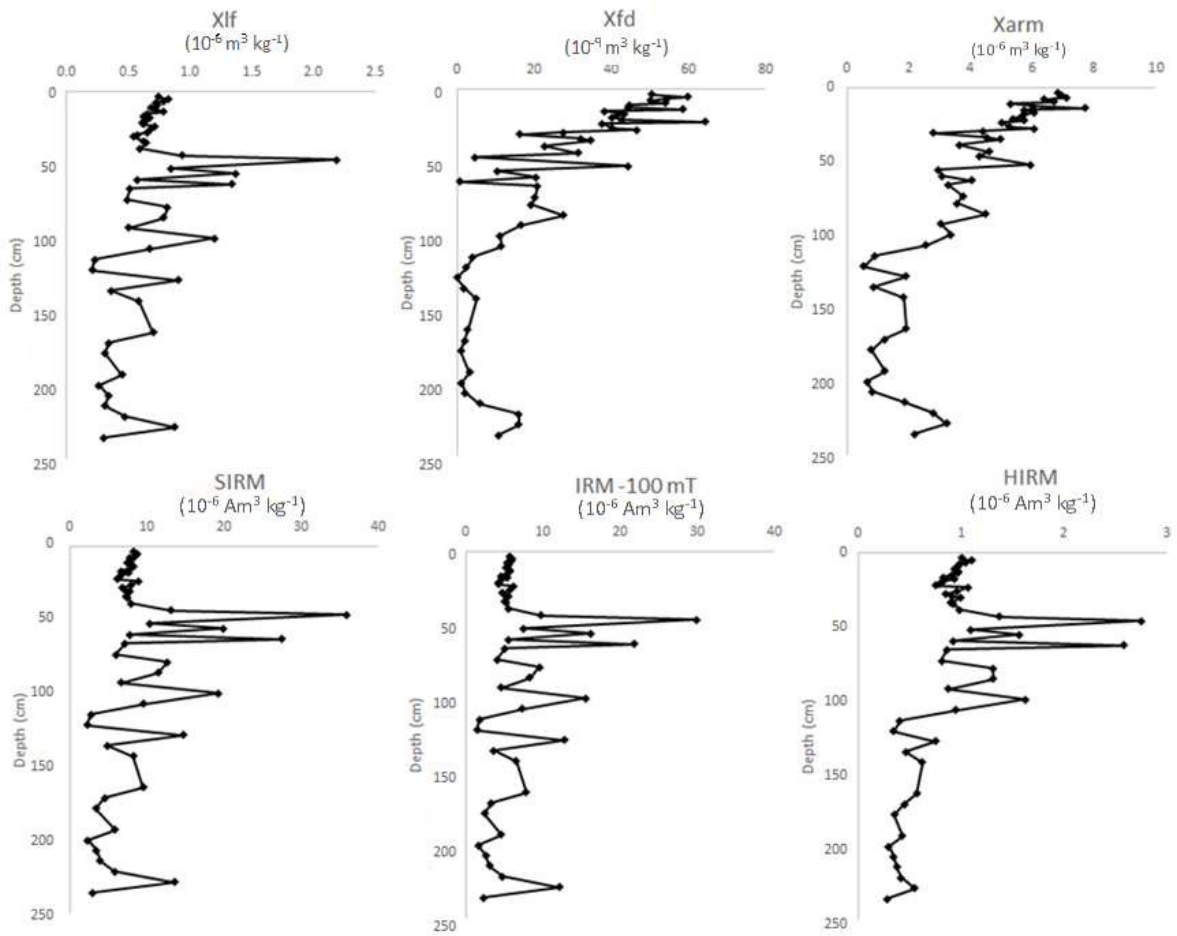


Figure 8: Down-core trends in magnetic signatures in the Dam 7 core.

1

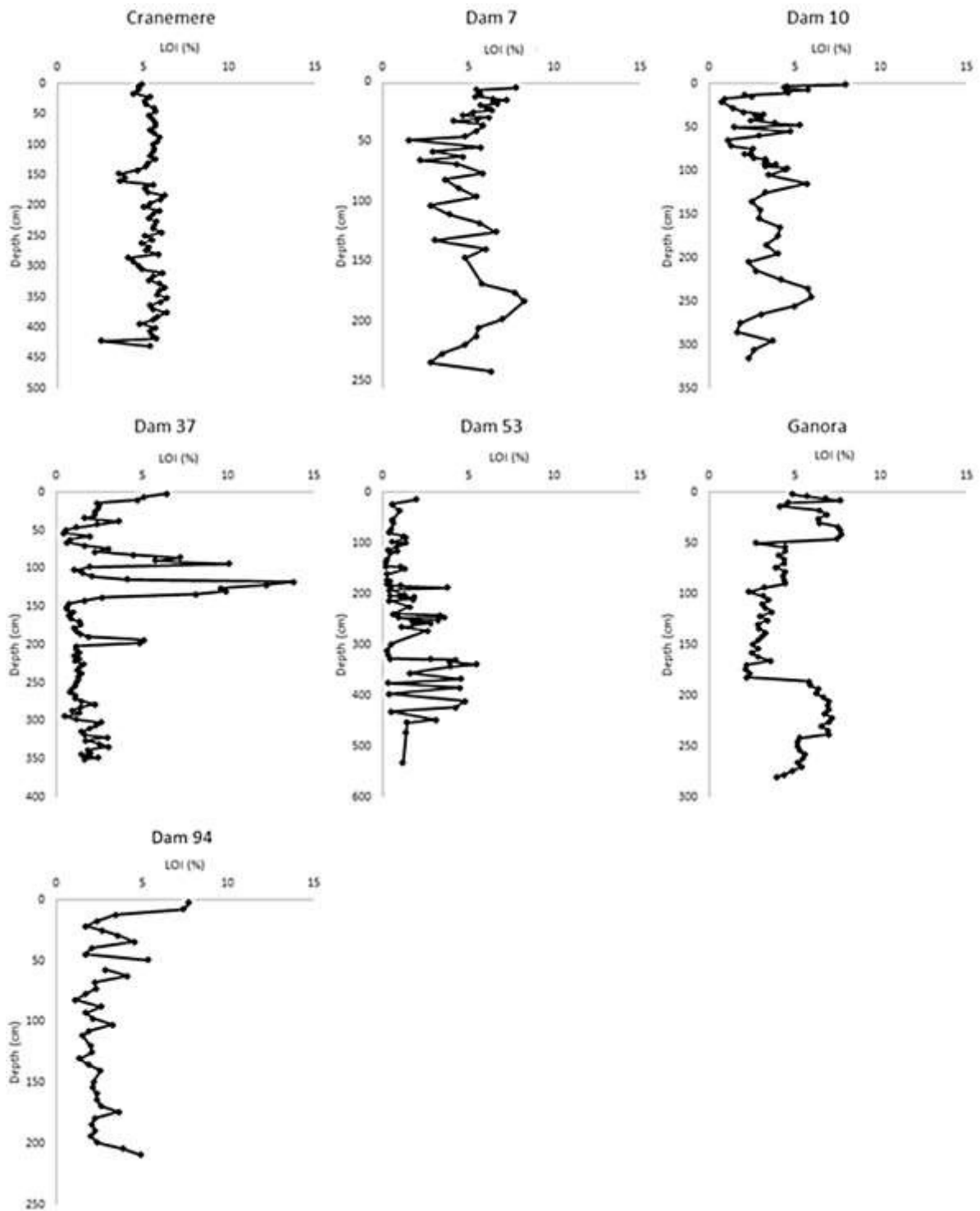
2 **Table 1: Characteristics of the study catchments, After Foster et al. (2012)**

	Compassberg Dam 7	Compassberg Dam 10	Compassberg Dam 37	Compassberg Dam 53	Compassberg Dam 94	Ganora	Craneme
Catchment topography							
Catchment area (ha)	630	148	3058	244	852/813*	258	575
Maximum altitude	2502	2113	2502	2092	2121	1741	1507
Maximum basin relief (m)	662	253	825	332	496	313	754
Percentage dolerite	65	0	5	10	45	5	5
Percentage sedimentary	35	100	95	90	55	95	95
Reservoir metrics							
Reservoir dam construction date	~1935	~1935	~1958	~1930's	~1914	1910	1843
Breach Date	2000	No	2010	1974	Probably 1974	No	No
Repair Date	No	No	2013	No	1976/7	No	No
Reservoir area (ha)	3.37	1.52	10.63	1.02	5.36/4.04*	5.23	30.2
Catchment to reservoir area ratio	187:1	98:1	288:1	239:1	159:1 / 196:1*	53:1	190:1
Erosion features							
Badlands	No	No	Yes	Yes	No	Yes	Limited
Gullies	Yes	Yes	Yes	Yes	Yes	Yes	Discontinued
Fans and hillslope storage areas	Minor	Minor				Yes	Yes
Land use							
Grazing	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Cultivation	Yes	No	Yes	No	No	No	Limited
Sampling year	2003	2003	2013	2013	2008	2006	2007

* Dam and catchment area reduced after breach repaired as new dam wall was built over the existing dam sediments and excluded a small northern tributary. Pre and post- new dam catchment areas are given as (pre/post) in Catchment Area, Reservoir Area and Catchment to reservoir area ratio

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Online supplementary data

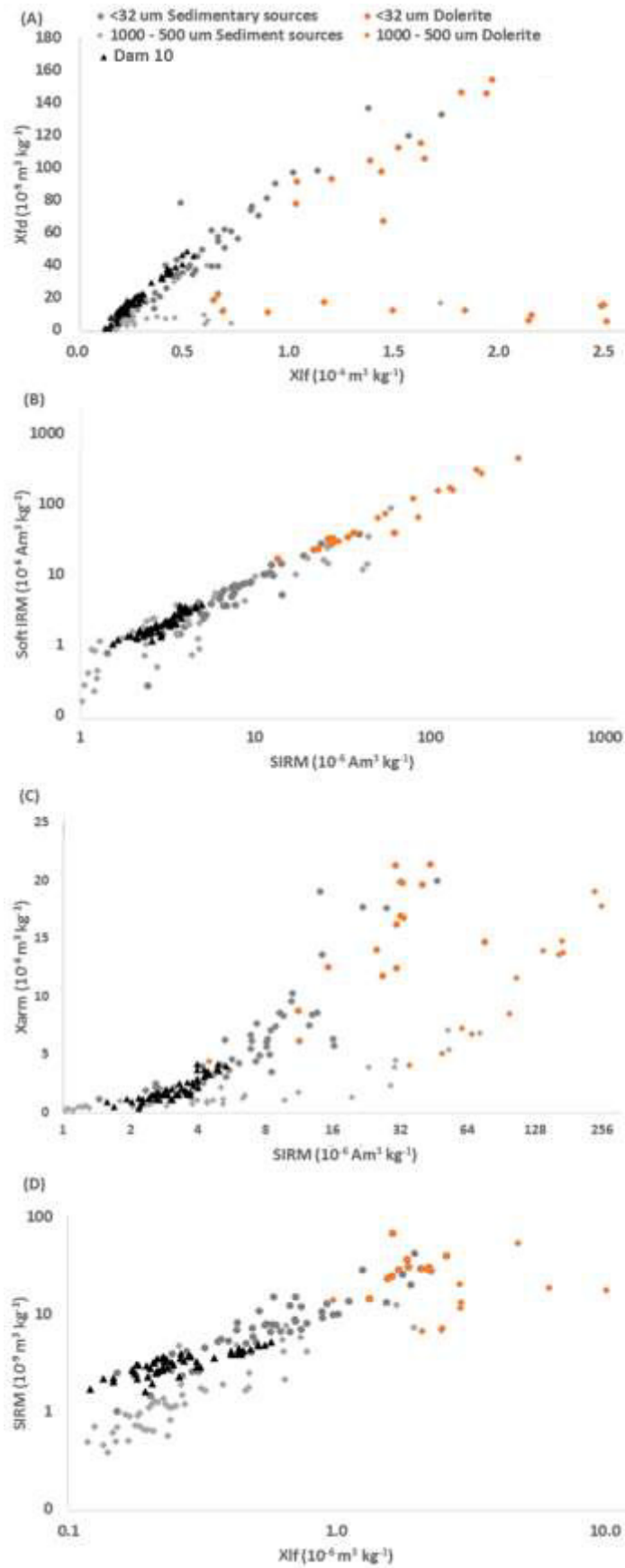


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Figure S1: Down-core trends in loss on ignition.

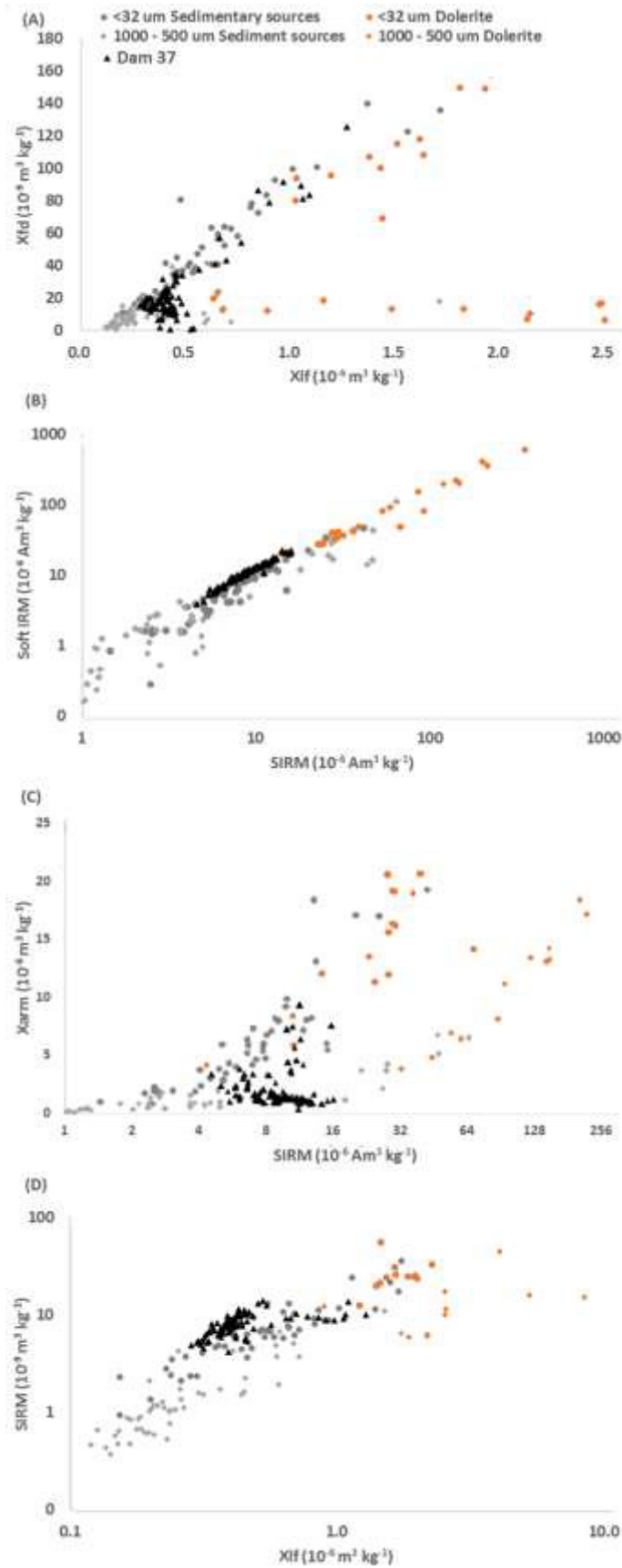
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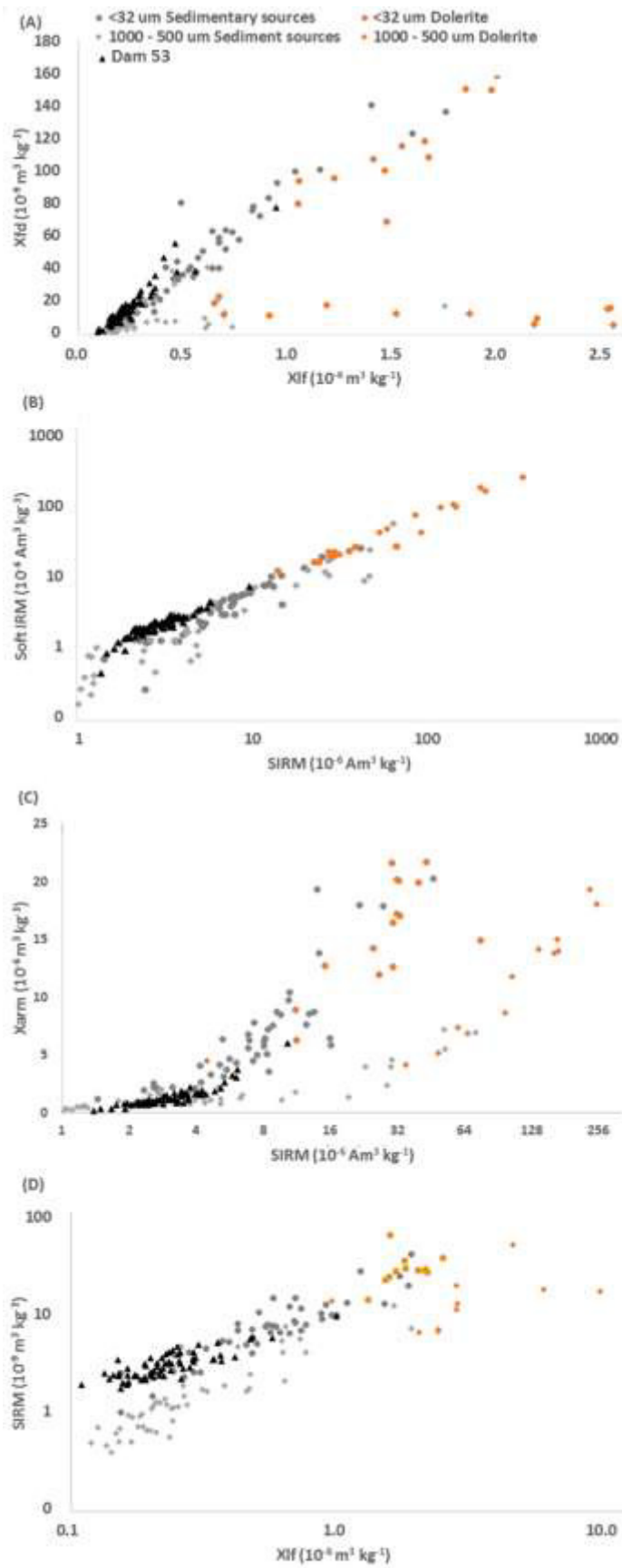
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13 **Figure S2: A comparison between source samples and the Dam 10 sediment core using**
 14 **bi-plots of magnetic signatures.**



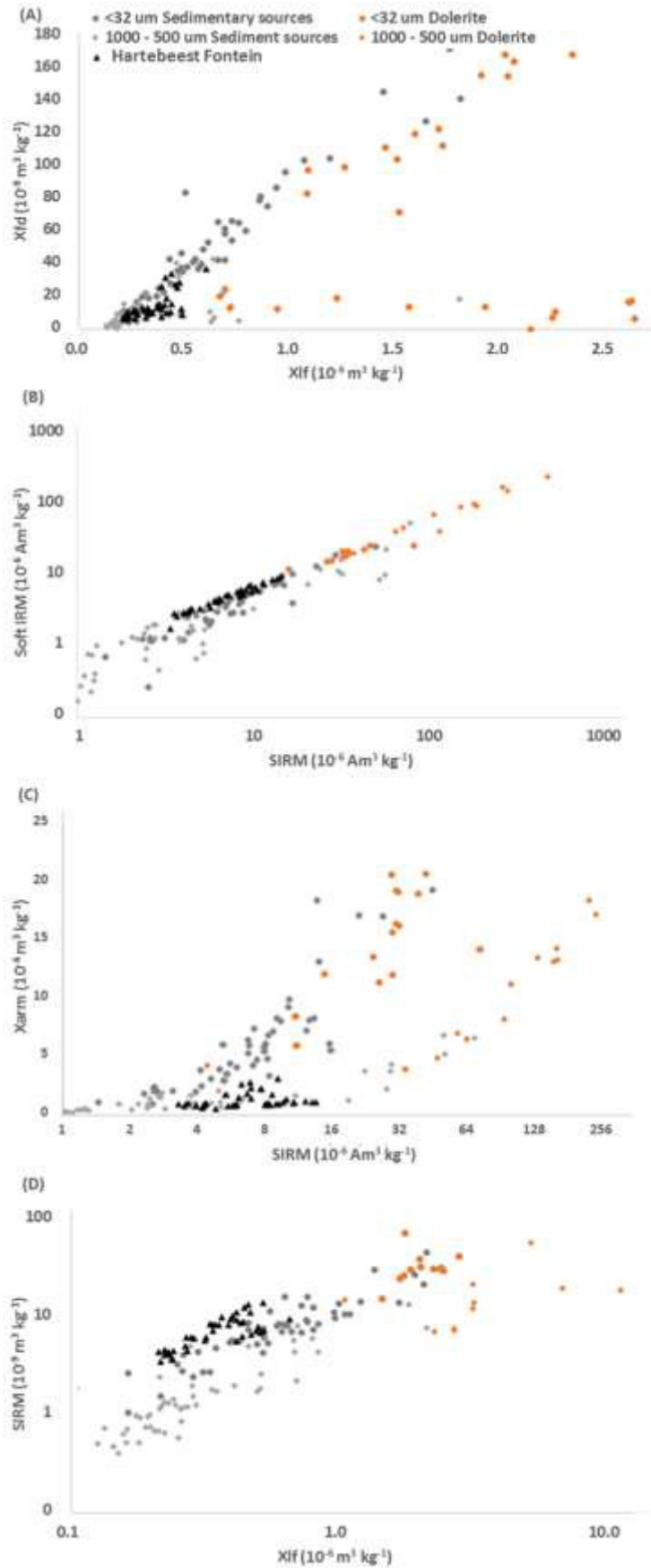
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16 **Figure S3: A comparison between source samples and the Dam 37 sediment core using**
 17 **bi-plots of magnetic signatures.**



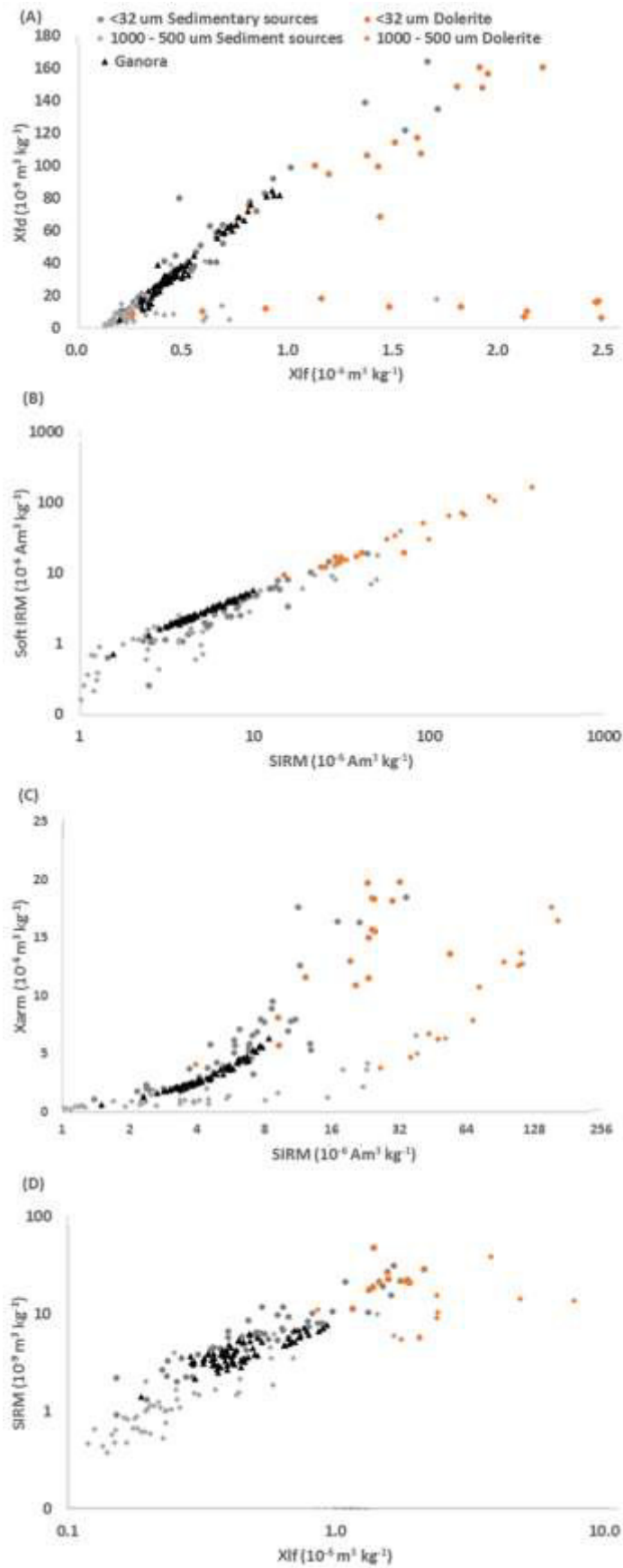
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19 **Figure S4: A comparison between source samples and the Dam 53 sediment core using**
 20 **bi-plots of magnetic signatures.**



21

22 **Figure S5: A comparison between source samples and the Dam 94 sediment bi-plots of**
 23 **magnetic signatures.**



24

25 **Figure 9: A comparison between source samples and the Ganora sediment core using**
 26 **bi-plots of magnetic signatures.**

