# Stream sediment geochemistry as a tool for enhancing geological understanding: An overview of new data from south west England

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## ABSTRACT

The requirements for quantitative data in geological surveillance are ever increasing; traditional geological maps and 3D models are evolving into quantitative conceptual models based on a broad range of analytical measurements of surface and subsurface properties. The British Geological Survey's Geochemical Baseline Survey of the Environment (G-BASE) project provides one such source of data: national coverage of stream sediment, stream water and soil geochemistry. While this geochemical data is of obvious benefit to our understanding of the present day surface environment, the rich geological diversity of south west England provides an ideal setting in which to showcase the potential of such data to enhance our understanding of the underlying bedrock.

In this paper we use compositional data analysis to extract lithostratigraphic information from G-BASE stream sediment data. We find that variations in G-BASE stream sediment geochemistry correspond very closely to mapped variations in bedrock geology. Geochemical variations between the 16 lithostratigraphic domains into which we classify the region provide insight into the distinct geological histories of the lithologies within each domain, particularly in relation to depositional environments and sediment provenance.

## 1. Introduction

As the British Geological Survey's work moves into the 21st century the requirements for quantitative data are ever increasing. Legacy geological maps and 3D models based on qualitative observations of rock properties are being updated into quantitative conceptual models on the basis of analytical measurements of surface and subsurface properties. The Geochemical Baseline Survey of the Environment (G-BASE) project provides one such line of data: national coverage of stream sediment, stream water and soil geochemistry. The most recent regional dataset to become available is that of south west England. This is a geologically diverse region consisting of a spectrum of geological formations which preserve various stages of the region's Paleozoic tectonic cycle from passive margin to collisional orogenesis and subsequent erosion (Shail and Leveridge, 2009). While surface geochemical data is of obvious benefit to our understanding of the present day surface environment, south west England, with its rich geological history, provides an ideal setting in which to assess the potential of such quantitative datasets to enhance our understanding of the underlying bedrock.

Geochemical techniques are widely utilised for a variety of applications (Rollinson, 2014) but the high costs generally limit the number of samples that can be analysed and their use is often restricted to focused study areas as a result. In south west England rock sample geochemistry has been applied to various focused studies of metasediments (Dodson and Rex, 1970; Primmer, 1985; Warr et al., 1991), the granites (Floyd, 1972; Alderton et al., 1980; Charoy, 1986; Chesley et al., 1993; Darbyshire and Shepherd, 1994; Psyrillos et al., 1998) and other igneous lithologies (Floyd, 1984; Kirby, 1984; Floyd et al., 1993a; Sandeman et al., 1997; Clark et al., 1998). Previous work has been conducted towards gauging the geochemical baseline of various lithologies (Scott et al., 2002; LeBoutillier, 2004) but these have been limited in terms of sampling density and extent. Some other, wider scale geochemical surveys of soil and stream sediment which have focused on exploration for metallic ore deposits are reviewed in Moon (2010). The Wolfson geochemical atlas (Webb et al., 1978) provided full stream sediment coverage of England and Wales but has now been succeeded by the G-BASE stream sediment survey in terms of sensitivity of measurements and the range of analytes. Thus the new G-BASE data provides us with the best insight into the major and trace element geochemistry of south west England.

In this paper we use compositional data analysis to provide an overview of the geochemical signatures of bedrock domains in south west England. This study focuses on a selection of elements which have not been heavily remobilised by hydrothermal activity and mineralisation relating to the intrusion of the Cornubian Batholith, and are identified as having primarily lithostratigraphically constrained distributions. We implement domain-weighted compositional principal component analysis on the data to identify and maximise the geochemical contrasts between domains, and map the results of the data analysis in

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geographic space to allow a visualisation of the relationships between stream sediment geochemistry and regional scale bedrock geology. We then relate the geochemical features of each domain to their bedrock composition to examine what new evidence this data provides that may enhance geological understanding.

## 2. A brief geological history of south west England

The geology of south west England (summarised in Fig. 1) predominantly consists of a range of metasediments which were deposited in a series of east–west trending sedimentary palaeo-basins both in a passive margin setting during the Devonian (Rhenohyercynian passive margin sediments) and a retro-arc setting during the Carboniferous (Carboniferous foreland basin sediments). The granites of the Cornubian batholith were then intruded following the late Carboniferous to early Permian Variscan Orogeny. Post-Variscan sediments are also preserved in the east of the region but are fairly limited in extent within the adopted boundaries of the study area.

The tectonic evolution of the region began with a north–south extensional regime set up within the Avalonian terrane (the basement beneath south west England) at the start of the Devonian. The extension was caused by either slab rollback or slab-pull stresses as a result of the initiation of subduction in the Rheic Ocean (Stampfli and Borel,

2002), an ancient ocean which separated Avalonia from Gondwana to the south. This intra-Avalonian extensional zone, termed the Rhenohercynian zone, developed to form a narrow oceanic basin in the Devonian that was analogous in profile to the Red Sea today (Davies, 1984). This basin was the Gramscatho Basin (Leveridge and Shail, 2011a) and is where the contents of the Lizard Complex, the Start Complex and our two Gramscatho Basin domains were formed.

Though the Gramscatho Basin was the only basin to reach full oceanic maturity, a sequential series of east–west striking half grabens and grabens extended the rift zone northwards throughout the Devonian. Each basin was initially fed by sediment derived from the continent to the north, in parts intercalated with basalts, as the listric faulting provided conduits for magma. These were the Looe, South Devon and Tavy Basins, whose subsidence began in the Lower Devonian, late Lower Devonian and late Middle Devonian respectively (Leveridge, 2011) and continued throughout the Devonian so that each basin's sedimentation became increasingly pelagic. Meanwhile to the north the North Devon basin was subsiding independently throughout the Devonian but remained a fairly shallow marine environment thanks to a high rate of sediment input from northern uplands (Whittaker and Leveridge, 2011).

Closure of the Rheic Ocean was completed at the end of the Devonian, when Gondwana collided northwards into Avalonia (Nance et al.,
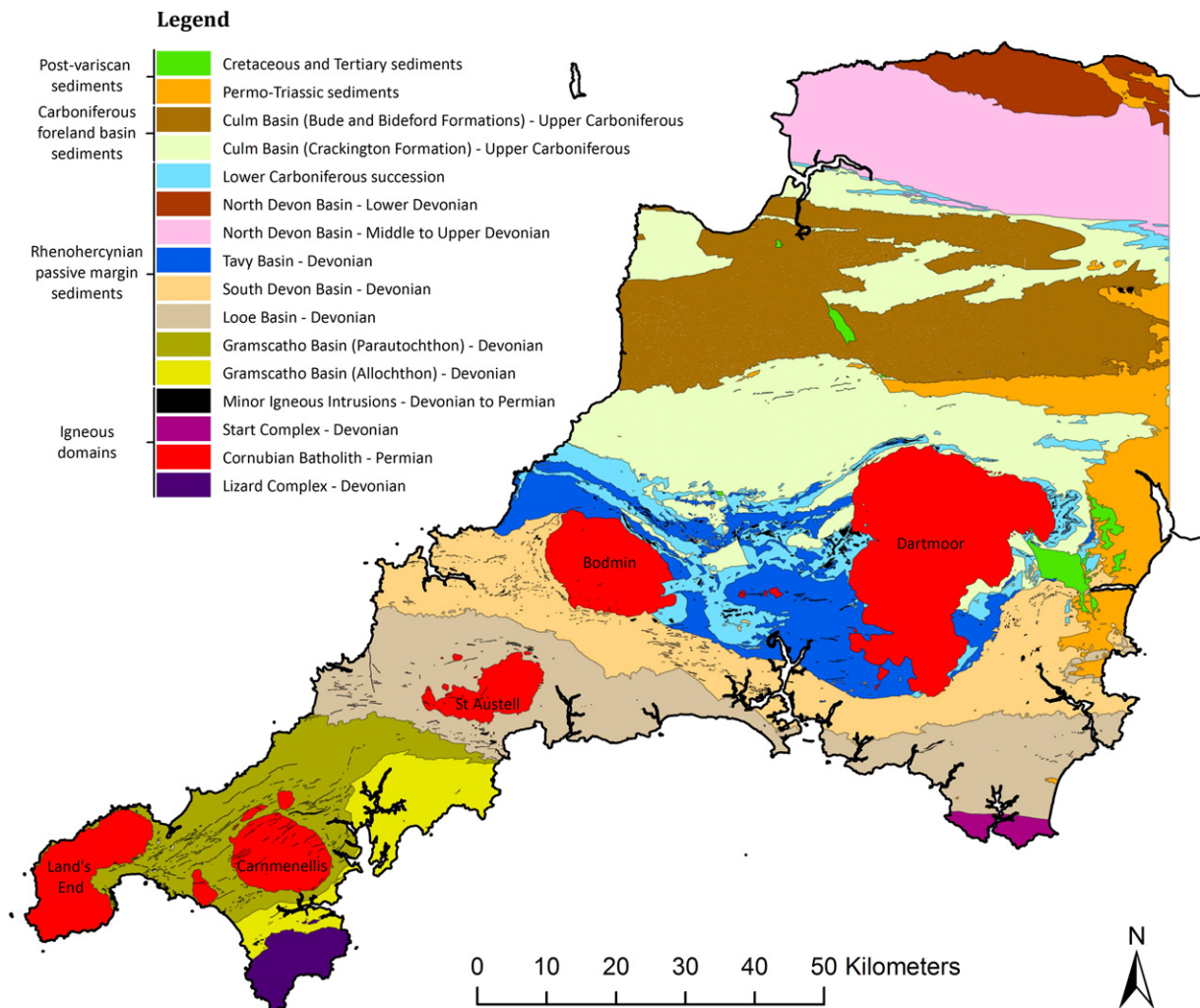


**Fig. 1.** The regional scale geology of south west England, classified into 16 geological domains for this study. The five major granites are labelled by name. Adapted from DiGMapGB-50 (Jackson and Green, 2003) after Shail and Leveridge (2009). See Fig. 2 for location in national context.
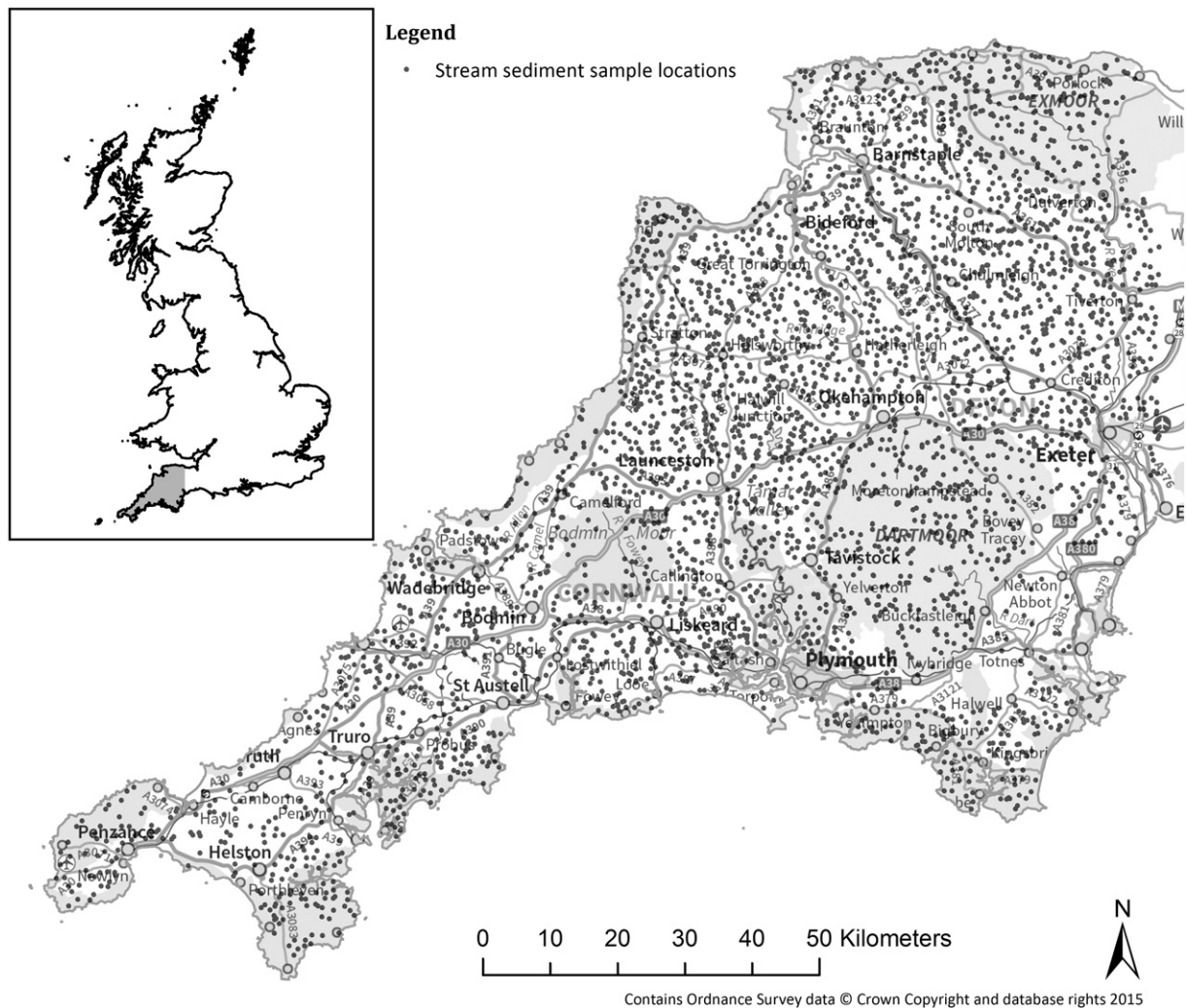
**Fig. 2.** Locations of all 3745 G-BASE stream sediment samples available within south west England. The inset map shows the region (shaded grey) in reference to the rest of Great Britain.

2010), resulting in the northwards progression of an accretionary wedge system and the inversion of south west England's Devonian basins (Leveridge and Hartley, 2006) into a mountain belt. Known as the Variscan Orogeny, this collision culminated in the formation of the supercontinent Pangaea. As the orogeny developed, the increasing topographic load of the mountain belt's thickening crust resulted in downward flexure of the surrounding crust. This produced a retro-arc foreland basin to the north; the Culm Basin, within which the sediments of our Culm Basin domains were both deposited and eventually inverted during the Carboniferous.

Variscan convergence across south-west England ended in the late Carboniferous (Edwards et al., 1997) and gave way to a NNW–SSE extensional regime. The structure of this regime exerted strong control on the emplacement of the granites of the Cornubian batholith during the early Permian (Chen et al., 1993) and on subsequent granite-related hydrothermal mineralisation (Shail and Wilkinson, 1994; Scrivener, 2006). The extent of bedrock preserving post-Variscan influences is relatively minor within the study area: Permo-Triassic 'New Red Sandstone' forms the bulk of the post-Variscan sedimentation preserved in south west England, and contains material eroded from the Variscan orogenic belt. Minor packages of Cretaceous and Tertiary sediments are also preserved in very limited extent, and are dominated by clays and sands; the weathering products of the Variscan granites (Edwards, 1976).

## 3. Materials and methods

### 3.1. G-BASE stream sediment geochemical data

The stream sediment baseline geochemistry data used in this study is measured from samples collected across south west England during summer field campaigns in 2002 and 2012 following standard G-BASE methods (Johnson et al., 2005). A total of 3745 samples were collected at an average sampling density of one sample per 2.5 km$^2$, varying locally depending on drainage patterns (Fig. 2). Sediment was primarily collected from 1st and 2nd order streams and wet-sieved to <150 μm. The <150 μm fraction sediment was air dried at <30 °C and subsequently freeze dried. The samples were analysed for the concentrations of 52 major and trace elements by X-Ray Fluorescence Spectrometry (XRF; Table 1) according to standard G-BASE procedures (Johnson et al., 2005). Any reported values below the accepted lower limit of detection were set to half the lower limit of detection. Data quality was assured by the inclusion of certified reference materials and duplicate samples within the analytical runs. Linear corrections were applied to normalise the data for systematic drift (Johnson et al., 2005; Lister and Johnson, 2005), ensuring that data is consistent across all analytical runs.

It is important to note that the G-BASE sampling procedures, which have changed little since the 1970s, were initially designed for the purpose of mineral exploration (Johnson and Breward, 2004). Plant (1971)

**Table 1**
Lower limits of detection for all elements in the G-BASE data used. Units are mg/kg unless otherwise stated.

| Element | LDL | Element | LDL | Element | LDL |
|---------|------|---------|-------|---------|-------|
| Ag | 0.5 | I | 0.5 | $SiO_2$ | 0.10% |
| $Al_2O_3$ | 0.20% | In | 0.5 | Sm | 2 |
| As | 0.9 | $K_2O$ | 0.01% | Sn | 0.5 |
| Ba | 1 | La | 1 | Sr | 1 |
| Bi | 0.3 | MgO | 0.30% | Ta | 1 |
| Br | 0.8 | Mn | 40 | Te | 0.5 |
| CaO | 0.05% | Mo | 0.2 | Th | 0.7 |
| Cd | 0.5 | $Na_2O$ | 0.30% | $TiO_2$ | 0.02% |
| Ce | 1 | Nb | 1 | Tl | 0.5 |
| Cl | 200 | Nd | 4 | U | 0.5 |
| Co | 1.5 | Ni | 1.3 | V | 3 |
| Cr | 3 | $P_2O_3$ | 0.05% | W | 0.6 |
| Cs | 4 | Pb | 1.3 | Y | 1 |
| Cu | 1.3 | Rb | 1 | Yb | 1.5 |
| $Fe_2O_3$ | 0.05% | S | 1000 | Zn | 1.3 |
| Ga | 1 | Sb | 0.5 | Zr | 1 |
| Ge | 0.5 | Sc | 3 | | |
| Hf | 1 | Se | 0.2 | | |

conducted a thorough orientation study in order to optimise every stage of the sampling and analysis towards maximising the contrast in trace metal data. The most influential stage of the G-BASE sampling methodology is the sieving of the sample to <150 μm before analysis. This procedure is specifically designed to remove 'hydraulic-equivalent sized quartz' in order to concentrate heavy minerals and therefore the trace metals that they contain (Plant, 1971). It is also beneficial in that it ensures that the sample contains sufficient individual particles, each sourced from different points within the catchment, to provide valid representation of the catchment as a whole. However, as a result of the sieving the G-BASE stream sediment geochemical data does not represent the true bulk composition of the stream sediment, and is highly dependent on factors such as the grain size of the underlying bedrock and the variable ability of streams to mechanically or chemically weather these grains before they are sampled. None of these factors are yet understood well enough to be corrected for, and it is important to be aware of these limitations of the data.

### 3.2. Classification of the region into geological domains using geological maps

A geological domain system was created by reclassifying the British Geological Survey's DiGMapGB-50 bedrock geology map (Jackson and Green, 2003) into 16 domains based on the boundaries of the different sedimentary palaeo-basins and igneous formations represented in the region (Fig. 1). The domains summarise the lithostratigraphy of the region following authors such as Shail and Leveridge (2009) while retaining the detailed formation-level geological boundaries of DiGMapGB-50. The sixteen lithostratigraphic domains of south west England can be broadly assigned to four categories: Igneous domains, Rhenohercynian passive margin sediments, Carboniferous foreland basin sediments and Post-variscan sediments.

The name of the domain in which each sample is located was then appended to the data as a categorical variable using a spatial join. This allowed the stream sediment geochemical data to be processed on a domain by domain basis. The spatial join took no account of the catchment areas of each stream sediment sample, so there may be cases where samples located near domain boundaries contain a portion of material from neighbouring domains as well as from the domain over which the sample was taken. This adds a potential inaccuracy in terms of the representivity of the geochemical data assigned to each domain. This is especially true of the domains which are limited in extent within

the study area and thus contain few stream sediment samples. However, the high sampling density and comparatively vast scale of this study, which is based on domains rather than individual samples, means that most of the sampled catchments do sit entirely within a single domain. We therefore expect that this inaccuracy is unlikely to cause significant detriment to the overall quality of our results.

### 3.3. Sub-composition selection according to hydrothermal immobility and data quality

In order to best focus on the relationships between rock types and geochemistry it was first necessary to identify and exclude the most hydrothermally mobile elements from the geochemical sub-composition to be studied. South west England hosted significant granite-related hydrothermal activity following the early Permian emplacement of the Cornubian Batholith. The hydrothermal activity has allowed elements such as As, Bi, Cu, Pb, Sb, Sn, Tl, W and Zn to be remobilised in the areas surrounding the granites, and has resulted in widespread metalliferous mineralisation. As a result the spatial distributions of these elements in the stream sediment data reflect variations in palaeo-hydrothermal conditions and the occurrences of mineral deposits more than they reflect variations attributable to compositional differences between lithostratigraphic units. Therefore we exclude these nine elements as they do not provide information which closely relates to the primary geochemistry of the bedrock. Ag, Cd, Cl, I, In, S, Te and Yb were also excluded because of analytical issues resulting in an abundance of Not Available (NA) values for these elements. This resulted in a sub-composition of 35 selected elements (Table 2). Samples with NA or zero values for any element within our sub-composition were then omitted in order to allow the use of compositional data analysis techniques without complication, leaving values for 3538 samples in the data frame.

### 3.4. Data analysis

The use of compositional data analysis (CODA) methods is necessary when dealing with this kind of geochemical data, in which the concentrations of each element are not free to vary independently but must accommodate one another within the constraint of the closed composition. Fundamentally, the combined concentrations of all of the elements within a sample must sum to 100%, whether or not they have all been measured. An increase in one element's concentration must be accompanied by a decrease in others. It is therefore not the absolute concentrations that are important but the ratios between elements: each element provides only relative information. Aitchison (1981, 1982, 1986) realised this and proposed log-ratio transformations to enable the valid application of classical (Euclidean) statistical methods to compositional data. The field of compositional data analysis

**Table 2**
Categorisation of elements into those used in this study and those excluded for reasons of hydrothermal mobility and data quality.

| Category | No. of elements | Elements |
|----------|-----------------|----------|
| Elements used in this study. Our chosen sub-composition. | 35 | Al, Ba, Br, Ca, Ce, Co, Cr, Cs, Fe, Ga, Ge, Hf, K, La, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Rb, Sc, Se, Si, Sm, Sr, Ta, Th, Ti, U, V, Y, Zr |
| Elements excluded from the study due to their hydrothermal mobility | 9 | As, Bi, Cu, Pb, Sb, Sn, Tl, W, Zn |
| Elements excluded from the study due to analytical issues (concentrations often NA) | 8 | Ag, Cd, Cl, I, In, S, Te, Yb |
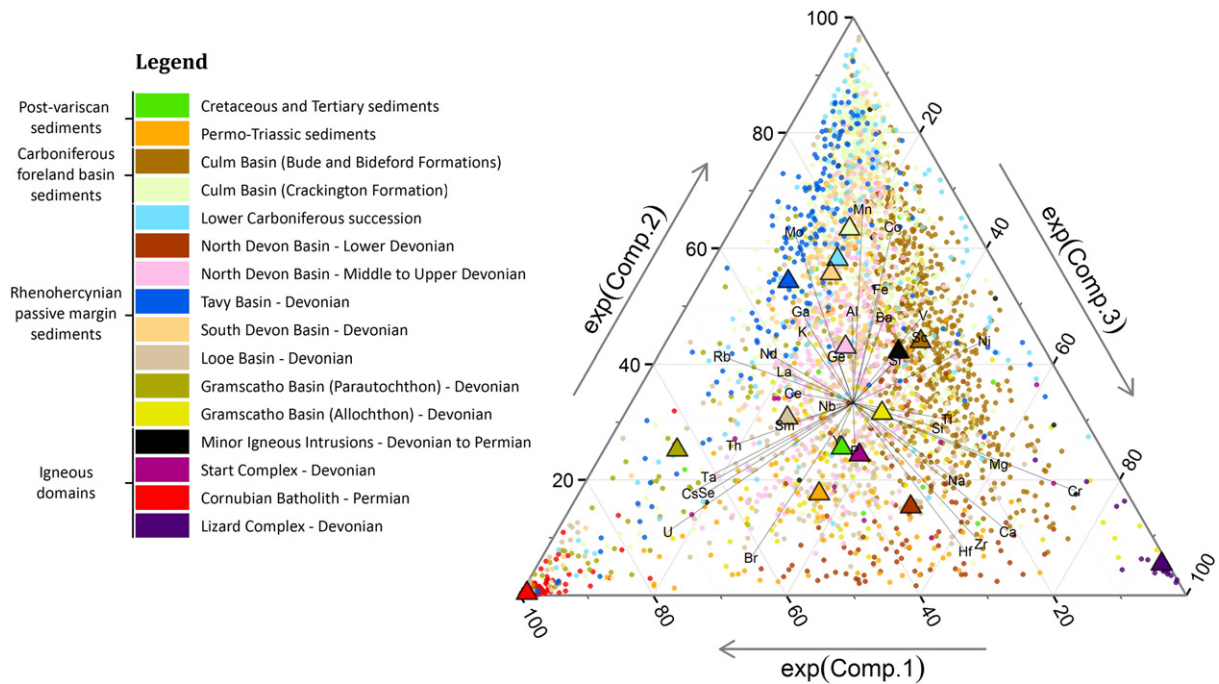
**Fig. 3.** Ternary plot of the exponential transformation of the first three domain-weighted compositional principal components of the stream sediment geochemistry of south west England. Individual samples are plotted as small dots, while large triangles indicate domain compositional centres. The element rays are a projection of the real element axes into the principal component space, and have been scaled by a factor of three to aid legibility. The colour scheme is the same as that used for the domain map (Fig. 2).

has been in development in the years since Aitchison's work (e.g. Pawlowsky-Glahn and Egozcue, 2001; Egozcue et al., 2003; Buccianti et al., 2006; Pawlowsky-Glahn and Buccianti, 2011; Van den Boogaart and Tolosana-Delgado, 2013) and a range of mathematical tools now exist for extracting meaningful results from compositional data.

In order to provide a holistic view of the geochemical differences between our 16 geological domains the data from our 3538 samples was processed using a compositional principal components approach based on isometric log-ratios (Egozcue et al., 2003). Compositional principal component analysis was conducted using a modified 'pcaCoDA' function from the 'robCompositons' (Templ et al., 2011) package in R (R Core Team, 2014) in which the sample weightings in the covariance matrix were adjusted so that each of the 16 domains were weighted equally. With this weighted covariance matrix the principal axes orientate to represent the geochemical variations between domains regardless of the number of samples they contain. However, the accuracy of the geochemical representation of each domain is still dependent on the number and placement of samples within the domain. The compositional centre (a compositionally valid average; Pawlowsky-Glahn and Egozcue, 2006) of each domain was then projected into the principal component space to allow the position of the average composition of each domain to be compared, both in principal component terms and in real element terms by subsequent back transformation.

## 4. Results

### 4.1. Domain-weighted compositional principal component analysis

The domain-weighted compositional principal component analysis successfully reduces the dimensionality of the data to allow holistic visualisation of the geochemical of the geological domains of south west England. The first three principal components account for at least 70% of the total structured data variation; this could be seen as a conservative estimate given that all subsequent principal components have eigenvalues <1. Closing the exponential transformation of the first three

principal components and displaying them on a ternary plot allows the geochemical contrasts between domains to be seen, and the inclusion of rays to indicate the orientations of the original element axes in the principal component space provides a convenient visualisation of the loadings on each element (Fig. 3).

In order to visualise the geochemical contrasts between domains in geographic space a map was produced by inverse distance weighted (IDW) interpolation of the values of the first three principal components from the sample sites to a raster grid (Fig. 4). The use of three principal components conveniently allows for full representation in the RGB colour space. Due to the fact that there is still some potentially useful geochemical variation outside of the first three principal components, and to allow for element-specific examination of the geochemical contrast between domains, parallel coordinate plots were also produced (Fig. 5). These plots display the position of the compositional centre of each domain in terms of the real element axes, but retaining the centre and scale of the domain-weighted principal component space. The numerical values displayed in the parallel coordinate plots are presented in Table 3, and the unscaled compositional centres of each domain (and of all the samples together) in Table 4.

### 4.2. The ability of G-BASE stream sediment geochemical data to capture geological variation

The degree to which the mapped regional lithostratigraphic boundaries (domain boundaries) are represented within the principal component map (Fig. 4) provides a visual indication of the ability of G-BASE stream sediment geochemical data to capture variations in bedrock geology. However the limitations of the IDW interpolation as a method of mapping stream sediment geochemistry (the samples of which represent material sourced from the upstream catchment rather than from the sample location) and the fact that a three channel map is unable to display all of the geochemical variation, as it can represent only three of the principal components, must be considered in this evaluation. Nevertheless, it is clearly evident that variations in bed rock
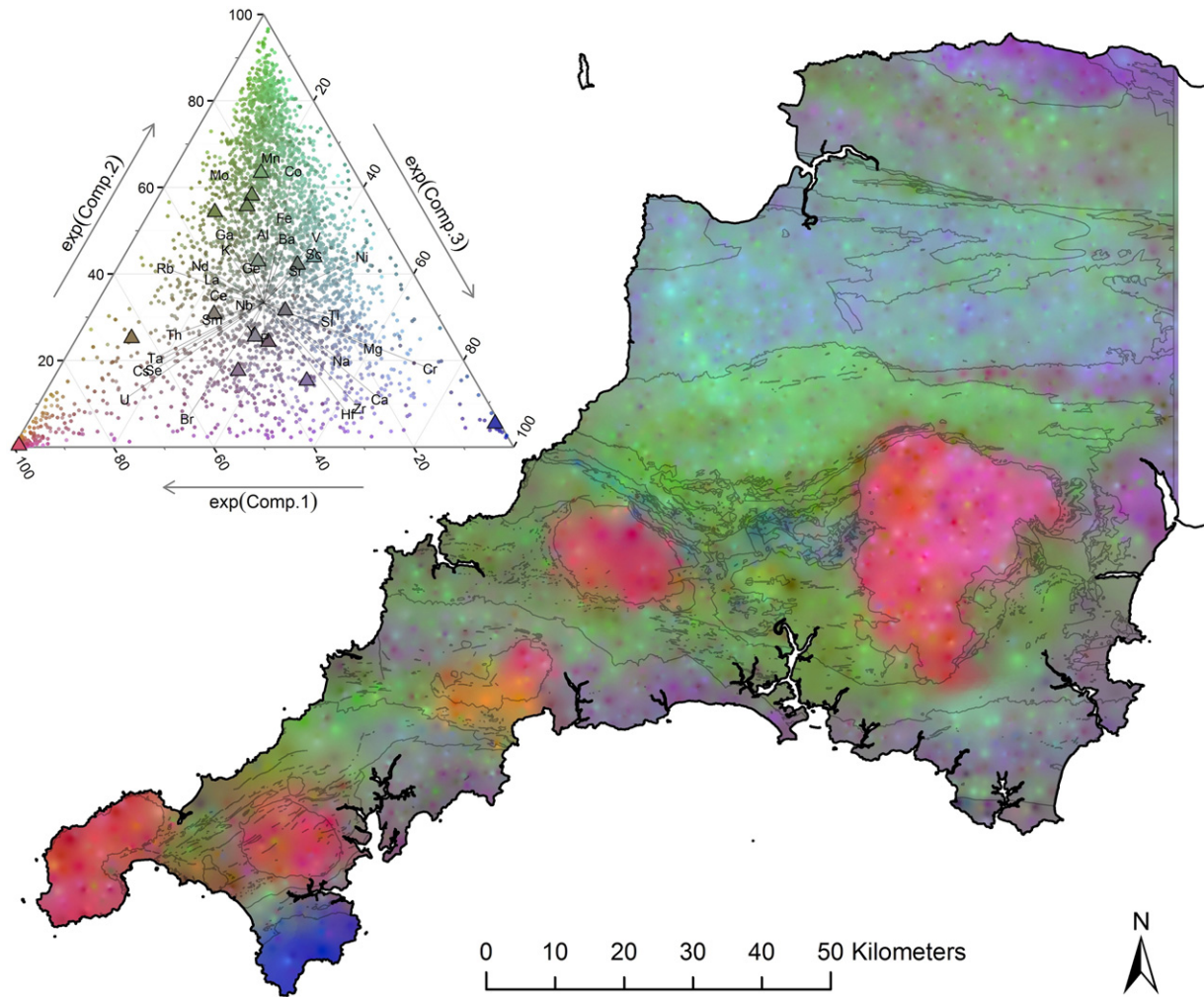
**Fig. 4.** Inverse distance weighted interpolation of the first three domain-weighted compositional principal components of the stream sediment geochemistry of south west England coloured according to a RGB ternary scheme in which red = exp(component 1), blue = exp(component 2) and green = exp(component 3). Domain boundary line work is overlain.

geology are captured in the stream sediment geochemical data, albeit at a spatial resolution limited by the sampling density (and catchment sizes) of the survey.

The granites of the Cornubian Batholith represent the endmember of component 1, on which the concentrations of elements such as U, Cs, and Ta have strong control, and are highlighted in red. Component 1 can thus be considered as a measure of the felsic-compositional content of the bedrock. The peridotite rich Lizard Complex represents the endmember of component 2, on which the concentrations of elements such as Cr, Ca and Mg exert strong control, and is highlighted in blue. Component 2 can be considered as a measure of the (ultra)mafic-compositional content of the bedrock. Between those igneous endmembers, the other domains are differentiated by more subtle colour changes due to their compositions being relatively more similar. However we still clearly see differences as a result of the geochemical data successfully capturing differences in bedrock composition, particularly in the green channel of component 2, on which the concentrations of elements such as Mn, Co, Mo and Fe have strong control. Component 2 can perhaps best be considered as a measure of argillaceousness in sedimentary terms.

In areas where the geochemistry appears to fail to represent the bedrock geology (e.g. the limited geochemical acknowledgement of the mapped northern section of the Crackington Formation) it should be considered that the geological map is an amalgamation of the work of many individuals, produced on the basis of field-observable factors

which have been interpolated using educated guesswork. It would not be unreasonable to suggest that consistent geochemical surveys like G-BASE have the ability to highlight inconsistencies in traditional geological mapping. Nevertheless the geological map is the accepted benchmark from which we take our domain boundaries.

## 5. Discussion

### 5.1. Igneous domains

#### 5.1.1. Cornubian Batholith

The lithology of the Cornubian Batholith domain consists entirely of S-Type, peraluminous granites intruded in the early Permian as a result of the Variscan orogeny (Chappell and White, 1974; Charoy, 1986; Chappell and Hine, 2006). Though compositional differences within the granites have been mapped in the field (Hawkes et al., 1987), their appearance in the principal component map (Fig. 4) is fairly uniformly red. This uniform appearance is to be expected: intra-granite compositional variations are minor within the regional context of the principal component analysis. The most notable exception to this is the more yellowish colouration of the western side of the St Austell Granite, which is mostly likely caused by the abundant hydraulic China clay (kaolinite) mining activity in the area (Portmann, 1970) resulting in anthropogenically elevated concentrations of kaolinite and other fine clays in the stream sediments. The geochemical signature of the granites (Fig. 5) is
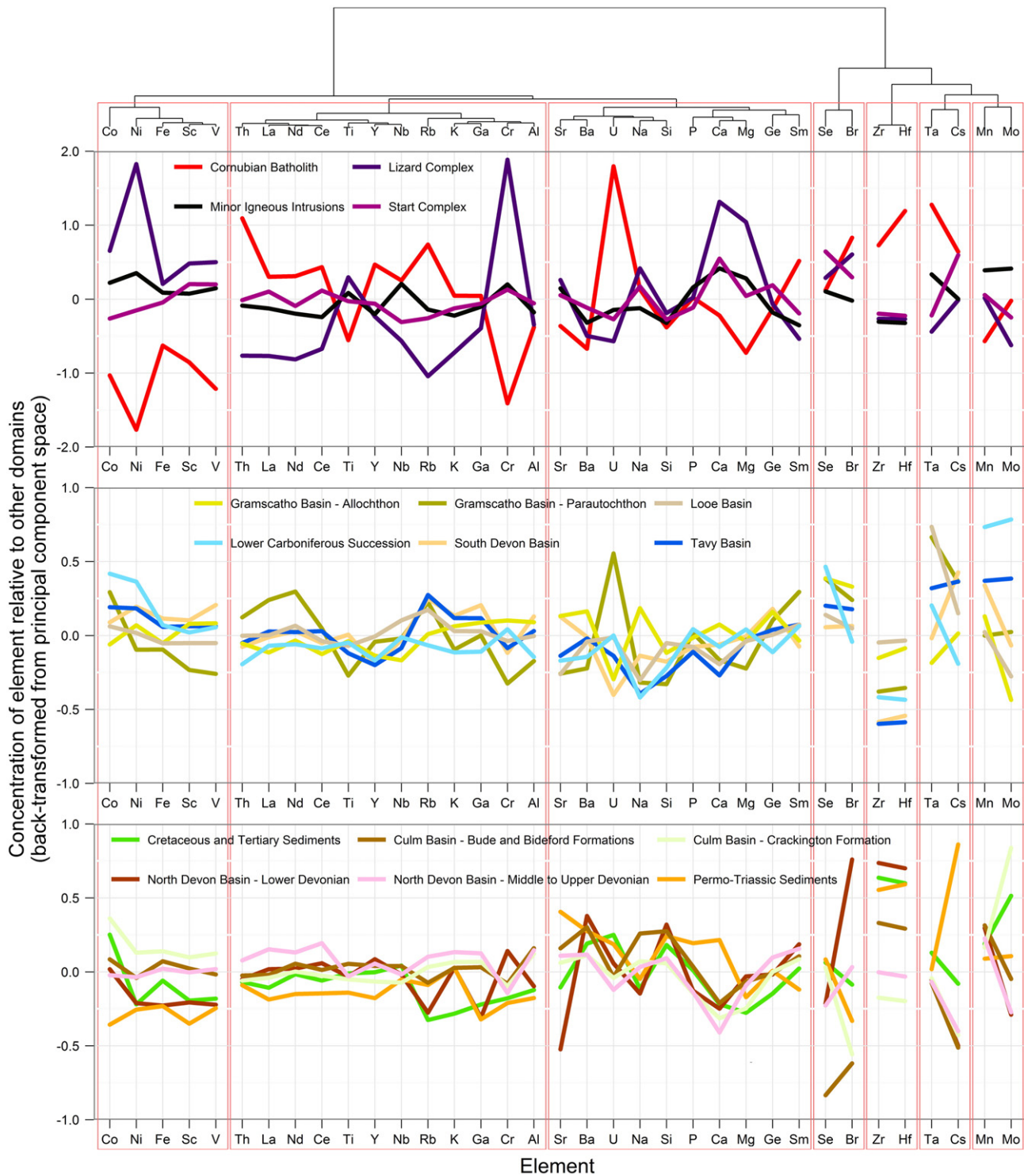
**Fig. 5.** Parallel coordinate plots of the compositional centre of each domain in real element terms centred and scaled according to their position in the domain-weighted compositional principal component space for comparison of relative geochemical features between domains. The elements are arranged on the x axis according to compositional clustering using the variation matrix (Pawlowsky-Glahn and Buccianti, 2011): elements are clustered according to the stability of their relationships. Stable relationships suggest that their distributions are controlled by similar processes. A dendrogram of this clustering is shown at the top of the figure.

characterised by low concentrations of mafic-associated elements such as Ni, Cr, V, Co, Sc, Fe and Mg and high concentrations of felsic-associated elements such as U, Ta, Hf, Th and Rb. This signature reflects the fact that this domain is the 'felsic endmember' of the region's geochemistry.

### 5.1.2. Lizard Complex

The Lizard Complex is in summary an ophiolitic assemblage of gabbro, basalts and peridotites representing Lower Devonian oceanic crust and mantle material (Kirby, 1979; Floyd, 1984; Cook et al., 2000) from within the Gramscatho Basin. Its appearance in the principal

**Table 3**

Compositional centre of each domain centred and scaled according to the domain-weighted compositional principal component analysis.

| Domain | Samples | Al | Ba | Br | Ca | Ce | Co | Cr | Cs | Fe | Ga | Ge | Hf | K | La | Mg | Mn | Mo | Na |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cornubian Batholith | 329 | −0.38 | −0.67 | 0.83 | −0.22 | 0.43 | −1.03 | −1.41 | 0.64 | −0.63 | 0.04 | −0.13 | 1.19 | 0.05 | 0.30 | −0.73 | −0.57 | −0.02 | 0.13 |
| Lizard Complex | 20 | −0.35 | −0.50 | 0.60 | 1.32 | −0.67 | 0.65 | 1.88 | −0.01 | 0.21 | −0.39 | −0.07 | −0.27 | −0.72 | −0.77 | 1.04 | 0.02 | −0.62 | 0.41 |
| Start Complex | 11 | −0.06 | −0.12 | 0.29 | 0.55 | 0.11 | −0.26 | 0.13 | 0.60 | −0.04 | −0.06 | 0.19 | −0.22 | −0.12 | 0.10 | 0.04 | 0.06 | −0.25 | 0.17 |
| Minor Igneous Intrusions | 9 | −0.18 | −0.32 | −0.02 | 0.42 | −0.24 | 0.22 | 0.20 | 0.00 | 0.09 | −0.10 | −0.18 | −0.32 | −0.22 | −0.13 | 0.28 | 0.39 | 0.41 | −0.12 |
| Gramscatho Basin – Allochthon | 116 | 0.09 | 0.16 | 0.33 | 0.07 | −0.13 | −0.06 | 0.10 | 0.01 | −0.05 | 0.09 | 0.16 | −0.09 | 0.06 | −0.12 | −0.04 | 0.13 | −0.44 | 0.18 |
| Gramscatho Basin – Parautochthon | 99 | −0.17 | −0.22 | 0.24 | −0.17 | 0.05 | 0.29 | −0.32 | 0.36 | −0.10 | 0.00 | 0.10 | −0.36 | −0.10 | 0.24 | −0.22 | 0.00 | 0.02 | −0.32 |
| Looe Basin | 347 | 0.00 | −0.04 | 0.05 | −0.19 | −0.04 | 0.06 | −0.04 | 0.15 | −0.05 | 0.03 | 0.00 | −0.03 | 0.03 | 0.00 | −0.04 | 0.02 | −0.28 | −0.30 |
| South Devon Basin | 229 | 0.13 | −0.01 | 0.06 | −0.06 | −0.05 | 0.09 | −0.12 | 0.43 | 0.11 | 0.20 | 0.18 | −0.54 | 0.13 | −0.01 | −0.01 | 0.34 | −0.07 | −0.14 |
| Tavy Basin | 198 | 0.03 | −0.02 | 0.18 | −0.27 | 0.03 | 0.19 | −0.09 | 0.36 | 0.06 | 0.12 | 0.04 | −0.59 | 0.12 | 0.03 | −0.03 | 0.37 | 0.38 | −0.39 |
| North Devon Basin – Middle to Upper Devonian | 358 | 0.15 | 0.12 | 0.03 | −0.41 | 0.19 | −0.02 | −0.14 | −0.40 | 0.02 | 0.13 | 0.10 | −0.03 | 0.13 | 0.15 | −0.09 | 0.23 | −0.27 | 0.03 |
| North Devon Basin – Lower Devonian | 93 | −0.10 | 0.38 | 0.76 | −0.25 | 0.06 | 0.02 | 0.14 | −0.50 | −0.23 | −0.31 | −0.02 | 0.70 | 0.03 | 0.02 | −0.03 | 0.30 | −0.29 | −0.15 |
| Lower Carboniferous Succession | 138 | −0.15 | −0.14 | −0.04 | −0.08 | −0.09 | 0.42 | 0.04 | −0.19 | 0.07 | −0.11 | −0.11 | −0.44 | −0.11 | −0.07 | 0.04 | 0.73 | 0.78 | −0.42 |
| Culm Basin – Crackington Formation | 785 | 0.12 | 0.11 | −0.56 | −0.31 | −0.03 | 0.36 | −0.10 | −0.43 | 0.14 | 0.07 | 0.00 | −0.20 | 0.07 | −0.04 | −0.25 | 0.16 | 0.84 | 0.07 |
| Culm Basin – Bude and Bideford Formations | 661 | 0.16 | 0.30 | −0.62 | −0.21 | 0.01 | 0.08 | −0.08 | −0.51 | 0.07 | 0.03 | −0.01 | 0.29 | 0.03 | −0.02 | −0.07 | 0.31 | −0.05 | 0.26 |
| Permo-Triassic Sediments | 134 | −0.18 | 0.28 | −0.33 | 0.22 | −0.15 | −0.36 | −0.21 | 0.86 | −0.23 | −0.32 | 0.01 | 0.59 | 0.03 | −0.19 | −0.17 | 0.09 | 0.11 | −0.05 |
| Cretaceous and Tertiary Sediments | 11 | −0.12 | 0.19 | −0.09 | −0.22 | −0.06 | 0.25 | −0.18 | −0.08 | −0.06 | −0.22 | −0.15 | 0.60 | −0.28 | −0.11 | −0.28 | 0.19 | 0.51 | −0.11 |

**Table 3** (*continued*)

| Domain | Nb | Nd | Ni | P | Rb | Sc | Se | Si | Sm | Sr | Ta | Th | Ti | U | V | Y | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cornubian Batholith | 0.25 | 0.31 | −1.77 | 0.02 | 0.74 | −0.85 | 0.12 | −0.38 | 0.52 | −0.36 | 1.28 | 1.09 | −0.55 | 1.80 | −1.21 | 0.47 | 0.73 |
| Lizard Complex | −0.57 | −0.82 | 1.83 | 0.02 | −1.04 | 0.48 | 0.29 | −0.19 | −0.54 | 0.26 | −0.44 | −0.77 | 0.30 | −0.57 | 0.50 | −0.24 | −0.27 |
| Start Complex | −0.31 | −0.09 | −0.15 | −0.12 | −0.26 | 0.20 | 0.64 | −0.28 | −0.19 | 0.05 | −0.22 | −0.01 | −0.03 | −0.27 | 0.20 | −0.06 | −0.20 |
| Minor Igneous Intrusions | 0.21 | −0.20 | 0.35 | 0.16 | −0.14 | 0.07 | 0.10 | −0.32 | −0.35 | 0.14 | 0.33 | −0.09 | 0.08 | −0.15 | 0.15 | −0.20 | −0.31 |
| Gramscatho Basin – Allochthon | −0.17 | −0.03 | 0.07 | −0.02 | 0.01 | 0.08 | 0.39 | −0.12 | −0.04 | 0.13 | −0.19 | −0.05 | −0.04 | −0.30 | 0.08 | −0.14 | −0.15 |
| Gramscatho Basin – Parautochthon | −0.02 | 0.30 | −0.10 | 0.02 | 0.22 | −0.23 | 0.38 | −0.33 | 0.29 | −0.26 | 0.66 | 0.12 | −0.27 | 0.55 | −0.26 | −0.04 | −0.38 |
| Looe Basin | 0.10 | 0.07 | 0.02 | −0.08 | 0.17 | −0.05 | 0.14 | −0.05 | 0.07 | −0.26 | 0.73 | 0.00 | −0.07 | −0.01 | −0.05 | −0.01 | −0.05 |
| South Devon Basin | −0.03 | 0.03 | 0.19 | −0.08 | 0.25 | 0.10 | 0.06 | −0.18 | −0.08 | 0.13 | −0.02 | −0.08 | 0.01 | −0.40 | 0.21 | −0.20 | −0.58 |
| Tavy Basin | −0.09 | 0.02 | 0.18 | −0.11 | 0.27 | 0.06 | 0.20 | −0.27 | 0.07 | −0.14 | 0.32 | −0.05 | −0.12 | −0.14 | 0.06 | −0.20 | −0.60 |
| North Devon Basin – Middle to Upper Devonian | −0.02 | 0.13 | −0.04 | −0.14 | 0.10 | 0.00 | −0.23 | 0.09 | 0.16 | 0.11 | −0.07 | 0.08 | −0.03 | −0.12 | 0.02 | 0.06 | 0.00 |
| North Devon Basin – Lower Devonian | −0.02 | 0.02 | −0.21 | −0.13 | −0.28 | −0.21 | −0.21 | 0.32 | 0.19 | −0.52 | −0.05 | −0.05 | −0.03 | 0.06 | −0.22 | 0.09 | 0.74 |
| Lower Carboniferous Succession | −0.01 | −0.06 | 0.36 | 0.04 | −0.07 | 0.02 | 0.46 | −0.22 | 0.06 | −0.17 | 0.20 | −0.19 | −0.05 | 0.00 | 0.06 | −0.17 | −0.17 |
| Culm Basin – Crackington Formation | −0.07 | 0.00 | 0.13 | −0.14 | 0.03 | 0.10 | 0.03 | 0.06 | 0.09 | 0.06 | −0.04 | −0.06 | −0.05 | −0.04 | 0.12 | −0.07 | −0.17 |
| Culm Basin – Bude and Bideford Formations | 0.04 | 0.06 | −0.04 | 0.03 | −0.07 | 0.02 | −0.83 | 0.27 | 0.11 | 0.16 | −0.07 | −0.03 | 0.05 | −0.04 | −0.02 | 0.04 | 0.33 |
| Permo-Triassic Sediments | −0.05 | −0.15 | −0.26 | 0.19 | −0.09 | −0.35 | 0.08 | 0.24 | −0.12 | 0.41 | 0.02 | −0.09 | −0.14 | 0.19 | −0.25 | −0.18 | 0.55 |
| Cretaceous and Tertiary Sediments | 0.04 | −0.02 | −0.22 | 0.01 | −0.33 | −0.19 | 0.06 | 0.18 | 0.02 | −0.11 | 0.13 | −0.07 | −0.01 | 0.25 | −0.18 | 0.00 | 0.64 |

component map (Fig. 4) is uniformly blue. Just as in the case of the granites, the Lizard Complex is so geochemically distinct from the rest of the region that it is confined to the edge of our principal component space. The geochemical signature of the Lizard Complex (Fig. 5) is characterised by low concentrations of felsic-associated elements such as Rb, K, Th and rare earth elements (REE) and high concentrations of mafic-associated elements such as Cr, Ni, Ca and Mg. This signature reflects the fact that this domain is the 'mafic endmember' of the region's geochemistry.

### 5.1.3. Start Complex

The likely Lower Devonian Start Complex consists of hornblende schists, believed to represent the metamorphosed remains of mid ocean ridge basalt (Floyd et al., 1993a) and mica schists representing sediments from the same basin. Its appearance in the principal component map is heterogeneous as a result of the mixture of the two rock types within the domain (Fig. 4). The western tip is coloured blue, indicating the mafic signature captured by the one sample that appears to have picked up significant hornblende schist-derived material. The rest of the domain appears as various shades of purple, indicating a clay-poor metasedimentary signature. The geochemical signature of the Start Complex as a whole (Fig. 5) is characterised by high Se, Ca and Na and low Si, U and Nb. In general the geochemical signature is fairly average with respect to the other domains of the region but with some mafic influence. The notable high Se concentration suggests abundant sulphides within the domain, perhaps a product of the basaltic magmatism responsible for the hornblende schist's protolith.

### 5.1.4. Minor Igneous Intrusions

The Minor Igneous Intrusions domain exists as numerous small scattered polygons, each representing minor intrusions that collectively range in composition from felsic to mafic and with both pre and post-Variscan ages (Floyd et al., 1993b). The main collections of minor igneous intrusions are found as NE–SW trending quartz-porphyry and rhyolite dykes around the Carnmenellis granite (Smedley, 1991) and as approximately E–W trending melange of mostly mafic dykes in the heavily faulted area between the Dartmoor and Bodmin granites (e.g. Polyphant Igneous Complex, Bennett et al., 1980). The latter appears as an area of blue shading on Fig. 4 and can be attributed to a mafic influence on stream sediment composition. The appearance of the former is less easy to discern in the principal component map, but could be interpreted as being indicated by the spread of reds and oranges to the zone north and west of the Carnmenellis granite, though this area is within the aureole of the granites in any case. The geochemical signature of the domain (Fig. 5) is collectively represented as being slightly mafic overall (with high Ca, Mg, Ni, Cr and low K, Rb). It is worth noting that the signature is likely to be strongly contaminated by that of other domains, because the catchments for all of the samples which overlie the Minor Igneous Intrusions are likely to extend beyond the perimeter of the intrusion that they overlie (a limitation of our catchment-oblivious approach is cross-contamination near domain boundaries).

### 5.2. Rhenohercynian passive margin sediments

### 5.2.1. Gramscatho Basin (Allochthon)

The lithology of the Allochthonous succession of the Gramscatho Basin is dominated by lithic and feldspathic sandstone turbidites (e.g. Porthscatho Formation) laid down in the Gramscatho Basin during the Middle to Upper Devonian (Floyd and Leveridge, 1987; Leveridge and Shail, 2011a). Technically the Lizard Complex is also considered part of the Allochthon, as it too has been transported from its original location by thrust faulting during continental collision, but we class it as a separate domain. The Allochthonous Gramscatho Basin domain appears on the principal component map (Fig. 4) as a greyish purple. It is in fact the most average (central) of all our domains in the principal component space. The geochemical signature of the domain (Fig. 5) is

characterised by low Mo, U and Ta and (slightly) high Na, Ba and Ge. This signature represents a fairly indistinct sedimentary composition though perhaps devoid of direct input of felsic material. The low Mo concentration (the one single feature that separates it from other domains) can be interpreted as an indication of a well oxygenated depositional environment (perhaps also poor in organic material) as Mo fixation in ocean sediments is dependent on redox conditions (Crusius et al., 1996).

### 5.2.2. Gramscatho Basin (Parautochthon)

The Parautochthonous succession of the Gramscatho Basin is dominated by the Middle to Upper Devonian slaty mudstones of the Porthtowan and Mylor Slate formations (Leveridge and Shail, 2011a). The domain has a varied appearance on the principal component map due to the inseparable influence of hydrothermal alteration on the sediments surrounding the Carnmenellis granite. The central axis of the Cornubian Batholith does in fact underlie the domain at shallow depth (Willis-Richards and Jackson, 1989). It may also be an effect of transport of stream sediment off the granite to the non-granite sample sites. As a result the 'true' composition of the domain is represented on Fig. 4 by the green areas over the northern part of this domain, and a granite-influenced composition in the oranges over the southern part. The geochemical signature of the domain as a whole (Fig. 5) features high concentrations of U, Rb, Th and Rare Earth Elements (REEs) such as La, Nd, Ce, and Sm, with low concentrations of Cr and Ti. All of these features indicate cross-contamination from granite however REEs are believed to be mobile in these hydrothermal conditions (Alderton et al., 1980) and so it is not necessarily entirely a limitation of our catchment-oblivious stream sediment analysis. The 'true' slaty composition of the domain is suggested by the low Zr and Hf concentrations, which are interpreted to reflect low volumes of resistate minerals such as zircon.

### 5.2.3. Looe Basin

The lithology of the Looe Basin consists of a conformable progression from the Early Devonian fluvio-lacustrine deposits of the Dartmouth Group to the Middle Devonian shallow marine facies of the Meadfoot Group, documenting the subsidence of the basin by north–south extensional rifting during this period (Shail and Leveridge, 2009; Leveridge and Shail, 2011b). The basin now forms an east–west trending anticline, with the older Dartmouth group rocks exposed along the central axis. On the principal component map (Fig. 4) we see this central axis coloured in mild purple tones indicating clay-poor sediments while the Meadfoot Group at the edges of the basin is coloured green according to their more argillaceous marine composition (Humphreys and Smith, 1989). The geochemical signature of the Looe Basin (Fig. 5) is fairly indistinct but features high Ta and Rb, and low Na, Ca and Mo. The elevated Ta and Rb concentrations are likely to correspond to the presence of anthropogenic contamination by China clay mining activity around the St Austell granite. The low Mo concentrations can be interpreted as an indication of a well oxygenated depositional environment.

### 5.2.4. South Devon Basin

The lithology of the South Devon Basin consists of steeply dipping northward-younging Middle Devonian Slates such as those of the Porthcothan, Treyarnon and Constantine Bay formations in the west (Beese, 1982) and their Tamar Group equivalents in the east (Leveridge, 2011). The appearance of the domain on the principal component map (Fig. 4) is a fairly uniform grey-green representative of the 'shaleyness' of the sedimentary protolith. The geochemical signature of the domain (Fig. 5) is characterised by high Mn and Cs and low Zr, Hf and U. The high Mn and Cs both indicate the fine grained, high clay composition of the domain's bedrock and the low Zr, Hf and U indicate an absence of the input of zircon and other dense late stage differentiate

**Table 4**

Compositional centre of each domain expressed in element concentrations (mg/kg). The compositional centre of all of the samples used in the study is also included.

| Domain | Samples | Al | Ba | Br | Ca | Ce | Co | Cr | Cs | Fe | Ga | Ge | Hf | K | La | Mg | Mn | Mo | Na |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cornubian Batholith | 329 | 70,000 | 267.0 | 61.8 | 5560 | 150.1 | 10.1 | 30.8 | 31.3 | 28,600 | 24.8 | 1.13 | 40.1 | 28,100 | 73.4 | 5300 | 1030 | 1.18 | 8950 |
| Lizard Complex | 20 | 59,500 | 260.0 | 40.5 | 21,260 | 40.8 | 44.9 | 683.1 | 13.4 | 54,100 | 13.1 | 1.00 | 7.7 | 10,700 | 20.7 | 25,500 | 1520 | 0.53 | 9760 |
| Start Complex | 11 | 89,200 | 428.0 | 33.3 | 11,050 | 100.6 | 20.1 | 132.2 | 27.6 | 47,200 | 20.5 | 1.44 | 9.0 | 21,800 | 55.4 | 10,500 | 1780 | 0.86 | 8570 |
| Minor Igneous Intrusions | 9 | 85,500 | 378.0 | 26.3 | 10,490 | 76.3 | 35.4 | 153.8 | 16.6 | 58,400 | 21.3 | 1.08 | 8.8 | 21,400 | 47.8 | 14,500 | 2690 | 1.81 | 6920 |
| Gramscatho Basin — Allochthon | 116 | 94,600 | 519.0 | 31.7 | 6310 | 72.6 | 22.6 | 118.0 | 14.2 | 43,000 | 21.8 | 1.28 | 9.4 | 24,100 | 40.9 | 8900 | 1750 | 0.66 | 7960 |
| Gramscatho Basin — Parautochthon | 99 | 84,300 | 409.0 | 33.6 | 5750 | 100.1 | 37.3 | 89.4 | 23.3 | 47,700 | 23.2 | 1.40 | 8.4 | 23,900 | 67.6 | 8600 | 1790 | 1.21 | 5580 |
| Looe Basin | 347 | 87,300 | 428.0 | 24.2 | 4880 | 80.2 | 25.9 | 104.0 | 16.4 | 43,500 | 20.8 | 1.11 | 10.1 | 23,600 | 46.5 | 9000 | 1600 | 0.78 | 4950 |
| South Devon Basin | 229 | 104,100 | 462.0 | 25.7 | 5830 | 82.7 | 27.8 | 100.4 | 22.7 | 53,800 | 26.0 | 1.38 | 6.3 | 27,400 | 48.0 | 9700 | 2290 | 1.01 | 6110 |
| Tavy Basin | 198 | 101,300 | 490.0 | 30.9 | 5090 | 96.3 | 33.0 | 111.2 | 22.9 | 54,600 | 25.6 | 1.29 | 6.5 | 29,000 | 53.5 | 10,200 | 2540 | 1.69 | 5070 |
| North Devon Basin — Middle to Upper Devonian | 358 | 92,100 | 455.0 | 21.6 | 3580 | 91.9 | 21.6 | 84.9 | 8.6 | 42,500 | 20.9 | 1.11 | 9.2 | 23,800 | 49.1 | 7800 | 1780 | 0.71 | 6290 |
| North Devon Basin — Lower Devonian | 93 | 60,700 | 497.0 | 37.6 | 3540 | 67.5 | 18.9 | 95.0 | 6.6 | 27,900 | 11.4 | 0.83 | 16.0 | 18,000 | 36.1 | 6900 | 1610 | 0.59 | 4430 |
| Lower Carboniferous Succession | 138 | 84,700 | 432.0 | 24.7 | 6140 | 85.4 | 41.3 | 125.9 | 13.1 | 55,000 | 20.3 | 1.10 | 7.5 | 22,900 | 48.4 | 10,900 | 3630 | 2.52 | 4930 |
| Culm Basin — Crackington Formation | 785 | 90,400 | 456.0 | 12.1 | 3960 | 74.2 | 31.9 | 89.5 | 8.4 | 48,200 | 19.8 | 1.01 | 7.8 | 22,400 | 40.8 | 6700 | 1680 | 2.17 | 6580 |
| Culm Basin — Bude and Bideford Formations | 661 | 80,200 | 471.0 | 9.7 | 3750 | 65.8 | 20.6 | 77.7 | 6.6 | 38,400 | 16.3 | 0.85 | 10.9 | 18,400 | 35.5 | 6800 | 1670 | 0.76 | 6780 |
| Permo-Triassic Sediments | 134 | 61,400 | 492.0 | 13.8 | 6160 | 60.3 | 14.2 | 73.2 | 28.0 | 30,400 | 12.3 | 0.93 | 15.8 | 19,800 | 32.2 | 6600 | 1430 | 0.96 | 5350 |
| Cretaceous and Tertiary Sediments | 11 | 66,400 | 463.0 | 18.1 | 4090 | 67.4 | 26.8 | 77.4 | 11.2 | 37,000 | 13.9 | 0.82 | 16.3 | 14,800 | 35.7 | 6100 | 1620 | 1.47 | 5130 |
| All samples used in study | 3538 | 84,500 | 428.0 | 16.6 | 4360 | 79.9 | 21.3 | 81.5 | 10.8 | 41,200 | 19.5 | 0.98 | 9.5 | 22,500 | 44.0 | 7400 | 1370 | 1.00 | 6180 |

**Table 4** (continued)

| Domain | Nb | Nd | Ni | P | Rb | Sc | Se | Si | Sm | Sr | Ta | Th | Ti | U | V | Y | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cornubian Batholith | 30.4 | 60.6 | 10.1 | 1220 | 312.5 | 7.2 | 1.46 | 233,000 | 11.92 | 72.8 | 6.87 | 44.2 | 3980 | 26.24 | 39.6 | 66.0 | 940 |
| Lizard Complex | 11.0 | 16.2 | 301.3 | 1000 | 43.3 | 22.4 | 1.42 | 233,000 | 3.42 | 111.5 | 1.02 | 5.7 | 7660 | 2.02 | 180.7 | 26.9 | 286 |
| Start Complex | 15.9 | 37.3 | 46.7 | 980 | 106.4 | 19.0 | 2.26 | 239,000 | 5.40 | 101.7 | 1.42 | 13.5 | 6200 | 3.05 | 149.9 | 35.8 | 344 |
| Minor Igneous Intrusions | 28.9 | 36.4 | 83.8 | 1400 | 129.6 | 18.1 | 1.43 | 247,000 | 4.99 | 120.9 | 2.68 | 13.6 | 7530 | 3.76 | 154.1 | 33.7 | 334 |
| Gramscatho Basin — Allochthon | 16.8 | 36.3 | 53.5 | 990 | 127.4 | 15.4 | 1.61 | 257,000 | 5.80 | 101.0 | 1.35 | 11.9 | 5640 | 2.74 | 122.3 | 30.5 | 329 |
| Gramscatho Basin — Parautochthon | 22.6 | 58.6 | 52.5 | 1190 | 183.3 | 13.1 | 1.86 | 241,000 | 9.36 | 79.3 | 3.65 | 16.4 | 5180 | 7.43 | 100.7 | 38.8 | 304 |
| Looe Basin | 22.3 | 40.6 | 51.4 | 950 | 152.1 | 13.7 | 1.27 | 278,000 | 6.55 | 69.0 | 3.42 | 12.7 | 5530 | 3.67 | 108.3 | 35.1 | 370 |
| South Devon Basin | 20.4 | 40.9 | 64.2 | 990 | 171.5 | 16.7 | 1.22 | 256,000 | 5.90 | 106.4 | 1.68 | 12.3 | 6230 | 2.61 | 146.4 | 30.4 | 226 |
| Tavy Basin | 20.8 | 43.6 | 68.1 | 1030 | 188.8 | 17.2 | 1.52 | 250,000 | 7.35 | 87.7 | 2.53 | 13.5 | 5910 | 3.64 | 136.1 | 32.5 | 240 |
| North Devon Basin — Middle to Upper Devonian | 18.0 | 39.4 | 44.3 | 810 | 128.6 | 13.0 | 0.80 | 291,000 | 6.46 | 90.8 | 1.39 | 12.4 | 5220 | 2.99 | 105.5 | 34.0 | 352 |
| North Devon Basin — Lower Devonian | 15.1 | 29.7 | 31.2 | 690 | 74.2 | 8.9 | 0.68 | 308,000 | 5.61 | 40.6 | 1.19 | 9.2 | 4390 | 3.02 | 69.8 | 29.5 | 619 |
| Lower Carboniferous Succession | 22.3 | 40.1 | 81.3 | 1190 | 133.8 | 16.4 | 1.97 | 263,000 | 7.26 | 84.5 | 2.25 | 11.7 | 6330 | 4.17 | 134.8 | 33.4 | 286 |
| Culm Basin — Crackington Formation | 17.1 | 34.8 | 52.5 | 810 | 120.8 | 14.5 | 1.04 | 283,000 | 6.06 | 87.0 | 1.44 | 10.9 | 5150 | 3.27 | 118.0 | 30.3 | 298 |
| Culm Basin — Bude and Bideford Formations | 16.4 | 31.3 | 37.8 | 820 | 92.7 | 11.5 | 0.37 | 300,000 | 5.28 | 81.9 | 1.19 | 9.6 | 4880 | 2.81 | 87.4 | 28.7 | 422 |
| Permo-Triassic Sediments | 16.0 | 27.4 | 32.7 | 1040 | 98.0 | 8.5 | 1.01 | 312,000 | 4.52 | 112.5 | 1.40 | 9.7 | 4310 | 3.76 | 74.6 | 24.8 | 565 |
| Cretaceous and Tertiary Sediments | 18.0 | 32.1 | 34.8 | 890 | 79.2 | 10.2 | 1.01 | 301,000 | 5.34 | 69.1 | 1.60 | 10.2 | 5030 | 4.10 | 81.5 | 30.2 | 629 |
| All samples used in study | 18.8 | 37.2 | 40.2 | 870 | 130.4 | 12.4 | 0.79 | 277,000 | 5.95 | 80.6 | 1.49 | 12.5 | 5130 | 3.65 | 96.9 | 32.9 | 353 |

mineral detritus to the depositional environment. These geochemical features support the existing interpretations of a distal turbidite fan depositional environment (Beese, 1982).

#### 5.2.5. Tavy Basin

The Tavy Basin domain contains Upper Devonian slate lithologies, including those of the Tavy and Tredorn Slate formations (Jackson and Green, 2003; Leveridge, 2011). Its appearance on the principal component map (Fig. 4) is similarly green to the South Devon Basin and indicates an approximately equally argillaceous composition. However, the compositional centre of the Tavy Basin is shifted slightly towards the felsic endmember in the ternary plot (Fig. 3), quite possibly due to sharing extensive boundaries with the granites. The geochemical signature of the domain (Fig. 5) is quite similar to that of the South Devon Basin but with slightly elevated U and Rb concentrations indicating cross-contamination from the granites. The Zr and Hf content is also the lowest of all the domains, indicating the most notable deficiency in zircon. This, along with an increased Mo and Se concentration suggests a more distal, deeper and more anoxic environment of deposition than for any of the other Devonian domains.

#### 5.2.6. Lower Carboniferous Succession

The lithology of the Lower Carboniferous Succession domain consists of thrusted slices of various rock types, but is perhaps best typified by the St Mellion formation of sandstone turbidites; slumped plant-rich sandstone and interbedded dark grey mudstone (Leveridge and Hartley, 2006). On the principal component map (Fig. 4) the domain appears a very similar green colouration to the South Devon Basin, though its compositional centre appears slightly less argillaceous. It is at risk of cross-contamination from the numerous minor igneous intrusions in the area which impart scattered blue tints to the map owing to their mafic composition. Even so, the geochemical signature of the domain has some interesting features (Fig. 5). The Lower Carboniferous Succession has the highest concurrent concentrations of Se and Mo and the lowest concentration of Na of any domain. The high Se and Mo could be taken as an indication of high levels of organic matter within the domain while the low Na concentrations (the lowest of any domain) could either be interpreted as an indication of Na poor detrital input (poor in albite clasts for example) or an effect of hydrothermal alteration due to the proximity of the granites.

#### 5.2.7. North Devon Basin — Middle to Upper Devonian

The Middle to Upper Devonian North Devon Basin domain consists of a succession from slates (e.g. Ilfracombe Slates) to sandstones (e.g. Baggy Sandstone) as the east–west striking sediments young to the south (Leveridge and Hartley, 2006). The general east–west strike is apparent in the principal component map (Fig. 4) and the green appearance of the slates in the north does transition to more purple tones in the south in recognition of the sandier composition. The geochemical signature of the domain (Fig. 5) shows some interesting features. In comparison to the Devonian sedimentary domains of South Devon and Cornwall the Middle to Upper Devonian North Devon Basin has higher concentrations of Si, Zr, Hf and REEs. The domain's most distinctive feature is its low Ca concentration, which is lower than that of any other domain. These enrichments suggest a generally shallow marine environment with abundant terrigenous sediment input containing resistate minerals. The reason for the low Ca is unclear, but may provide a clue to sediment provenance or indicate poor habitat conditions for potential biogenic carbonate producers in the North Devon Basin.

#### 5.2.8. North Devon Basin — Lower Devonian

The Lower Devonian North Devon Basin is dominated by the Hangman Sandstone formation: a continental fluvial fan deposit of 'Old Red Sandstone' (Tunbridge, 1984; Tunbridge, 1986; Leveridge and Hartley, 2006). Its appearance on the principal component map (Fig. 4) is bluish purple, indicating the coarse, mature nature of the sands, and aligned

closely with the axes of Zr and Hf. This alignment ties in with the domain's elemental geochemical signature (Fig. 5): it has the highest Zr, Hf (and Si) content of any domain, representing the sandy composition of the domain, rich in resistate minerals. Low concentrations of Sr coincide with low concentrations of Ca, Na and Rb to suggest a relative absence of carbonate and feldspar minerals.

### 5.3. Carboniferous foreland basin sediments

#### 5.3.1. Culm Basin — Crackington Formation

The Crackington Formation consists of interbedded quartz-rich sandstone greywacke and pyrite rich shaley mudstone deposited during the Namurian and Westphalian epochs (Leveridge and Hartley, 2006) which are interpreted to have been deposited in a largely anoxic environment (Brenchley and Rawson, 2006). In the principal component map (Fig. 4) it appears as fairly homogeneous green, at least in its main southern part, and is in fact the closest domain to the component 2 endmember, broadly indicative of an argillaceous composition. The geochemical signature of the domain (Fig. 5) reveals a greatly elevated concentration of Mo and lesser concentration of Co coinciding with low concentrations of Br, Ca and Mg. The Mo spike can be taken as an indication of the anoxic depositional environment (Emerson and Huested, 1991) while the Co concentration suggests a fine grained composition. The low concentrations of Br (and to a lesser extent Ca and Mg) suggest a lower salinity (brackish or fresh water) depositional environment than that of the Devonian sediments.

#### 5.3.2. Culm Basin — Bude and Bideford Formations

The Bideford Formation only forms a minor constituent of this domain, striking east–west along the western half of the northern boundary. It consists of coarsening-up sedimentary cycles, from black mudstone to feldspathic sandstone (De Raaf et al., 1965). The Bude Formation conformably overlies the Crackington Formation and is dominated by thick beds and amalgamated units of feldspathic sandstone that are believed to have been deposited in a lacustrine environment (Higgs, 1991; Leveridge and Hartley, 2006; Leslie et al., 2008). On the principal component map (Fig. 4) the domain appears as a fairly unique dappled light blue-green colour representing its position in the principal component space: low in component 1 and approximately equal in components 2 and 3. The geochemical signature of the domain (Fig. 5) is best defined by its very low Se and Br concentrations, also accompanied by low Ca and Mg and high Si, Na and Ba. The high concentrations of Si, Na and Ba indicate the siliciclastic, feldspar rich mineralogy of the domain, while, as in the Crackington Formation, the low concentrations of Br, Ca and Mg indicate the brackish to fresh water depositional environment. The low Se values suggest that the domain is very poor in organic material (De Vos et al., 2006).

### 5.4. Post-variscan sediments

#### 5.4.1. Permo-Triassic Sediments

The Permo-Triassic Sediments domain consists of a range of mapped breccia, sandstone and mudstone lithologies that fall within the 'New Red Sandstone Supergroup' (Laming, 1968), and most of which are specifically assigned to the Exeter Group (Edwards et al., 1997). The domain appears mostly in varying shades of purple on the principal component map (Fig. 4) in accordance with the predominantly sandy composition. The geochemical signature of the domain (Fig. 5) is characterised by high Cs and Sr concentrations (accompanied by high Si, Ba and Ca) and low ferromagnesian elements such as Co, Sc, Ni, V, Fe and Mg. These enrichments suggest the presence of evaporites, and the high Si and low ferromagnesian concentrations indicate predominantly felsic mineralogy for the siliciclastic component of the sediments. The high Cs concentrations can be taken as an indication that some of the material in this domain is derived from the erosion of the Cornubian Batholith.

### 5.4.2. Cretaceous and Tertiary Sediments

The Cretaceous and Tertiary Sediments domain mostly consists of the tertiary sediments of the Bovey and Petrockstowe Basins, both of which lie along the NW–SE striking Sticklepath fault zone that cuts through the north of Dartmoor. These basins contain kaolinitic clays, lignites and sands (Edwards, 1976). The Cretaceous component of the domain consists of a limited extent of Upper Greensand Formation and Buller's Hill Gravel Member to the north east of the Bovey Basin, east of Dartmoor (Jackson and Green, 2003). In the principal component map (Fig. 4) the domain does not appear to stand out from its neighbours: the Petrockstowe Basin appears bluish like the surrounding Bude Formation, the Bovey Basin appears green like the surrounding Devonian basin sediments and the Cretaceous exposure appears purple like the Permo-Triassic sediments it overlies. This appears to be another example of cross-contamination from nearby domains due to the sample catchments spanning domain boundaries. Even so, the geochemical signature of the domain (Fig. 5) does exhibit features that are not just an average of neighbouring domains: Rb and K concentrations are the lowest of any sedimentary domain and Zr and Hf concentrations are higher than any neighbouring domains. Si is also high. These characteristics would appear to suggest a zircon-rich, siliceous composition for the domain as a whole, which is lacking in K-feldspar or K-feldspar derived clays.

## 6. Conclusions

G-BASE stream sediment geochemical data contains a huge amount of geological information. In contrast with traditional geological survey methods, the geochemical survey data is not limited by the availability of outcrop, and is highly consistent and sensitive to compositional variability. These aspects of the data give it great potential to enhance and unify regional geological interpretations. However, our methods in this paper have highlighted the limitations of using stream sediment geochemical data 'as is' for any spatially dependent analysis, particularly at fine scales. The development of mapping methods which account for the upstream sourcing of the sampled stream sediment material would allow sharper interpretations to be made.

The use of compositional principal component analysis has been demonstrated as a very effective method of data analysis for this type of geochemical data. The approach followed has a number of advantages, which allow the geochemical contrasts between domains to be gauged in a way that could be considered to be optimal: compositional validity was maintained; each element was weighted equally, each domain was weighted equally and dimensionality could be reduced all as part of the same process. This allowed each domain's relative geochemical signature to be visualised in ternary principal component space, on a ternary RGB coloured map, and in real element terms by back-transformation from the full principal component space.

Despite the broad scale and limitations of the survey methods, the data analysis has been able to reveal numerous geochemical features of geological interest. Many of these support previously published geological interpretations, but some add detail in the form of new geochemical interpretations that may not have been considered in the past. For example, the Crackington Formation's very low Br concentrations suggest that it was deposited in brackish or fresh waters; an interpretation that seems to have only previously been made for the overlying Bude Formation. The Crackington Formation is also very distinctly enriched in Mo relative to the other sedimentary successions of the region, which provides hard geochemical evidence for anoxia during its deposition. The pronounced low Se concentration of the Bude Formation is also noteworthy and may provide important palaeoenvironmental evidence. General geochemical differences between the Carboniferous and Devonian sedimentary domains serve to highlight the contrasts in their depositional environments and should be combinable with evidence from geological field surveys to reinforce and improve understanding of the tectonic history of the region.

It is also worth considering that while the geology of south west England is much studied and generally well understood, similar methods of data analysis applied to surface geochemistry in lesser-mapped regions could significantly enhance geological understanding.

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