Geochemical mapping using stream sediments in west-central Nigeria: implications for environmental studies and mineral exploration in West Africa

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Abstract

This paper provides an overview of regional geochemical mapping using stream sediments from central and south-western Nigeria. A total of 1569 stream sediment samples were collected and 54 major and trace elements determined by ICP-MS and Au, Pd and Pt by fire assay. Geostatistical techniques (e.g. correlation analysis and principal factor analysis) were used to explore the data, following appropriate data transformation, to understand the data structure, investigate underlying processes controlling spatial geochemical variability and identify element associations. Major geochemical variations are controlled by source geology and provenance as well as chemical weathering and winnowing processes, more subtle variations are a result of land use and contamination from anthropogenic activity.

This work has identified placer deposits of potential economic importance for Au, REE, Ta, Nb, U and Pt as well as other primary metal deposits. Areas of higher As and Cr (>2 mg/kg and >70 mg/kg respectively) are associated with Mesozoic and younger coastal sediments in southwest Nigeria.

High stream sediment Zr concentrations (mean>0.2%), from proximal zircons derived from weathering of basement rocks, have important implications for sample preparation and subsequent analysis due to interferences. Associated heavy minerals enriched in high field strength elements and notably rare earths' may also have important implications for understanding magmatic processes within the basement terrain of West Africa.

This study provides important new background/baseline geochemical values for common geological domains in Nigeria (which extend across other parts of West Africa) for assessment of anthropogenic contamination from urban/industrial land use changes and mining activities. Regional stream sediment mapping is also able to provide important new information with applications across a number of sectors including agriculture, health, land use and planning.

Keywords: Sediment geochemistry, Nigeria, Environmental studies, Mineral exploration

1 Introduction

A range of media including stream sediments, soils and waters have been used in many countries across different scales for geochemical mapping (e.g. Darnley, 1990; BGS, 1990; Reimann *et al*., 1998; Rice, 1999; Key *et al*., 2004; Salminen *et al*., 2005; Johnson *et al*., 2005). The resulting geochemical data are used for a range of purposes including mineral exploration, land use planning, agricultural development as well for environmental assessment of both natural and anthropogenic hazards (Appleton and Ridgway, 1992; Plant *et al*., 2001). The Nigerian Geochemical Mapping Technical Assistance Project (NGMTAP) carried out stream sediment sampling in two pilot areas (‘cells’) in west-central Nigeria, one in central Nigeria and one in south-western Nigeria (Key *et al*., 2010). In 2009 fieldwork was carried out by a team comprising geoscientist from the Nigerian Geological Survey Agency (NGSA), the Finnish Geological Survey (GTK), Nigerian Universities and the British Geological Survey (BGS), see Lapworth *et al*. (2010) and Knights *et al*. (2010). These pilot cells form the basis for the ongoing Nigerian regional geochemical mapping programme which commenced in 2008 (Ogedengbe *et al*., 2008).

The mapping project produced not only new geochemical information but provided training to more than a hundred Nigerian geoscientists who will form the body of expertise for both the continuing national geochemical mapping programme and an expanding mineral exploration industry (Lapworth *et al*., 2011). This work forms a crucial part of the Nigerian Government’s strategy in its efforts to diversify away from a hydrocarbon-based economy by attracting greater investment in the minerals sector. The geochemical mapping is part of a much broader national geoscience mapping programme, for example, an airborne geophysical survey of Nigeria is nearly completed. Nigeria with its comprehensive programme of geochemical, geophysical and geological mapping will have one of the most comprehensively mapped land areas of Africa.

The main purpose of this paper is to investigate the geochemical variations of the <150 μm stream sediment fraction within the two pilot cells. This is referred to as a regional geochemical baseline survey. However, it is important to note that this term does not have a precise definition (Salminen and Gregorauskienė, 2000), reflecting the varied purpose of any particular study, i.e. the media collected, sample density, and method of analysis to list just three factors. The geochemistry of a given drainage site will be a function of a complex relationship between a range of factors including catchment geology and size, flow dynamics, land use, weathering processes and redox geochemistry (Plant and Raiswell, 1983). These factors have a spatial as well as a temporal dimension, and vary significantly between different collected sample media. An assessment is also made on the validity of using stream sediments as an effective medium for regional geochemical mapping in sub-Saharan West Africa.

The spatial framework for the geochemical mapping of Nigeria is based on Global Reference Network (GRN) cells as defined by Darnley *et al*. (1995). For Nigeria, the NGSA has divided the country into the 44 cells based on 1½ degree latitude/longitude topographic map sheet boundaries (see Figure 1). Each cell is equivalent to nine 1:100 000 topographic map sheets with a size of approximately 160 km x 160 km. Surveys aimed at the recognition of large scale geochemical patterns can employ lower density sampling than those designed to detect individual mineral deposits but, in general, higher density sampling produces more useful and reliable data suitable for a wider range of applications. The sampling densities for the two pilot areas were different (1 sample per 20 km^2 for the central cell, and 1 sample per 90 km^2 for the south-western cell – but with comparable catchment sizes of 10 – 30 km^2) to reflect the overall ‘prospectivity’ (Key and Pitfield, 2009) of the region including non-geological considerations such as existing land use, population density, national security issues and cultural/traditional controls on land use (see Figure 1). The two cells include the main geological units represent the varied land use and climate found in Nigeria.

An overview of the stream sediment geochemical mapping component of the NGMTAP is provided with particular focus on the regional scale distribution of selected major and trace elements, the mineralogy of the stream sediments and the influence of geology, weathering and transport processes and anthropogenic activities on this distribution. Implications for future geochemical surveys in Africa are discussed.

2 Study areas: geology, mineralisation, climate and land use

2.1 *Geology*

Both study areas are underlain by Precambrian rocks within the Benin-Nigeria Shield (of the Dahomeyan Terrane) that separates the Archaean to Mesoproterozoic West African and Congo Cratons to the west and east of Nigeria respectively (Grant, 1968, 1969; Odeyemi, 1981; Wright, 1985;Ajibade *et al*., 1987; Ajibade and Wright, 1989). The Dahomeyan Terrane is part of the African network of Neoproterozoic-Ordovician Pan-African Orogenic Belts, and is also referred to as the Trans-Saharan Belt. It is a collage of Neoproterozoic and older Precambrian rocks (interpreted as originally forming parts of continental fragments, island arcs and intervening basins) formed during collision between various lithospheric plates, including the West African and Congo Cratons (Burke and Dewey, 1972; Dada, 2006). The Trans-Saharan Belt is divided into an Eastern Terrane and a Western Nigerian Terrane (that includes the field study areas). The Western Terrane comprises three major lithological units (Figure 1) – migmatitic gneisses, supracrustal/schist belts (within the migmatitic gneisses) and plutonic rocks of the Pan-African 'Older Granite Suite' (Russ, 1957; Hockey *et al*., 1963; Truswell and Cope, 1963; Jones and Hockey, 1964; Dempster, 1966; Grant, 1969; Oyawoye, 1976; Odeyemi, 1981; Fitches *et al*, 1985; Olarewaju, 1988; Odeyemi, 1988; Rahaman, 1988; Ferré *et al*., 1996; Odigi, 2002; Ajibade *et al*., 2008). There are extensive sedimentary sequences of Mesozoic to Recent age that overlie the crystalline basement: i) The Chad Basin in northern Nigeria and along the Niger border; ii) The Benue Trough and Bida Basin, central Nigeria, (the Nupe Group (Ajibade *et al*., 2008) that covers the south-western part of the central cell); iii) The coastal sedimentary strata and sediments of the Dahomey Basin of southern Nigeria (that covers the southern parts of the south-western cell), including the Niger Delta. The sedimentary fill comprises post-orogenic molasse facies and a few thin marine sediments (Adeleye, 1974). The general succession for the coastal sediments was established by Jones and Hockey (1964) and comprises grits, sandstones, mudstones and shales.

Areas directly underlain by Precambrian rocks are generally poorly exposed peneplains. Migmatitic gneisses and granitic rocks locally form impressive inselbergs as well as large flat rock pavements. The schist belts underlie more hilly countryside and the best rock exposures mostly occur in incised stream and river sections. The Mesozoic and younger sedimentary strata form featureless flat plains covered by feriallitic soils with very little rock exposure.

In this paper simplified geological domains will be used to explore the variations in stream sediments geochemistry. These include four basement domains: Migmatitic gneiss; metasediments and metavolcanites; Zungeru mylonites and the Older Granites

(Malamo, 2004). Sedimentary rocks are grouped together in a Mesozoic and younger sedimentary domain (see Figure 1).

2.2 *Known mineralisation in the study areas*

Major mining activities in both cells are presently confined to the quarrying of industrial building materials, ornamental stone and river sand and gravel. There are also small-scale alluvial gold extractions in both cells, but no mining of primary gold-bearing quartz veins (Russ. 1957; Truswell and Cope, 1963; Malamo. 2006). In the south-western cell other known mineral deposits include nickeliferous laterites, rare earth element (REE) bearing pegmatites, uranium hosted both in crystalline basement vein systems and overlying sedimentary cover sequences as well as lead-zinc deposits in the Cretaceous strata (Olanipekun, 2000; Salau *et al*., 2005; Okunlola and Oyedokun, 2009; Okunlola and Akinola, 2010). The central cell has Sn-Ta-Nb pegmatites genetically related to the Pan African Older Granites (Jacobson *et al*., 1964; Matheis, 1987; Garba, 2003) as well as potential for uranium mineralisation in both the basement and sedimentary units (Suh *et al.* 2000).

2.3 *Climate and land use*

Annual average rainfall is between 1800–2000 mm/yr in the south-western cell, the central cell receives between 1200–1500 mm/yr. The climate is characterised by a unimodal regime that is controlled by the West African Monsoon (Nicholson, 1981). The wet season in central Nigeria lasts from April until October and a hot, dry season from November until March, the dry season is less distinct in southwest Nigeria. Daytime temperatures in the cells vary from the low 20s to the low 40s^{o} C. From December through February, the northeast trade winds blow strongly and often bring with them a large load of fine dust from the Sahara. These dust-laden winds, known locally as the Harmattan, are more common in the north but affect the entire country except for a narrow strip along the southwest coast. Water flow is controlled by seasonal rains which vary from the extremes of flash flooding after torrential rain to stagnant water at the end of the 'dry season'. Floodwater is charged with fine sediment derived from weathered bedrock and tropical soils and seasonal flooding is clearly a major weathering process. The thickness of the weathered profile is variable with extremes of unweathered bedrock pavements with no soil cover to lateritic soil profiles at least several metres in thickness.

In central Nigeria the land cover is a mixture of agriculture (mixed arable and livestock) and savannah grassland, and the population densities are low compared to southwest Nigeria. The land use in the central cell is predominantly arable agriculture with some fruit and cocoa plantations and small areas of forest, and has a relatively high population density. There are many densely populated areas in west-central Nigeria, notably in the extended urban sprawl of major cities including, Kaduna, Minna, Suleja, Abuja, the northern edge of Lagos as well as Ibadan and Abeokuta, some or all of which fall inside the cells. Although every effort was made to avoid potential sources of contamination, in some cases this was unavoidable, Nigeria is the most populous country in Africa (*c*.150 million – UN (2008)) and very few environments are untouched by anthropogenic activity.

3 Methodology

In this study, sites with significant anthropogenic contamination were avoided and observations were made at each site regarding potential sources of contamination and land use (Johnson *et al*., 2008; Ridgway *et al*., 2009). Meta-data on local landuse, site contamination, sediment texture and observed upstream outcrop lithology was collected. All of these factors have important implications for the interpretation of the geochemical results from regional stream sediment surveys.

2.1 Field sampling programme

The required sediment size fraction was chosen following analyses during an orientation survey in the central cell (Ridgway *et al*., 2009). Sampling was carried out between August and December 2009. Two size fractions (<250 and <150 μm) were collected from 20 streams (4 duplicates for each site) which covered the same geological terrain as the south-western cell. It was determined from this orientation study, using nested analysis of variance (ANOVA), that a minimum of 100 g of the <150 μm fraction sediment was required for each sample to be representative of the sample site's stream sediment and to allow for enough for analyses and a proportion for archiving. Table S1, found in the supplementary on-line material, shows ANOVA results from the orientation survey, indicates that within site variance was significantly greater for the <250 μm fraction compared to the <150 μm fraction for most elements, and thus less suitable for the purposes of regional geochemical mapping. Although collecting the <150 μm fraction was more time consuming this was not found to be prohibitive.

Stream sediment sites were pre-planned by the field campaign leaders although teams in the field held the responsibility for the selection of the exact site to sample, paying special attention to avoiding all contamination sources (*e.g*. sampling upstream of crossing points, and avoiding observed contamination or disturbance to the natural channel). During the planning stage possible sample sites were selected at a higher density than was necessary thus allowing for sites to be dropped due to inaccessibility or poor suitability due to significant anthropogenic contamination. The catchment size for the samples was usually between 10-30 km^2, lower order streams (1st - 3rd) were selected at the 1:100 000 map scale.

The sampling methodology for the collection of stream sediments is summarised below:

i. Sediment was dug using a trenching tool from the stream bed, in the active part of the channel and away from collapsed overbank or soil material. Enough wet sediment was collected to yield the required amount of fine sediment, from several (five or more) places along the length of the stream channel (within a *c*.50 m length of the channel).

ii. Wet sediment was passed through a coarse, upper nylon sieve (2 mm gauge) by hand.

iii. The <2 mm sediment fraction was passed through a lower nylon sieve with 150 µm nylon mesh. The >150 µm fraction was retained and a portion panned to collect the heavy mineral concentrate. Observed common heavy minerals are described and documented. The panned sample was not routinely analysed but was archived for later use should the stream sediment sample indicate something of interest.

iv. The < 150 µm fraction of stream sediment was left to settle out and water decanted prior to collection. The collected sample was transferred into a Kraft paper sample bag and allowed to air dry.

2.2 Sample preparation and analyses

Stream sediment samples and secondary reference materials (SRMs) were initially prepared at the National Geosciences Research Laboratory (NGRL) in Kaduna, Nigeria. Each sample was split so that an archive of material is retained at the NGRL. Sample preparation was completed at the BGS Keyworth laboratories (pulverisation in agate ball mills) and 0.2 g of homogenised sample analysed by inductively coupled plasma mass spectrometry (ICP-MS). During the orientation survey it was observed that very high Zr concentrations, found in many of the samples, caused significant interferences with several trace element determinations when using X-ray fluorescence spectrometry (XRFS) analysis. This was one of the factors that supported the use of the ICP-MS method in the main field campaign. Samples were dissolved using an aggressive sodium peroxide fusion method followed by HCl and HF acid digestion (Watts and Johnson, 2010). This digestion method was chosen to provide a more aggressive dissolution of refractory minerals than a standard mixed-acid method.

A total of 1569 stream sediment samples as well as standards, duplicates and reference standards were analysed for 57 elements by the fusion-ICP-MS method: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Se, Si, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr. However, the ICP-MS analyses of Au, S and Se were found to be unsuitable for use due to the relatively high detection limit (S and Se) and due to the large nugget effect for Au. Gold, Pd and Pt were determined by fire assay using 30 g of homogenised sample powder.

Sixty stream sediment samples collected from both cells, including all the main geological units, were analysed in the BGS Keyworth laboratories by X-ray diffraction (XRD) to quantify their mineral composition, and investigate the host minerals for the elevated Zr concentrations found in many of the sediments. These XRD studies were reported in detail in a number of BGS internal reports (Kemp *et al*., 2011). In order to achieve a finer and uniform particle-size for powder XRD analysis, approximately 5 g portions of the pulverised material were micronised under deionised water for 10 minutes with 10 % (i.e. 0.5 g) corundum. The corundum-spiked samples were then spray-dried following the method and apparatus described by Hillier (1999). The spray-dried materials were then front-loaded into a standard stainless steel sample holders for analysis. Mineral quantification was achieved using least squares fitting of measured to calculate XRD profiles using a crystal structure databank (*e.g*. Snyder and Bish, 1989). Kemp *et al*. (2011) provides further details of the analytical techniques used for the XRD analyses.

2.3 Quality control

A quality control (QC) programme covered all aspects of the work programme from the planning stages of sample site collection, the actual sample collection procedures and subsequent sample preparation and chemical analysis and the recording of the field and laboratory data. The quality controls are based on the rigorous sampling protocols of the BGS G-BASE methodologies (e.g. Johnson *et al*., 2005, 2008). Random number lists were used to ensure that spatially correlated anomalies were not an artefact of any systematic bias in sample preparation or analysis. Alongside the collected samples, international and locally collected Nigerian control samples were inserted and analysed so that they were blind to the analyst. Thus two SRMs were collected from the central cell and prepared for use on the Nigerian Geochemical Mapping Programme. In each batch of one hundred samples, a sample was collected from one site in duplicate (a duplicate pair) and then sub-sampled to create replicate analytical samples. These are designed to investigate the within-site and within-sample element variability. In a batch of 100 samples there were six control samples (duplicates, replicates and SRMs). The results for the SRMs were also assessed as part of the QC process, and where discrepancies were found these were investigated to ensure that the final data set was of the highest quality.

All the analytical data were assessed for their fitness-for-purpose. Sulphur and Se results were determined to be unsuitable, with > 90% of values reported below the lower limit of detection and are not included in subsequent interpretations (Watts and Johnson, 2010). Nested analysis of variance (ANOVA) of the duplicate and replicate data was used to deduce which elements' data should be treated with caution in examining between-site variations. The results from these tests are shown in Table 1. In brief, most elements display an acceptably high proportion of between-site variability. Some elements should be 'treated with caution' (V, Bi, Cd, Sn, Cr, Mo, Li, Cu, Co and Ga); having 60 – 75% of variability attributed to between-site variation. The authors conclude that some data should only be used to interpret the high concentrations; of elements with a low proportion of variability attributed to between-site variation (Ni, Ag, As, P, Si, Be, Tl, and Au). The use of just 0.2 g of sample for analysis, using sample powders containing a high concentration of resistate minerals e.g. zircon, is thought to have increased the "within sample" variability.

Additional blanks, duplicates and CRMs were during the fusion analysis as part of laboratory QA procedures (Green *et al*, in preparation).

During interpretation an excellent correlation between Ag and Zr was observed. This was attributed to interference from ZrO on Ag during the ICP-MS determination requiring subsequent correction for samples with high Zr concentrations (Hu *et al*., 2002).

XRD – Simon do we need to add any detail on QC for this analysis?[djl]

2.4 Data Analysis

The geochemical results were explored using a range of common statistical techniques including descriptive summary statistics, box-plots, percentile-classified geochemical maps, spearman rank correlation analysis, cluster analysis and robust principal factor analysis (see Reimann *et al*., 2008; Grunsky, 2010). The purpose of using these techniques was to investigate the structure, trends and element associations within the data set, thus providing insights into the underlying geological, physical, geochemical, anthropological processes that are important in controlling the stream sediment geochemistry. The explanatory data procedures used in this study are summarised in Table 2.

For elements with <50% censored data (see Table 3) the mean values were estimated using the Kaplan and Meier (1958) method (nonparametric). For elements (Au and Cd) with 50-80% censored data, a robust Maximum Likelihood Estimation (MLE) method is used (Kroll and Stedinger, 1996), and for elements (Pd and Se) with >80% censored data the mean value is not estimated (see Helsel, 2005).

A Shapiro-Wilk test (Shapiro and Wilk, 1965) was used to assess the normality of untransformed and log-transformed element results. A nonparametric Wilcoxon rank sum test (Wilcoxon, 1945) was used to explore differences between median values from different data groups. Correlation analysis of geochemistry data was carried out using the Spearman rank sum method as it is nonparametric, less sensitive to outliers and does not assume a linear relation between variables (Spearman, 1904).

The box-plots data was log-transformed for most elements as untransformed plots can seriously underestimate the number of lower outlier values and overestimate the number of upper outlier values in strongly right-skewed data, which is often the case for stream sediment geochemistry (Filzmoser *et al*., 2009; Reimann *et al*., 2008). It was essential to transform the data prior to carrying out principal factor analysis (PFA) due to the issue of data closure and multiple populations. However, with appropriate data transformation this method is able to generate robust factors that relate to underlying processes controlling the spatial geochemical distribution in stream sediments. The multi-element chemical analysis consists of elements from a closed data set (i.e. constant value of 1,000,000 mg/kg = 100%) with markedly different concentrations, variability and distribution. As a result the data was centred log-ratio (CLR) transformed (Aitchison, 1986) for PFA. A robust PFA with Varimax (orthogonal) rotation method was chosen to explore the spatial variation of factors composed of multiple elements (Reimann *et al*., 2008). Silicon and elements with >2% censored data were excluded from the PFA and the rare earth elements (REE) were summed as light REE (LREE, La to Sm) and heavy REE (HREE, Eu to Lu) due to their large effect on PFA, such factors masking subtle internal structures within the data sets (Riemann *et al*., 2008). The number of factors extracted to describe the variance of the geochemical dataset was determined using a sum of squares scree-plot, in this case a cut off of 76% of explained variance was used including the first 5 factors. It must be stressed that factor analysis is only used to explore the data set for multivariate structures, and indicate certain element relations but does not in any way provide proof of the existence of certain processes (Reimann *et al*., 2002).

Hierarchical cluster analysis of the XRD traces (Q-mode) was carried out using a search-match algorithm to compare scans with each other, measured data were reduced to probability curves and each possible pair of probability curves was compared. A dendrogram was produced by agglomerative hierarchical clustering (Kaufman and Rousseeuw. 2005)

Maps of single elements and robust PFA scores were produced using box-plot (log scale) with percentile intervals of (0, 5, 25, 75, 95 and 100). Accentuated exploratory data analysis (EDA) symbols were used (Reimann *et al*., 2008) which emphasises the spatial structure of the data rather than simply highlighting the extreme high values as in the case of graduated symbols (Reimann, 2005).

The geochemistry data was stored in a relational MS ACCESS database and extracted into an MS EXCEL spreadsheet. Statistical analysis and plotting was carried out using the open source package R (R Core Development Team, 2010; Reimann *et al*., 2008).

The Th/Al ratio provides a measure of the 'winnowing' of stream sediment material from a combination of fluvial and wind-blown transport processes (Garrett *et al*, 2005). As such it acts as a ratio for the high-density and low-density minerals in the stream sediment, the 'winnowing index' (WI) was calculated using the method of Grunsky *et al*. (2009) in the following manner:

i. Log-centered Th/Al index created:

Index = (Th/Al – mean (Th/Al))/std. dev. (Th/Al)……*equation 1*

ii. Create an “Offset Index” to a minimum of zero and add 0.01 so there are no zero values:

Index’ = Index –minimum (Index) + 0.01…………….*equation 2*

iii. Rescale the Index’ between 0.01 and 3.0:

Interval = 3.0/maximum (Index)………………………*equation 3*

iv. Calculate the Winnowing Index (WI):

WI = Index’ x Interval……………………………….*equation 4*

4 Results

4.1 *Stream Sediment Geochemistry*

The summary statistics for the stream sediment geochemistry from both cells are shown in Table 3. In addition, the mean upper crust concentration (UCC– Taylor and McLennan. 1995; Wedepohl. 1995), and the probable effect level (PEL) concentrations (MacDonald *et al*., 2000; CCME, 2002) for freshwater sediments for a selection of trace elements is shown. Results from a Shapiro-Wilk test for normality are shown in Table 3 for all the elements (either untransformed or log transformed). Only the following elements; Al, Ti, Mg, Zr, Hf, Cs, Li, Zn, Cu, Co and Mo were found to have either a normal (only the case for Al) or a log-normal distribution ($p >$ 0.05) for the data from both cells, confirming the fact that normally distributed data rarely holds true for geochemical data, even when the data are assembled from multiple populations, i.e. different source geology. A Wilcoxon rank sum tests were used to test the equivalence of median stream sediment geochemistry values from the central and south-western cells, for the four main geological units that are also shown in Table 3. The null hypothesis is that the median values of the various elements in question are equal.

Table 4 shows a Spearman rank correlation matrix for selected major and trace elements for the different geological domains in both cells. The significance of the correlation for each pair of elements is indicated. Differences in stream sediment geochemistry between the two cells and between different land use, potential contaminant sources and sediment type were explored using box-plots (Figures 2-5) as well as Wilcoxon rank sum tests. A log scale was used for most plots with the exception of Pb for Figure 4c and 4f. The notches (Figures 2, 3 and 5) show the 95% confidence interval around the median value for a given group, thus allowing a rapid assessment of the significance (p <0.05) of different median values between differences groups of data. Solid horizontal lines show the censored values for the different elements, the long dash line is the UCC, and the dotted line the PEL (only plotted in Figures 3 and 4). Table 5 summarises results for the quantitative stream sediment mineralogy, the dendogram from cluster analysis using XRD data is available in the supplementary on-line material (Figure S1). Figure 6 shows the spatial distribution (percentile box plot method) for selected elements (K, Pb, As, Au, Ta and ΣLREE).

The PFA loading plots using the first 5 factors are shown in Figure 7. On the factor loading plot the y-axis is an expression of the communality of a variable (related to the multiple correlation coefficient R^2), on a scale of -1 to 1, only the highest coefficients <-0.3 or >0.3 are plotted (see Figure 7). The first 5 factors are briefly summarised below: Factor 1 explains 32% of the data variability and is dominated by positive loadings for transition metals (Cr, Cu, Mo, Ni, V, Zn, Co, Sn, Fe, Ti) and may be considered an Fe-oxide/hydroxide and ilmenite factor. Dominant negative loadings can be considered a large ion lithophile (LIL) factor (K, Ba, Rb and Sr) associated with K-feldspars and micas. Factor 2 explains 21% of the data variability with dominant positive loadings for LREE, HREE, Th, U and Y and may be considered a REE and resistate heavy mineral factor. Negative loadings have overall low coefficients and may be considered a phyllosilicate and Fe-oxide factor. Factor 3 explains a further 8% of variability; positive loadings have high coefficients for Fe, Mn, Mg and some trace elements and may be considered a ferromagnesian factor, indicative of the importance of olivine, pyroxene and hornblende. Negative loadings are dominated by Pb, Sn and U. Factor 4 explains 7% of variance, negative loadings are dominated by Hf and Zr (immobile elements) and can be considered a zircon mineral factor, and positive loading are dominated by Cs, Li, Rb (mobile elements) as well as Cu and Ni. Factor 5 explains 6% of variability and positive loadings are dominated by Ta, Nb, Ti and Sn that may be indicative of a coltan factor. Figure 8 shows factor score maps for the first five factors from the robust PFA analysis and these are discussed in Section 5.2.

4.2 *Mineralogy*

Table 5 summarises the XRD results from stream sediments from both cells (see Kemp *et al*., 2011). Cluster analysis of the raw mineralogy data revealed two dominant clusters within this data. The first cluster is composed of four groups (1-4, see Figure S1) which show broadly similar mineralogical characteristics of moderate-high amounts of quartz, low-moderate K-feldspar (microcline), plagioclase and 'kaolin' together with low/no 'mica' and ferromagnesian minerals and variable zircon concentrations. These samples typically correspond to catchments composed of migmatitic gneiss geology. The second cluster, a combination of the next three groups (5-7), is composed of low-moderate amounts of quartz, high amounts of K-feldspar (microcline and orthoclase) and plagioclase, moderate but variable amounts of 'mica', 'kaolin' and ilmenite together with occasional traces of epidote, amphibole, sillimanite, monazite and zircon concentrations. These samples appear to be derived from a mixture of Older Granites and migmatitic gneiss catchment lithologies.

The single remaining sample (Group 8, shown in black, site 198) is clearly very different to all the other stream sediments. This sample has a very quartz-rich mineralogy (95%), the catchment geology is formed of Mesozoic and younger strata and sediments.

5 Discussion

5.1 *Stream sediment geochemistry and mineralogy of major geological domains*

5.1.1 Distribution of the major elements

The basement-derived sediments have significantly higher Fe, K, Ca and Mg compared to the more recent sedimentary domains (Figure 2). In the case of K and Ca in the sedimentary domains have concentrations that are significantly higher in the central cell, reflecting the greater proportion of basement-derived material within this basin contrasting with the marine signature of the south-western cell. Silicon concentrations in the sedimentary domains are higher than those from the basement domains, but both cells are depleted in Si compared to UCC (see Table 3). Within the basement domains there are few significant differences within domains (between cells) or between domains for major elements (Figure 2, Table 4). Compared to UCC the basement sediments have comparable concentrations of Fe, but are depleted in Al, K, Ca and Mg reflecting the maturity of the chemical weathering processes.

It can be seen that for all these elements there are strong geological controls on distributions in stream sediments both within the different Mesozoic sediments within each cell as well as within the basement domains of each cell (Figure 6). Potassium is highly depleted in the Mesozoic sediments of both cells compared to the basement units reflecting the higher quartz content of these domains.

It is apparent from the correlation matrix (Table 4) that when the data is grouped by source geology they yield very different correlation structures. The influence of quartz and aluminous minerals are clearly reflected in the significant negative correlations of Si, and significant positive correlations of Al, with other elements. Significant positive correlations between K (and Ba, not shown here) suggest that the distribution of K is controlled by clay and mica (Table 4).

5.1.2 Distribution of trace elements

High field strength elements (HFSE) (*e.g.* Zr, Hf, Ti, U, Th, Ta and Nb) including the REE (La-Lu and Y) and are significantly enriched in stream sediments across the two cells compared to UCC, while other incompatible large ion lithophiles (*e.g*. Sr, Ba and Rb) are not enriched (Table 3) reflecting their relative solubility and the maturity of the weathering processes. The LREE have significantly different concentrations between the two cells as do the HREE, Eu, Gd and Tb for all the simplified geology domains, while the other HREE (Dy-Lu and Y) are not significantly different for the stream sediments draining migmatitic gneiss and Older Granite rocks (Table 3). Compared with other regional stream sediment studies in Africa, Asia and Europe (*e.g*. Key *et al*., 2004; Chandrajith *et al*., 2000, 2001; Salminen *et al*., 2005) the results from the this study show relativly high concentrations for REE, Y, U, Ta, Nb, Zr and Hf. Zinc, Pb, Ni, Cr, V as well as other trace elements are enriched in basement rocks compared to UCC (Figure 3). There are significantly higher concentrations of Zn, Pb and Sn within all basement domains of the south-western cell compared to the central cell, and higher As concentrations within the basement rocks of the central cell compared to the south-western cell (Figure 3, Table 3). Arsenic concentrations within the younger sediments of the south-western cell are significantly higher than all other geological domains. There are highly significant positive Spearman rank correlation coefficients between As and Fe and As and Al ($R=0.67$ and $R=0.38$, $p<0.001$, respectively), as is the case for other trace elements ($R>0.6$ for V, Co, Zn, Cr, Ni, Cu), suggesting that Fe oxides/hydroxides and phyllosilicates are important in controlling trace element geochemistry (*e.g*. Goldberg, 2002; Chakraborty *et al*., 2007). Biogeochemical processes, as well as provenance (younger sedimentary system) could explain the higher As concentrations in these sediments (Figure 6c) which have high organic matter, and have been subjected to anaerobic conditions (Ogban and Babalola, 2003; Akpan and Ufondike, 2005). The more prevalent reducing environments present in stream sediments in the humid delta areas, and microbial activity, fuelled by greater dissolved organic carbon flux, may be involved in releasing As and Fe from the geologial materials. This is then oxidised in the stream and co-precipitated and absorbed on Fe hydroxide surfaces – this cycle is repeated resulting is relative enrichment in the younger sedimentary deposits.

Arsenic (and Sb) was found to be a useful pathfinder for Au in the central cell (Knights *et al*., 2010). However, this relationship breaks down in south-western cell due to the higher background As concentrations associated with younger coastal sediments (see Figure 6c), with important implications for its use as a pathfinder element across West Africa. The highest density of anomalous gold concentrations are associated with the metasediments in both cells (Figure 6d), highlighting the importance that physical processes play in controlling the distribution of Au in placer deposits. The LREE and Ta are elevated in both the Mesozoic and migmatitic gneiss and depleted in the Older Granite catchments in the Central cell, while LREE are depleted in the Mesozoic rocks of the south-western cell (Figure 6f).

5.1.3 Mineralogy

XRD analysis showed that the stream sediments are predominantly composed of quartz with subordinate amounts of feldspar (various species of plagioclase and K-feldspar), mica (undifferentiated but possibly including muscovite, biotite, illite and illite/smectite), 'kaolin group minerals' (undifferentiated but possibly including kaolinite, halloysite etc) ± traces of ilmenite, zircon, amphibole, epidote, haematite, monazite, sillimanite, pyroxene and anatase (Table 5).

Cluster analysis of XRD data (see Figure S1) indicates eight specific mineralogical groups which can be combined to produce two clusters with similar characteristics. One cluster comprises samples with moderate to-high amounts of quartz, low to-moderate K-feldspar (only microcline), plagioclase and 'kaolin' together with low/no micas, ferromagnesian minerals and variable zircon concentrations. A second cluster has low to-moderate amounts of quartz, high amounts of K-feldspar (microcline and orthoclase) and plagioclase, moderate but variable amounts of micas, 'kaolin' and ilmenite together with occasional traces of epidote, amphibole, sillimanite, monazite and variable zircon concentrations. The first cluster is dominated by samples from samples with migmatitic gneiss source geology, the second cluster from samples dominated with Older Granite and migmatitic gneiss geology. Relatively few samples from the Mesozoic sediments were analysed by XRD, but are characterised by higher amounts of quartz.

Zircon was the only Zr-bearing phase identified by XRD in the stream sediments and its concentration shows a strong linear relationship (R^2 = 0.91) with Zr from geochemical analysis. The variable zircon content of the stream sediments suggests that its presence is not indicative of any particular catchment lithology. While recent results from LA-MC-ICP-MS U-Pb dating of detrital and country rocks in Nigeria by Key *et al*. (in preparation) suggest that these sedimentary zircons are from proximal sources, wind-blown sources of immobile elements from these chemically weathered terrains also are important (Moreno *et al*., 2006).

The XRD total feldspar shows a good linear relationship with Ba (R^2 = 0.78) due to its presence in the majority of alkali feldspars and to a lesser degree in plagioclase (Deer *et al.*, 1966). There is a good linier relationship between ilmenite and total Fe (R^2 = 0.78), suggesting that it is the dominant Fe-bearing mineral. A good correlation between monazite and REE and P concentrations, suggests that this is the dominant REE host mineral. The REE distributions and mineralogy is explored in more detail in Knights *et al*. (in preparation).

5.1.4 Stream sediment texture

Figure 5 shows box-plots for a selection of elements that represent clay minerals (Al), feldspars (K), elements that tend to be part of the crystal structure or absorb to the surface of Fe-Mn oxy-hydroxides (Fe, Mn, Zn, Cu) and elements associated with heavy minerals (Th, Zr). The winnowing indices (WI) are shown for the two principle sediment types: clay-type sediments (group one) and sand and gravel type sediments (group two). Aluminium, Cu and Zn have significantly higher concentrations in the 'clay' type sediments, while K, elements associated with heavy resistant minerals Th and Zr, and the WI, as well as Mn, associated with surface absorption processes, have significantly higher median values in coarser textured sediments.

The sediment type (clay dominated or sand and gravels) reflects the nature of the geology in the catchment of the stream, the prevailing weathering and stream-flow conditions: coarser sediments are transported by higher energy flow regimes, and the fluvial dynamics determine the rate and nature of bedrock weathering and sediment deposition (Robert, 2003). The Harmattan winds winnow clays from unprotected interfluves as well as from dry stream beds. For the areas surveyed this combination of both an extreme wet season and a dry season with very strong unidirectional winds is believed to be responsible for the concentration of heavy minerals, including zircon, in the stream sediments of the two cells.

An understanding of the variation in sediment types is useful as some transition elements have an affinity for adsorbing onto fine-fraction mineral particulate surfaces such as clay minerals, iron oxy-hydroxides (Petersen *et al*., 1996; Owens *et al*., 2005) whilst others are incorporated into minerals that resist physical weathering to the finer fractions or on the surface of sand and gravel (e.g. Mn, see Figure 5). The variable nature of stream sediment is one of the prime reasons for consistently sampling at the same size fraction in a regional-scale survey.

5.2 *Spatial variation in multivariate geochemical signatures*

There are a number important processes that explain the majority of the data variability in stream sediment geochemistry, these include source geology and mineralisation, physical hydromorphic processes (transport and winnowing), and chemical processes (e.g. the important effects of Fe-Mn-oxyhydroxide and Fe-oxides on trace element distributions) and weathering processes.

The PFA factor score maps (Figure 8) clearly discriminate between the sediments derived from basement sources and those derived from young marine sediment sources (see Figures 8a-8c).

Factor 1: Fe-trace element associations. A large proportion of data variability (32%) is explained by this factor and high scores for Factor 1 are found in the sediments draining the Mesozoic and younger strata in the south-western cell (Figure 8a).

Factor 2: HFSE associations (Figures 6f and 8b). High scores for this factor are a function of catchment geology, the occurrence of REE pegmatities intruding the basement country rocks (Garba, 2003; Okunlola and Akinola, 2010), as well as the winnowing processes that occur during sediment transport (see spatial correlation with WI, Figure 8f).

Factor 3: Ferromagnesian factor has a clear spatial relationship with catchment geology, positive scores are found associated with the Older Granite rocks, perhaps indicative of the importance of olivine, pyroxene and hornblende in the mineral assemblage.

Factor 4 shows a distinct N-S trend, highlighting perhaps an overprint of Harmattan deposition (Moreno *et al*., 2006) and/or the retention of relatively mobile large ion lithophile elements in more arid regions relative to immobile elements, Zr and Hf, due to chemical weathering processes (see Figures 7 and 8d).

Factor 5: Ta-Nb (coltan) mineralisation (Figure 8e and see also Figure 6e). The high positive scores of this factor are found in both the sedimentary placer deposits as well as over intrusive granite bodies in both cells. Tin-and coltan-bearing pegmatites and Ta-Nb mineralisation are well documented across Nigeria (Kinnaird, 1983, 1985; Ogunleye *et al*., 2006; Obaje, 2009; Okunlola and Oyedokun, 2009). Following weathering of magmatic host rocks deposition in alluvial placer deposits can reach economic grades (Dill, 2010).

5.3 *Geochemical variations in relation to land use, potential contamination and environmental guidelines*

The variation in stream sediment geochemistry for Zn, Cd and Pb, three trace elements associated with anthropogenic contamination, are shown for sites with contrasting major land use (forest, arable, pasture and semi-urban/industrial) and potential contamination (mine/industrial, household, agricultural and sites with no observed contamination) from field observations are shown in Figure 4. Overall it can be seen that there are higher Zn, Cd and Pb concentrations at sites with observed contamination from mining and industrial activity (n=21), as well as sites with semi-urban and industrial landuse, although the numbers of sites were small (n=16).

Cadmium concentrations were lower for sites within forest compared to sites with obvious anthropogenic activity. A Wilcoxon rank sum test was used again to test equivalence in the median values from the contaminated sites with those from non-contaminated sites. The null hypothesis is that the underlying distributions of the various elements in question are equal in contaminated and non-contaminated sites. There was no significant difference (p>0.05) between the sites with no observed contamination and those with observed contamination for most elements (Cu, Ni, Zn, Sn, Cd, Cr, As), however, there are notable exceptions (p<0.05) for Pb, Sb and B. Anthropogenic contamination from a variety of sources including household waste (*e.g.* soaps and plastic bags), agricultural waste and chemicals (e.g. fertilisers and $CuSO_4$ spraying in cocoa plantations) and mining activities has led to elevated element concentrations (including As, Sn, Cd, Ni, Sb, Cu, Pb and Zn) in waters, sediments and soils in Nigeria (Ajayi and Mombeshora, 1989; Oyedele *et al*., 1995; Nriagu *et al*., 1997; Scheren *et al*., 2002; Ololade and Ajayi, 2009; Ohioma *et al*., 2009; Azeez *et al*., 2009).

In stream sediments the proportion of organic matter and fine clay-sized fraction and surface area all have important controls on trace element mobility (Horowitz and Elrick, 198; Salminen and Tarvainen, 1997; Tack *et al*., 1997; Grosbois *et al*., 2007). The sediment type reflects the nature of the geology in the catchment of the stream and the prevailing weathering and stream-flow conditions. Coarser sediments are transported by higher energy flow regimes, and the fluvial dynamics determine the rate and nature of bedrock weathering. An understanding of the variation in sediment types is useful as some elements have an affinity for adsorbing to fine-fraction mineral particulate surfaces (such as clay minerals and iron oxy-hydroxides) whilst others remain incorporated in minerals that resist physical weathering to the finer fractions. The variable nature of stream sediment types is one of the prime reasons for using a consistent size fraction in a regional-scale survey, as well as always sampling from the active stream channel below the surface oxidised layer of sediment.

The sedimentary units derived from the weathering of basement material (group 2, Figure 3) have lower trace element concentrations compared to basement catchments. The highest median Cr, Ni and As concentrations were found in the sedimentary units of the south-western cell, which could reflect both the high population density in this area as well as the prevailing redox conditions. However, there are also a significant number of trace element outliers in all the basement groups (Figure 3). A number of these outliers have total concentrations exceeding the PEL for freshwater sediments (Ni, Cr and Cd), while only a few outliers exceed the PEL for As, Pb, Cu and Zn. Any inference on potential toxicity should be considered in light of the fact that the chemical analytical method used identified total element concentrations (<150 µm) sediment fraction. As such these concentrations provide the worst case scenario, and an overestimation of the truly bioavailable fraction of trace elements in the fine sediment fraction. Overall, median concentrations of Pb, Ni, Cu, Cr, Cd and As are all lower than those found in regional stream sediment surveys in USA and Europe (Rice, 1999; Salminen *et al*., 2005).

Many targeted studies in urban environments in Nigeria have reported elevated concentrations of metal pollution in sediments from urban and industrialised areas (e.g. Tijani *et al*. 2004; Odukoya, 2007; Tijani *et al*. 2007; Abimbola and Olatunji, 2011). While previous studies have suggested that the elevated concentrations of trace metals in urban freshwater sediments in south-western Nigeria reflect basement source rocks and mineralisation (Ajayi and Mombeshora. 1989), there is obvious concern regarding the impact of anthropogenic activity on environmental degradation in many urban and sub-urban settings across Nigeria (e.g. Okoye *et al*., 1991; Ogunsola *et al*, 1994; Ohioma *et al*., 2009; Abimbola and Olatunji. 2011).

In the central cell a cluster of anomalous Pt and Pd are found in stream sediments sampled in the Abuja–Suleja urban area with Pt values $\geq 95^{th}$ percentile of 1.2 µg/kg; and Pd values $\geq 95^{th}$ percentile of 0.88 µg/kg. These may be derived from abandoned motor vehicle parts, such as catalytic converters (Lesniewska *et al*., 2004), rather than mafic or ultramafic sources (*e.g* Angeli. 2005).

An important result of the survey described here is that it provides new information on the trace element distribution in stream sediments from the major geological terrains in Nigeria. This background or baseline data is an essential part of assessing contamination due to anthropogenic activity.

5.4 *Implications for geochemical mapping in West Africa*

Stream sediments have been shown to be a reliable media for rapid regional geochemical mapping in West Africa. Across a range of climate zones this type of survey provides new information that can be used to improve the geological maps, identify new mineralisation, as well as contamination from anthropogenic activities. They provide important data for other agricultural (*e.g.* K and trace elements), environmental health (*e.g.* As, Cr, Cd, and Pb) landuse and planning purposes (Appleton and Ridgway, 1992). Given the rapid expansion of urban and industrial landuse and population across sub-Saharan Africa (Cohen, 2003; Ambe, 2003), and the associated potential risk to the environment and human health (e.g. Azeez *et al*., 2009), there is a clear need to quantify the baseline geochemistry to enable assessments of contamination due to anthropogenic activity. Stream sediment data and other surface parameters have also been shown to be an effective proxy for soil and groundwater geochemistry (e.g. Appleton *et al*., 2008; Winkel *et al*., 2008; Goldhaber *et al*., 2009; Barringer *et al*., 2011), and this may be particularly important in parts of Africa where there is a scarcity of geochemical data across a range of media.

This survey indicates that the combination of old basement terrains, high weathering rates and sediment winnowing processes (wind-blown and fluvial) have resulted in stream sediments that are highly enriched in heavy minerals including zircon and associated HFSE minerals. These are from largely proximal sources (Key *et al*, in preparation) and many provide important new tools for understanding magmatic processes within basement terrains of West Africa.

Mean Zr concentrations in stream sediments in this study were >0.2%. This has important implications for both sample preparation and analysis. If XRFS is used as the analytical method then there is significant interference from Zr on some other trace element spectra if present in high concentrations. Optical emission or mass spectroscopy methods are better suited for trace element analysis, particularly the REEs, although interferences on Ag as a result of high concentrations of Zr do need to be corrected. During the sample preparation process a high concentration of zircons in the fine sediment will mean longer times needed for sample preparation because of the presence of hard resistant minerals. Poor homogenisation of samples due to high zircon content will lead to greater analytical variability, particularly if small amounts of sample are used in the extraction procedure.

Stream sediment geochemistry is characterised by a high degree of spatial heterogeneity due to a combination of multiple controlling processes. In order to have reliable data with which to assess these processes it is critical to ensure that data is collected at the appropriate density, and that quality control is maintained at every stage of the survey, from sample collection through to sample preparation and analysis. The orientation survey was a critical component of this study, and will be a necessary part of future work in different climatic/geological terrains across Nigeria and West Africa. This study has demonstrated that using contrasting sample densities (*c*.1 per 20 km^2 and 1 per 90 km^2) regional geochemical processes can be readily assessed. However, the use of higher density sampling will enable better characterisation of more subtle processes such as anthropogenic contamination and landuse controls.

6 Conclusions

This overview from recent work carried out in Nigeria has shown that stream sediment sampling provides a rapid and practical approach for regional geochemical mapping in West Africa. As a first stage in mineral exploration and baseline environmental geochemical assessments it is able to provide important new information for use in a range of sectors.

This study has identified placer deposits of potential economic importance including Au, REE, Ta, Nb, U and Pt as well as other primary metal deposits. Ongoing detailed studies are focused on characterising some of these deposits of potential economic significance. This study provides important new background/baseline geochemical values for common geological domains in Nigeria (which extend across other parts of West Africa) for assessment of anthropogenic contamination from urban/industrial landuse changes and mining activities. Areas of high As and Cr (>2 mg/kg and >70 mg/kg respectively) are associated with young coastal sediments in southwest Nigeria.

The very high stream sediment Zr concentrations, from proximal zircons derived from weathering of basement rocks, have important implications for sample preparation and analysis. Associated proximal heavy mineral HFSE mineralisation may have important implications for provenance studies and elucidating magmatic processes within the basement terrain of West Africa.

Commonly used geostatistical techniques (e.g. robust PFA) have been applied to explore the results to understand the underlying processes controlling spatial geochemical variability following appropriate data transformations. Major geochemical variations are controlled by source geology and provenance, as well as winnowing processes. More subtle variations are a result of landuse and contamination from anthropogenic activity.

Given the lack of fundamental geochemical data across much of Nigeria (and more generally across West Africa), i.e. data from soil, surface water and groundwater, this new stream sediment data may be useful in informing future studies related to agriculture, environment and health in Nigeria and other parts of West Africa with similar geological terrains.

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8 Appendix A

Supplementary data, Table S1 and Figure S1 associated with this article can be found in the online version.

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Table captions:

Table 1. Summary ANOVA results from paired duplicate and replicate samples.

Table 2. Summary of explanatory data analysis procedures used in this study.

Table 3. Geochemical results for stream sediments in the central and south-western Nigeria.

Table 4. Correlation matrix for major and minor elements in stream sediments from different geological domains in Nigeria using the Spearmans rank sum method.

Table 5. Summary mineralogy results for stream sediments from central and south-western Nigeria.

Figure captions:

Figure 1. Simplified regional geology map of Nigeria and location of pilot Cells for stream sediment sampling in central and south-western Nigeria. Based on Malamo (2004) national geological map of Nigeria. Inlay shows the global geochemical reference network (GRN) cells for Nigeria (Darney *et al*.,1995), and those covered in this study.

Figure 2. Box-plots (notched) of major elements grouped by cell and geological domain: a) Al, b) Fe, c) K, d) Ca, e) Mg. Solid horizontal lines show the method detection limit, long dashed line the UCC (Wedepohl, 1995; Taylor and McLennan, 1995). Geological grouping on x-axis: 1) Mesozoic south-western cell, 2) Mesozoic central cell, 3) Metasediments south-western cell, 4) Metasediments central cell, 5) Migmatitic gneiss south-western cell, 6) Migmatitic gneiss central cell, 7) Older Granite south-western cell, 8) Older Granite central cell, 9) Zungeru Mylonites central cell.

Figure 3. Box-plots (notched) of trace elements grouped by cell and geological domain: a) Zn, b) Pb, c) Ni, d) Cu, e) Cr, f) Cd, g) As. Solid horizontal lines show the method detection limit, long dashed line the UCC (Wedepohl, 1995; Taylor and McLennan, 1995), and dotted line the PEL (MacDonald et al., 2000;CCME, 2002). Geological grouping on x-axis: 1) Mesozoic south-western cell, 2) Mesozoic central cell, 3) Metasediments south-western cell, 4) Metasediments central cell, 5) Migmatitic gneiss south-western cell, 6) Migmatitic gneiss central cell, 7) Older Granite south-western cell, 8) Older Granite central cell, 9) Zungeru Mylonites central cell.

Figure 4. Box-plots of Zn, Cd and Pb variation in samples from sites with different major landuse (4a to 4c) and sites with different potential contamination (4d to 4f),

the dotted line shows the PEL (CCME, 2002). Note log scale on y-axis for all elements except Pb.

Figure 5. Box-plots (notched) of selected elements grouped by major sediment types, i) clay and organic rich sediment and ii) sandy and gravel sediments: a) Al, b) K, c) Fe, d) Cu, e) Mn, f) Zn, g) Zr, h) Th, i) Winnowing Index - WI (Grunsky *et al*., 2009). Note log scale on y-axis for all elements.

Figure 6. Box-plot percentile maps (log scale, percentile intervals: 0, 5, 25, 75, 95 and 100), from the central and south-western cells: a) K, b) Pb, c) As, d) Au, e) Ta, f) ΣLREE. All units in mg/kg except Au which is in μg/kg. Symbols used are accentuated EDA symbols (Reimann *et al*., 2008)

Figure 7. Robust Principal Factor Analysis (PFA) loading plots for selected elements using centred logratio (CLR) transformed data (not including Si or elements with >2% censored data and REE summed by LREE and HREE) and correlation coefficients >0.3 and <-0.3.

Figure 8. Box-plot percentile maps of robust PFA factor scores (figures a-e, log scale, percentile intervals: 0, 5, 25, 75, 95 and 100), for first 5 factors from the central and south-western cells: a) Factor 1, b) Factor 2, c) Factor 3, d) Factor 4 and e) Factor 5 and f) box-plot percentile map of the Winnowing Index (WI, see Grunsky *et al*., 2009). Symbols used are accentuated EDA symbols (Reimann *et al*., 2008)

Supplementary data:

Table S1. Summary ANOVA table for within and between variance (%) for <150μm and <250 μm fraction of stream sediment.

Figure S1. Dendogram from hierarchical cluster analysis using stream sediment XRD mineralogy data showing eight distinct mineral assemblages (Group 1 to Group 8, shown on x-axis). Catchment geology codes for samples: MY=Mesozoic and younger strata, MG=Migmatitic gneiss, MM=Metasediments and metavolcanics, OG=Older Granites, ZM= Zungeru Mylonites.

Figures

Figure 1.

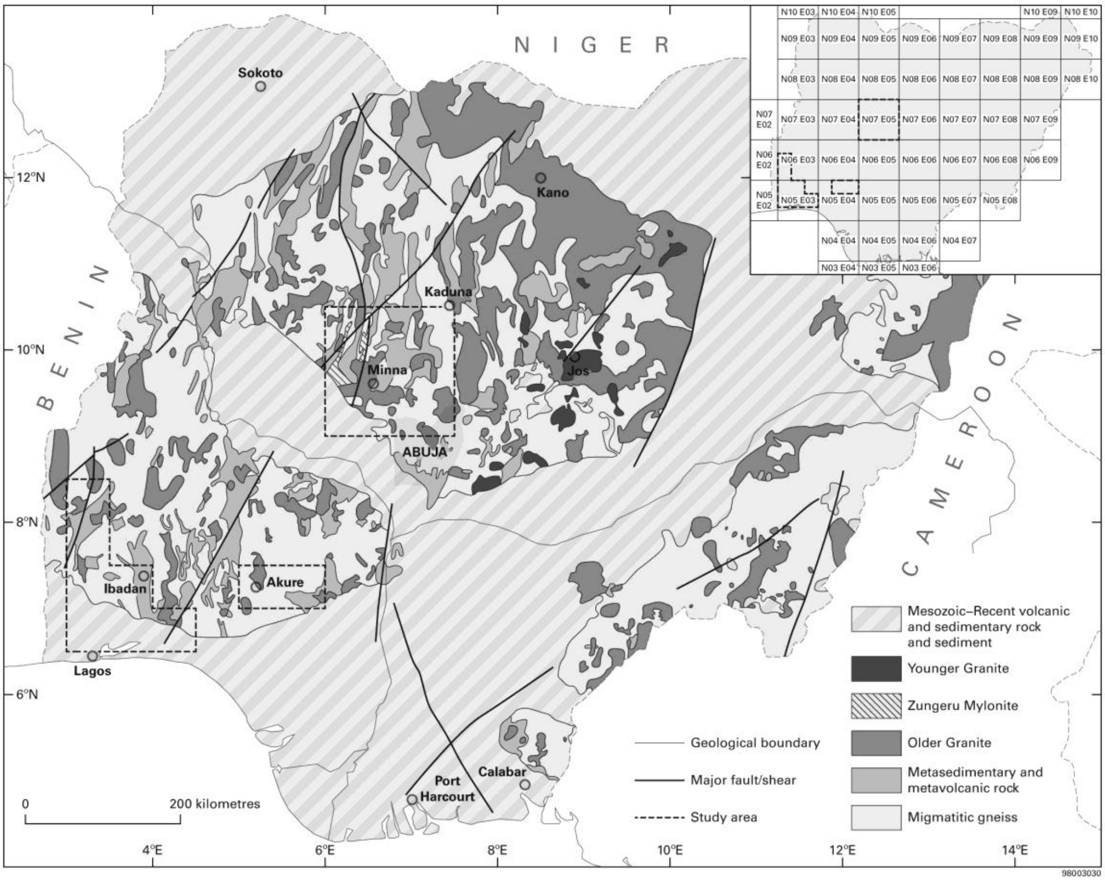


Figure 2.

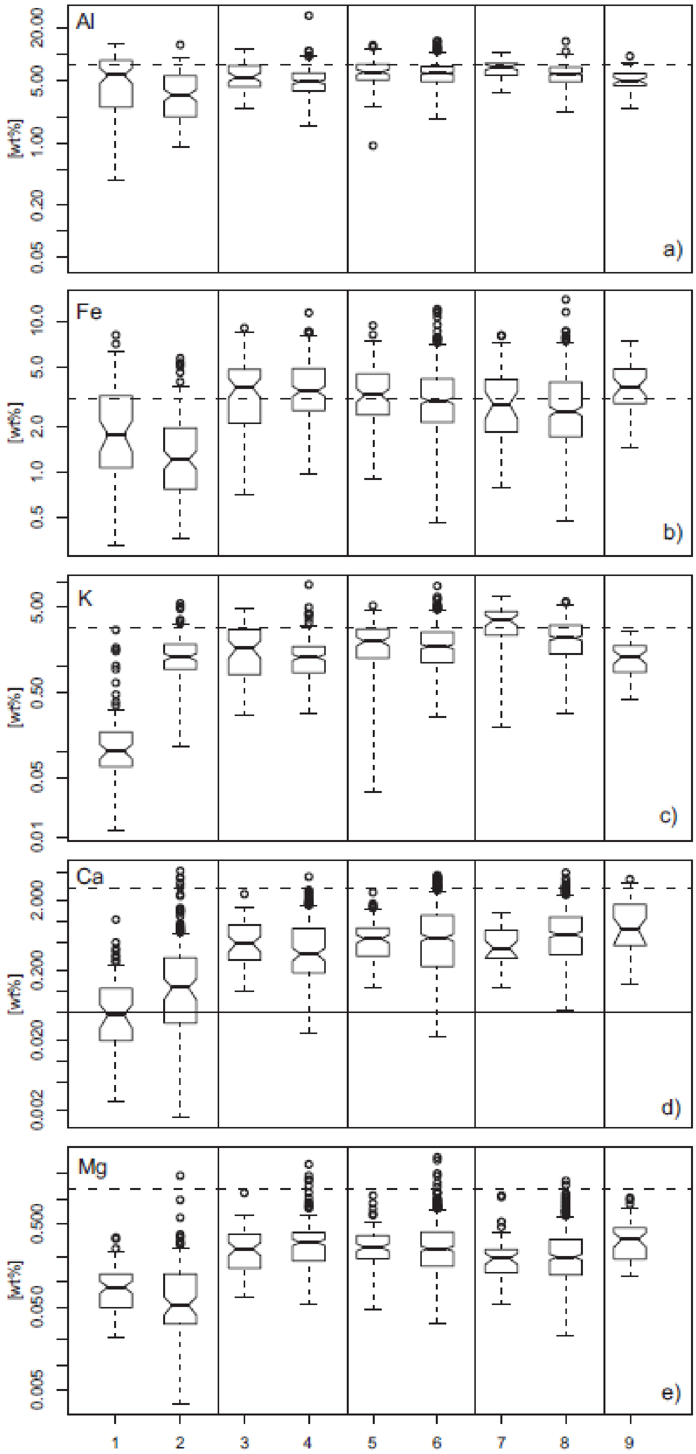

Al
a)
Fe
b)
K
c)
Ca
d)
Mg
e)
[wt%]
20.00
5.00
1.00
0.20
0.05
10.0
5.0
2.0
1.0
0.5
0.50
0.01
2.000
0.200
0.020
0.002
0.500
0.050
0.005
1
2
3
4
5
6
7
8
9

Figure 3.

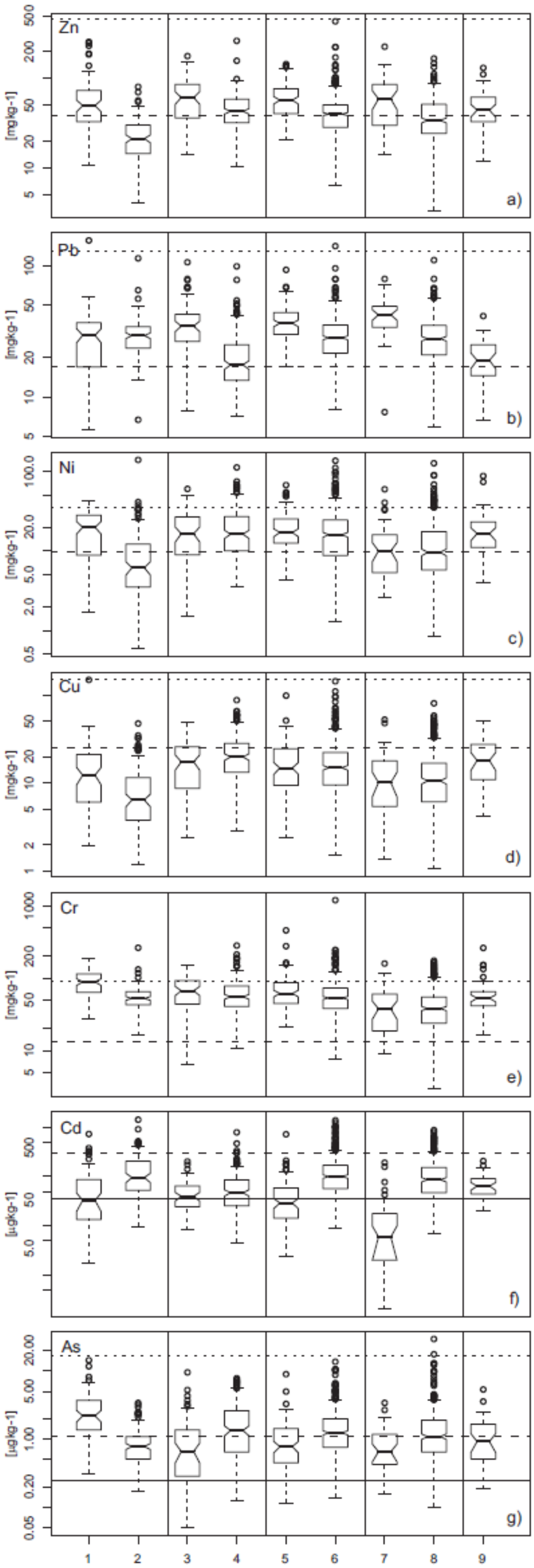

Zn
[mgkg-1]
a)
Pb
[mgkg-1]
b)
Ni
[mgkg-1]
c)
Cu
[mgkg-1]
d)
Cr
[mgkg-1]
e)
Cd
[µgkg-1]
f)
As
[µgkg-1]
g)
1
2
3
4
5
6
7
8
9

Figure 4.

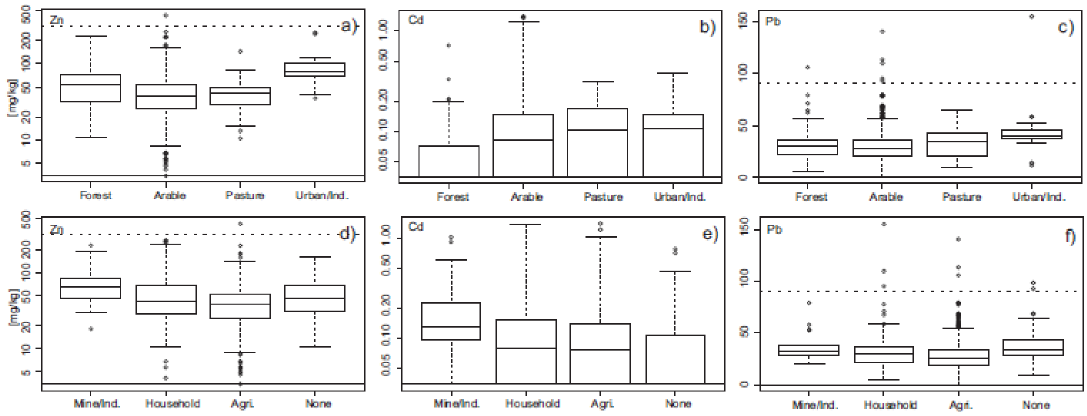

Zn
a)
Cd
b)
Pb
c)
[mg/kg]
Forest
Arable
Pasture
Urban/Ind.
Zn
d)
Cd
e)
Pb
f)
[mg/kg]
Mine/Ind.
Household
Agri.
None

Figure 5.

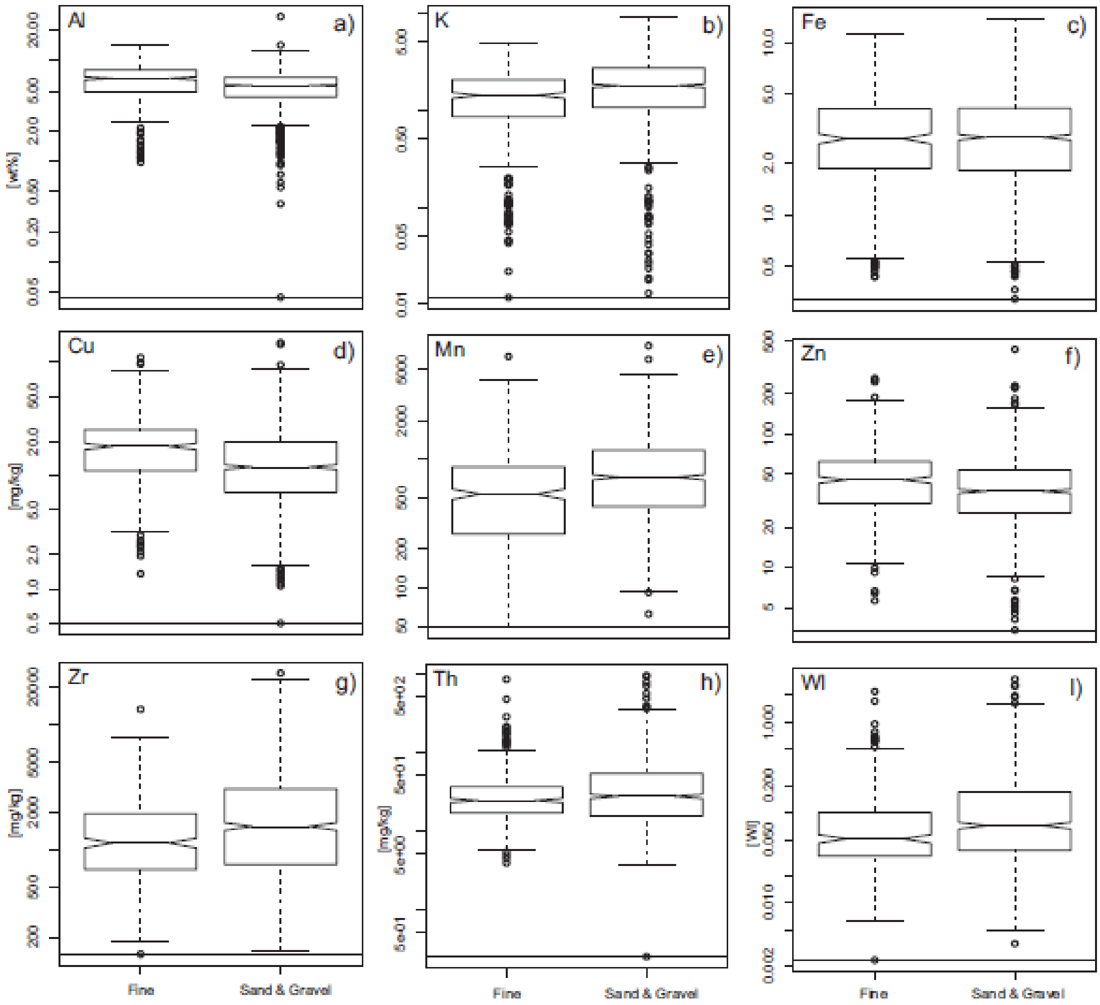

Al
a)
K
b)
Fe
c)
Cu
d)
Mn
e)
Zn
f)
Zr
g)
Th
h)
WI
i)
[wt%]
[mg/kg]
[WI]
Fine
Sand & Gravel

Figure 6. Figures 6 and 8 are snap-shots, the original files have good resolution [djl]

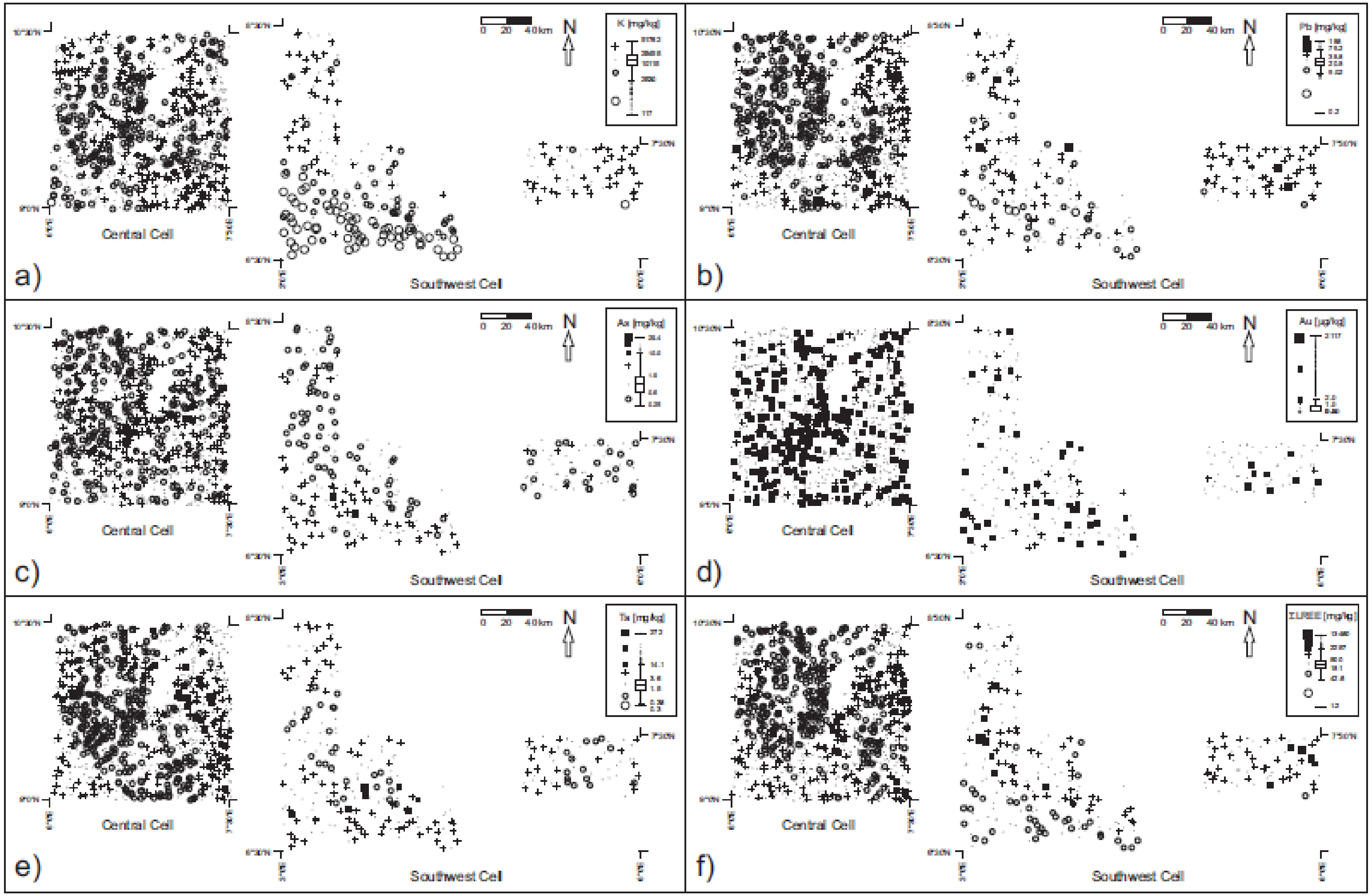
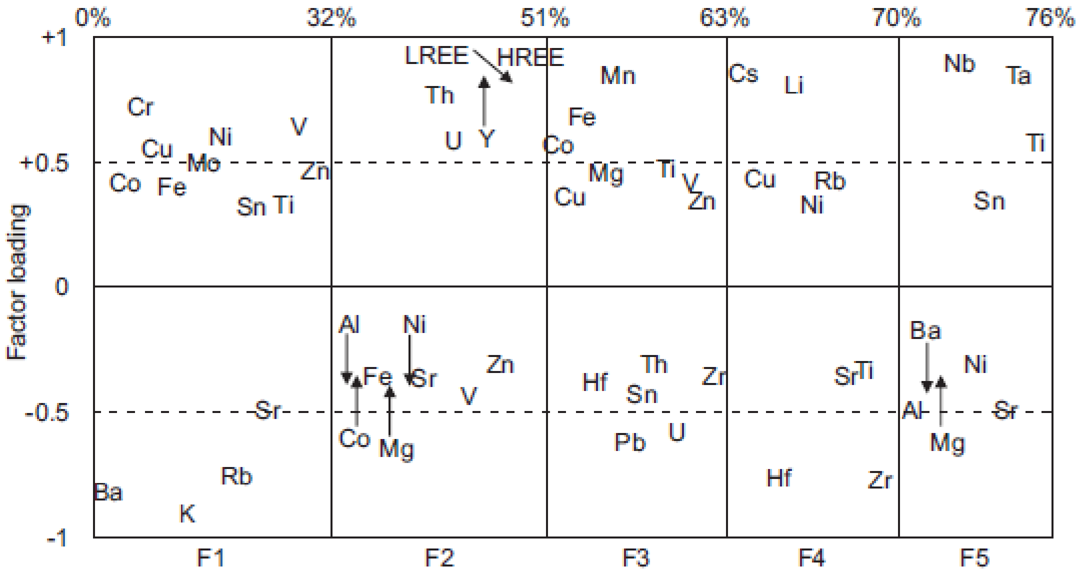


Figure 7.


0%
32%
51%
63%
70%
76%
+1
+0.5
0
-0.5
-1
Factor loading
Cr
Cu
Ni
Mo
V
Zn
Co
Fe
Sn
Ti
Sr
Rb
Ba
K
LREE
HREE
Th
U
Y
Al
Ni
Fe
Sr
Zn
V
Co
Mg
Mn
Fe
Co
Mg
Ti
V
Zn
Cu
Hf
Th
Sn
Zr
Pb
U
Cs
Li
Cu
Rb
Ni
Sr
Ti
Hf
Zr
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Ta
Ti
Sn
Ba
Ni
Al
Sr
Mg
F1
F2
F3
F4
F5

Figure 8.

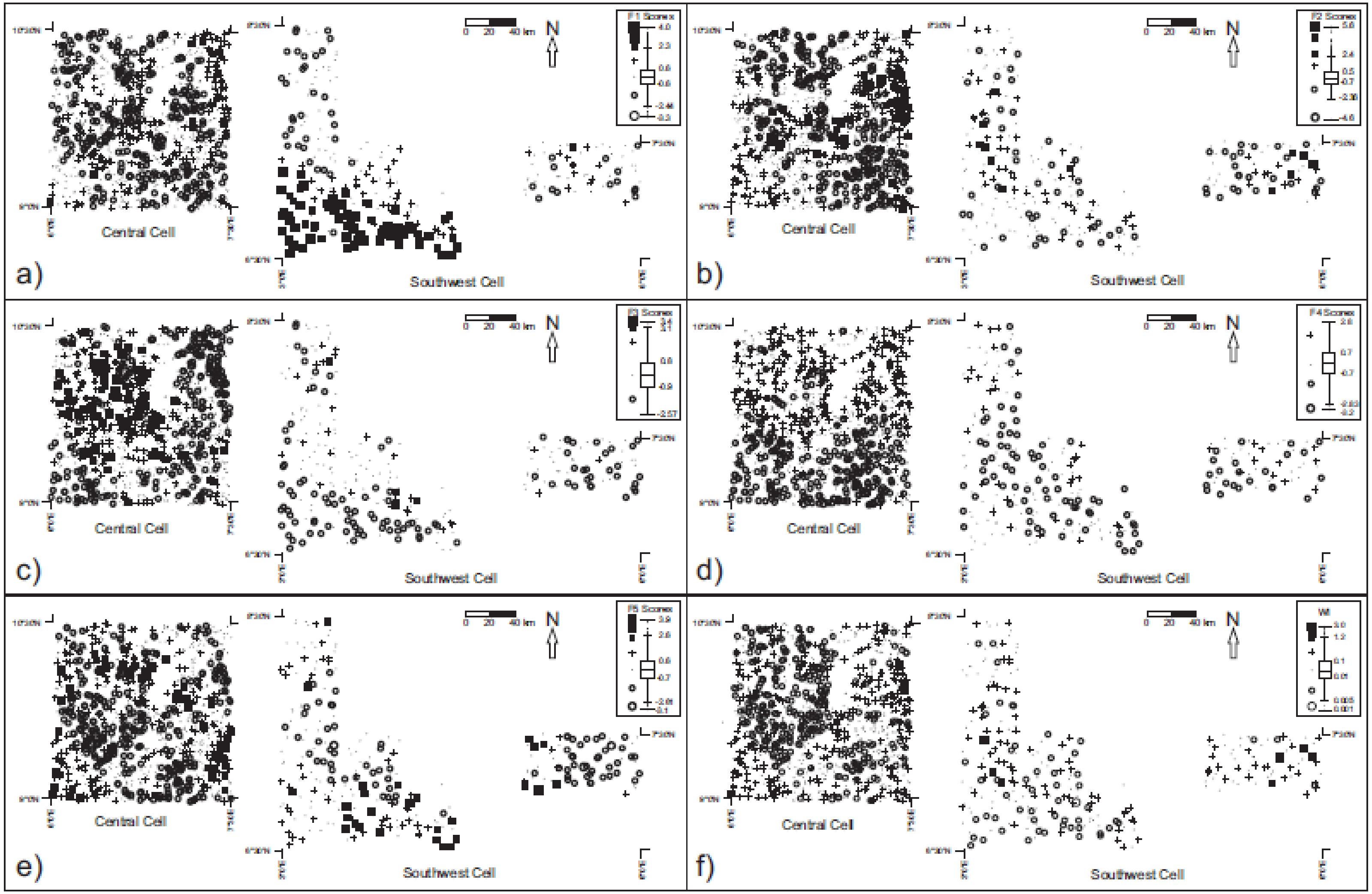
a)
Central Cell
Southwest Cell
b)
Central Cell
Southwest Cell
c)
Central Cell
Southwest Cell
d)
Central Cell
Southwest Cell
e)
Central Cell
Southwest Cell
f)
Central Cell
Southwest Cell

Figure S1.

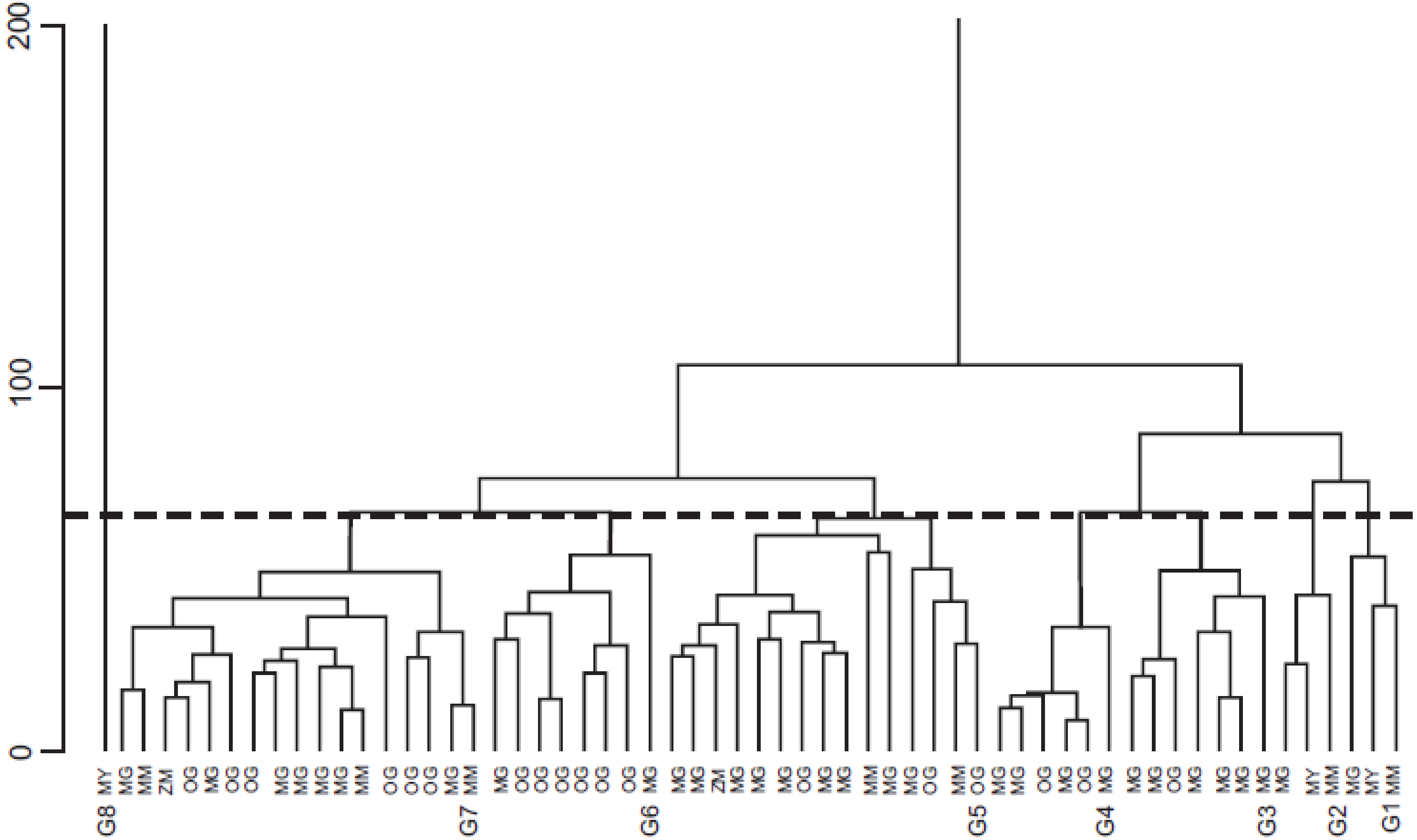

Table 1.

Element	Between Site %	Between Sample %	Within Sample %
Sr	99.26	0.47	0.27
Ba	98.7	1.05	0.25
K	98.2	0.98	0.82
Rb	96.63	2.79	0.57
Nb	91.29	8.14	0.57
Mn	90.4	9.22	0.38
Al	90.11	9.34	0.55
Ti	89.7	9.72	0.58
B	89.63	2.8	7.57
Ca	89.57	1.84	8.59
Tm	89.26	8.97	1.77
Fe	88.91	10.58	0.51
La	88.78	10.82	0.4
Nd	88.74	10.69	0.56
Pr	88.7	10.86	0.43
Yb	88.45	10.12	1.43
Er	88.2	10.98	0.82
Sm	88.14	11.18	0.68
Sb	88.12	4.5	7.38
Ho	87.78	11.32	0.9
Y	87.65	11.64	0.71
Lu	87.62	10.34	2.04
Ce	87.55	12.04	0.41
Gd	87.18	12.37	0.45
Tb	86.53	12.93	0.54
Dy	86.22	13.18	0.59
Th	85.3	13.46	1.24
U	85.04	13.73	1.24
Ta	84.33	10.2	5.47
Zn	83.67	13.13	3.2
Eu	82.65	14.87	2.48
Pb	82.41	13.22	4.37
Hf	81.73	10.26	8.01
Zr	81.56	9.5	8.94
Cs	80.35	17.98	1.67
Mg	79.82	-7.84	28.03
V	73.87	25.1	1.03
Bi	73.53	10.8	15.66
Cd	73.32	12.74	13.94
Sn	71.5	20.25	8.25
Cr	70.83	28.1	1.06

Mo	70.74	27	2.26
Li	67.06	28.65	4.28
Cu	61.83	15.7	22.48
Co	61.81	37.32	0.87
Ga	61.04	0.17	38.79
Ni	56.1	35.98	7.92
Ag	56.02	23.13	20.85
As	52.11	11.17	36.72
P	49.73	13.47	36.81
Si	43.51	1.43	55.06
Be	42.78	9.29	47.92
Tl	26.58	2.94	70.47
Au	25.68	-29.47	103.79

Table 2.

Purpose	Method	Notes	Reference
Estimate mean value	Kaplan-Meier	<50% censored data, nonparametric	Kaplan and Meier (1958)
Estimate mean value	Maximum likelihood estimation	50-80% censored data, log transformed	Kroll and Stedinger (1996)
Test for normal data distribution	Shapiro-Wilk test	log transformed data	Shapiro and Wilk (1965)
Test for equivalence in median values	Wilcoxon rank sum	nonparametric test	Wilcoxon (1945)
Correlation analysis	Spearman rank sum	nonparametric test	Spearman (1904)
Visual comparison of data groups	log box-plot	log transformed data, notched	Reimann *et al*., (2008)
Explore multivariate data structure	Robust PFA	CLR transformed data, Varimax rotation	Reimann *et al*., (2008)
Explore multivariate data structure	Hierarchical cluster analysis	Q-mode analysis, agglomerative	Kaufman and Rousseeuw (2005)
Calculate 'Winnowing index'	Th/Al method	CLR transformed data	Grunsky *et al*., (2009)

PFA = Principal factor analysis, CLR = centred log-ratio

Table 3.

Element	SW [a]	%cens [b]	South-western cell (n=281) Min	Mean	Median	Max	Central cell (n=1288) Min	Mean	Median	Max	UCC [c]	PEL [d]	Wilcoxon rank sum test [e] G1	G2	G3	G4
Si		0	2.27	21.8	22.2	47.1	4.45	27.8	28.5	101	30.3		***	***	***	
Al	**	0	0.378	6.3	6.16	13.3	0.0445	5.78	5.78	27.6	7.7		***	•		**
Fe		0	0.323	3.26	2.84	9.37	0.365	3.12	2.81	13.9	3.1		***			
K		0	0.0117	1.74	1.63	6.67	0.115	1.93	1.68	9.18	2.9		***			***
Ti	*	0	0.262	1.19	0.974	6.51	0.0702	1.01	0.792	9.79	0.3		•	•	•	
Ca		31,25	<0.1	0.515	0.381	2.59	<0.1	0.83	0.539	5.24	2.9		*			•
Mg	*	0,1.5	0.0213	0.235	0.196	1.18	<0.0005	0.29	0.221	3.17	1.4		•			
Mn		0	49.9	779	611	7630	83.5	846	686	5990	527		***		•	
P		10,33	<100	615	495	4620	<100	369	274	2880	665		***	***	***	***
Ba		0	22.2	773	782	3490	5.33	808	644	4310	668		***	***	***	*
Sr		0,0.1	5.76	150	132	804	<2.5	201	128	1820	316		***	***		
U		0	0.965	11.6	7.62	224	1.14	8.09	6.03	138	2.5		***	***	***	***
Th		0,0.1	4.39	65.6	29.2	922	<0.25	40.8	25.3	835	10.3		***	***	***	*
La		0,0.1	8.94	171	85.9	3190	<0.25	99.9	64.4	1770	32.3		***	***	***	**
Ce		0,0.1	20.5	368	193	6670	<0.25	211	135	3550	65.7		***	***	***	***
Pr		0,0.1	2.04	37.8	18.7	711	<0.025	22.6	14.7	402	N/A		***	***	***	**
Nd		0	8	137	69.7	2430	0.327	85.6	56.8	1370	25.9		***	***	***	*
Sm		0	1.56	22.8	12.2	468	0.376	15.9	10.6	295	4.7		***	***	***	*
Eu		0	0.31	2.3	1.82	60.4	0.307	1.9	1.69	12.5	0.95		***	***	*	•
Gd		0,0.1	1.45	17.1	10.3	416	<0.015	3.3	1.56	88.4	2.8		***	***	***	***
Tb		0	0.239	2.38	1.54	62.9	0.259	11.6	7.96	269	0.5		***	***	***	***
Dy		0,0.1	1.59	13.7	9.28	361	<0.015	12	8.44	258	2.9		***	***		
Ho		0	0.316	2.57	1.78	66.9	0.25	2.4	1.7	48.5	0.62		***	***		

Er		0,0.1	0.907	7.97	5.53	203	<0.005	7.3	5.25	132	2.3		***	***		
Tm		0,0.1	0.151	1.16	0.809	28.7	<0.002	1.12	0.815	19	0.33		***	***		
Yb		0,0.1	0.99	8.11	5.72	183	<0.005	7.74	5.72	123	1.5		***	***		
Lu		0,0.1	0.181	1.25	0.89	26.2	<0.0025	1.18	0.885	16.2	0.27		***	***		
Y		0,0.1	8.58	71.7	49.9	1700	<0.05	66.3	46.6	1310	20.7		***	***		
Zr	**	0	146	2980	1900	25800	153	2100	1300	22800	237		*	***	***	**
Hf	**	0	4.12	78.5	50.4	676	4.32	55.3	36	529	5.8		*	***	***	**
Ta		0	0.477	5.23	2.78	272	0.312	3.27	2.16	53.2	1.5		***			
Rb		0	0.828	74.4	67.3	280	5.86	76.7	66.9	415	110		***	***		*
Cs	*	0	0.10	2.37	1.72	32.3	0.26	2.78	2.08	21.4	5.8		***			***
Li	**	0	2.8	15.8	13	85.8	1.1	14.8	12.1	103	22		•		***	
B		38,30	<7.5	71	36.7	1070	<7.5	49.7	26.2	792	17		***			
Be		8,10	<0.3	1.85	1.6	6.5	<0.3	1.6	1.45	9.38	3.1		***		***	
Au		72	<0.5	-	<0.5	658	<0.5	29.5	N/A	2120	0.0018			***		***
Pt		18,30	<0.05	1.34	0.3	204	<0.05	0.501	0.2	66.3	N/A					
Pd		87	<0.25	-	<0.25	3.2	<0.25	-	<0.25	10.7	N/A		*		***	
Ag		23,30	<0.05	0.295	0.202	1.81	<0.05	0.256	0.157	2.76	0.055					
Zn	**	0	10.7	65	57.2	256	3.38	41	36.8	433	52	315		***		
Pb		0,0.1	5.67	36.3	34.5	155	<0.25	28	26.6	141	17	91.3	***	***	***	**
Ni		0,1.4	1.52	19	16.4	67.8	<0.5	16.9	13.1	141	18.6	36		***	***	***
Cu	*	0,0.1	1.37	17.2	14.9	148	<0.5	16.5	13	143	14.3	197	***		•	
Sn		0.4,0	<0.25	6.33	3.52	211	0.503	2.97	2.38	79.8	2.5		***			
V		0	15.7	86.1	79.7	254	6.31	80.4	71.5	558	53		***	***	*	*
Cr		0	6.33	72.9	65.4	458	2.91	56.4	48.3	1200	35	90	***		*	
Cd		78, 41	<0.035	-	<0.035	0.719	<0.035	0.138	0.085	1.4	0.102	3.5	***	•	***	***
Co	*	0	1.29	15	11.7	81	0.817	11.3	8.7	75.1	11.6			*	***	*
Nb		0	5.17	38.3	31.9	332	3.51	29.1	25.5	209	26		*	***		***

Mo	*	0	0.131	1.04	0.784	3.98	<0.05	0.727	0.581	5.17	1.4		***			•
W		9, 1.2	<0.005	1.78	1.6	9.06	<0.005	1.85	1.63	23.2	1.4		*		***	•
Ga		3, 0.4	<0.5	14.9	14.4	34.3	<0.5	13.6	13.2	64.6	14		***			**
Tl		22, 32	<0.035	0.188	0.15	0.86	<0.035	0.154	0.115	0.749	0.75			***	***	***
As		26,17	<0.25	1.61	0.989	14.3	<0.25	1.62	1.14	29.4	2	17	***	***	***	•
Sb		33,19	<0.075	0.368	0.221	19.5	<0.075	0.345	0.261	4.5	0.31		***	*	***	•
Bi		6,0.5	<0.015	0.444	0.2	28.3	<0.015	0.276	0.2	6.3	0.123		***		***	

Units are in weight % for major elements (Si to Mg), mg/kg for trace elements and µg/kg for Au, Pd , Pt

[a] % censored data for south-western cell, % censored for the central

[b] SW= Shapiro-Wilk test for normality, significant codes: <0.001' ',0.05'*',0.1'**' for either cell

[c] UCC= Mean upper continental crust: Wedepohl (1995) and Taylor and McLennan (1995)

[d] PEL= Freshwater sediment probable effect level: CCME (2000), also known as the Canadian PELs, see MacDonald et al., 2000 for Ni value.

[e] Nonparametric test of equivalence between median stream sediment values in both cells, significance codes: 0.0001'***', 0.001'**', 0.01'*', 0.05'•', ' ' >0.05

Geology abbreviations: G1 =Mesozoic and younger strata, G2 =metasediments, G3 =migmatitic gneiss, G4 =Older Granites

Table 4.

	Si	Al	Ca	Fe	K	Mg	Mn	P	Ti	Sr
	G1	***	•	**	**	**		*	*	*
	G2	***	***	***		***	***	***	***	***
Si	G3	***	*	***	*	***		***		***
	G4	***		***		***	***	***	*	
	G5	***		***		***	***	***	***	
	-0.5			***	***	***		***		***
	-0.6		***	***		***	***	***	***	***
Al	-0.4		***	***	***	***		***	*	***
	-0.4		*	***	***	***		***	***	***
	-0.4		***	***	***	***		***	***	***
	-0.2	0.02		*	**	*	**	**		*
	-0.4	0.46		***		***	***		***	***
Ca	-0.1	0.23		•		***	***			***
	-0.1	0.1		***		***	***	*		***
	-0.1	0.21		**	***	***	***			***
	-0.4	0.59	0.24		***	***	***	***		***
	-0.6	0.81	0.56			***	***	***	*	***
Fe	-0.3	0.44	0.11		***	***	***	***	***	
	-0.4	0.36	0.13		***	***	***	***	***	**
	-0.5	0.16	0.14		***	***	***	***	***	***
	-0.4	0.46	0.35	0.48		***	**	***		***
	-0.04	0.14	-0.13	-0.12					**	***
K	-0.1	0.4	<0.001	-0.23			***	***	***	***
	0.03	0.16	0.04	-0.4			***		***	***
	0.02	0.28	-0.23	-0.46		***	***	•	***	***
	-0.3	0.76	0.27	0.56	0.66		**	***		***
	-0.5	0.75	0.64	0.76	0.04		***	***	***	***
Mg	-0.3	0.52	0.48	0.55	0.07		***	•		***
	-0.3	0.49	0.62	0.49	0		***	***	**	***
	-0.4	0.35	0.36	0.71	-0.29		***	***	***	*
	-0.2	0.15	0.32	0.59	0.38	0.34		*	***	*
	-0.5	0.62	0.62	0.79	0.08	0.75		***	**	***
Mn	-0.1	0.06	0.26	0.71	-0.33	0.4		*	***	
	-0.1	-0.01	0.5	0.63	-0.21	0.41		***	***	***
	-0.2	-0.06	0.36	0.68	-0.37	0.41		***	***	
	-0.3	0.61	0.3	0.66	0.52	0.66	0.26			***
	-0.4	0.29	0.13	0.36	-0.03	0.39	0.36			**
P	-0.4	0.48	-0.01	0.3	0.23	0.12	0.15		*	***
	-0.4	0.28	-0.08	0.39	-0.03	0.24	0.16		***	
	-0.3	0.32	-0.05	0.42	0.08	0.36	0.28		***	
	-0.3	0.12	0.05	0.14	-0.01	0.18	0.41	-0.01		

	0.32	-0.5	-0.43	-0.22	-0.27	-0.45	-0.23	0.1		***
Ti	-0.01	-0.14	0.07	0.45	-0.34	0.09	0.66	0.14		*
	-0.1	-0.2	0.02	0.55	-0.34	0.11	0.63	0.23		***
	-0.2	-0.25	-0.07	0.74	-0.33	0.42	0.62	0.31		***
	-0.3	0.62	0.26	0.49	0.74	0.8	0.27	0.65	<0.001	
	-0.4	0.58	0.69	0.49	0.44	0.67	0.69	0.25	-0.54	
Sr	-0.3	0.33	0.65	-0.05	0.32	0.27	0	0.28	-0.14	
	-0.1	0.17	0.81	-0.12	0.35	0.47	0.25	-0.04	-0.16	
	-0.03	0.29	0.71	-0.21	0.18	0.11	0.03	-0.06	-0.36	

G1= Mesozoic (SW cell), G2=Mesozoic (Central cell) G3=Metasediments & Metavolcanics, G4=Mig.Gneiss, G5=Older Granite, ***(p<0.001), **(p<0.01), *(<=0.1p<0.05),"•"(0.05<=p<0.1), blank(p<=0.1). Coefficients >0.5 or <-0.5 highlighted in white, all others shown in grey.

Table 5.

Geology	G1 (n=3)			G2 (n=7)			G3 (n=30)			G4 (n=18)			G5 (n=2)		
Statistic	Min	Med.	Max	Min	Med.	Max	Min	Med.	Max	Min	Med.	Max	Min	Med.	Max
Silicates															
quartz	77.3	78.1	94.9	33.8	61.7	70.8	24.8	67	87.6	33.8	54	77.5	60.6	62.55	64.5
[a]plagioclase 1	<LQ	<LQ	2.7	<LQ	<LQ	4.9	<LQ	<LQ	25.3	<LQ	2.95	26.9	8	9.1	10.2
[b]plagioclase 2	<LQ	<LQ	1.8	<LQ	11.7	17.5	<LQ	5	32.9	<LQ	0.45	14	<LQ	<LQ	<LQ
[c]K-feldspar 1	2.7	3.2	6.2	4.8	11.2	23.9	4.2	14.5	35.6	6.6	19.3	35.9	10.5	14.7	18.9
[d]K-feldspar 2	<LQ	<LQ	<LQ	<LQ	<LQ	8.7	<LQ	<LQ	15	<LQ	<LQ	7.9	<LQ	<LQ	<LQ
pyroxene	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	0.7	<LQ	<LQ	0.9	<LQ	<LQ	<LQ
amphibole	<LQ	<LQ	1	<LQ	1.2	5.7	<LQ	<LQ	2.3	<LQ	<LQ	2.6	1.2	1.7	2.2
epidote	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	6.8	<LQ	<LQ	6.3	<LQ	<LQ	<LQ
sillimanite	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	5	<LQ	<LQ	2.9	<LQ	<LQ	<LQ
zircon	<LQ	<LQ	2.1	<LQ	1.4	4.6	<LQ	0.6	3.7	<LQ	0.3	2.4	<LQ	<LQ	<LQ
Oxides, Phosphates															
anatase	<LQ	<LQ	0.8	<LQ	<LQ	0.8	<LQ	<LQ	0.6	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
hematite	<LQ	<LQ	<LQ	<LQ	<LQ	1.3	<LQ	<LQ	2.3	<LQ	<LQ	<LQ	<LQ	0.4	0.8
ilmenite	<LQ	<LQ	2.3	1.3	1.9	5.7	<LQ	1.35	6.4	<LQ	0.85	10.2	2.2	3.95	5.7
monazite	<LQ	<LQ	<LQ	<LQ	<LQ	0.6	<LQ	<LQ	1.1	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
Phyllosilicates															
'mica'	<LQ	<LQ	4	<LQ	<LQ	5.1	<LQ	4.4	11	<LQ	3.75	7.9	4.4	5.55	6.7
'kaolin'	2	4	15.5	<LQ	6.7	21.6	<LQ	3.4	11.7	<LQ	1.35	12.1	1.2	1.75	2.3

G1 = Mesozoic and younger strata, G2 =Metasediments, G3 =Migmatitic gneiss, G4 =Older Granites, G5 =Zungeru Mylonites

Med.=Median, , <LQ = below limit of quantification (<0.5%), [a]plagioclase 1 = $Na_{0.84}Ca_{0.16}Al_{1.16}Si_{2.84}O_8$

[b]plagioclase 2 = $Na_{0.75}Ca_{0.25}Al_{1.26}Si_{2.74}O_{8,}$ [c]K-feldspar 1 = microcline, [d]K-feldspar 2 = orthoclase

'mica' = undifferentiated mica species, possibly including muscovite, biotite, illite, illite/smectite

'kaolin' = undifferentiated kaolin-group species, possibly including kaolinite, halloysite etc

Table S1.

Element	<150 micron fraction Between site (%)	<150 micron fraction Within site (%)	<250 micron fraction Between site (%)	<250 micron fraction Within site (%)
Sr	99.9	0.1	99.8	0.2
Ca	99.8	0.2	99.8	0.2
K	99.7	0.3	99.3	0.7
Na	99.5	0.5	99.4	0.6
P	99.5	0.5	98.9	1.1
Rb	99.5	0.5	97.6	2.4
Pb	98.9	1.1	95.3	4.7
Hf	98.8	1.2	97.8	2.2
Ti	98.6	1.4	98.2	1.8
Y	98.6	1.4	93.3	6.7
V	98.3	1.7	98.9	1.1
W	97.9	2.1	87.8	12.2
Zr	97.8	2.2	95.2	4.8
Nb	97.4	2.6	98.2	1.8
Mg	97.4	2.6	97.4	2.6
Hg	97.4	2.6	95.7	4.3
Fe	97.3	2.7	98.3	1.7
Mn	97.1	2.9	98	2
Yb	97.1	2.9	93	7
Cr	97	3	96.1	3.9
Ga	97	3	93.9	6.1
U	97	3	93.6	6.4
Nd	96.9	3.1	92.9	7.1
Se	96.7	3.3	93.8	6.2
Th	96.7	3.3	92.5	7.5
Sc	96.6	3.4	96.7	3.3
Tl	96.6	3.4	92.3	7.7
Bi	96.3	3.7	93.6	6.4
Cu	96.1	3.9	90.9	9.1
Sm	95.9	4.1	91.7	8.3
Si	95.8	4.2	92.3	7.7
Zn	95.7	4.3	95.9	4.1
Al	95.6	4.4	90.8	9.2
Co	94.7	5.3	94.4	5.6
Ni	94.1	5.9	92.7	7.3
Br	92	8	91.8	8.2
Ta	89.7	10.3	85.2	14.8
S	89.6	10.4	84.2	15.8
Cl	88.8	11.2	83.4	16.6
Mo	88.5	11.5	94.4	5.6

As	88.2	11.8	82.9	17.1
Ge	74.9	25.1	69.5	30.5