Geochemistry of Caesium and Fluoride in Cornwall and Devon: Evidence from TellusSW

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The TellusSW geochemical survey provides comprehensive data on concentration of Cs in stream sediments, soils and water as well as fluoride in waters. Devon and Cornwall are one of the most enriched areas in Cs in Western Europe. This reflects Cs concentration in fine-grained granite of west Dartmoor, late stage Li-F rich granites in St Austell, Tregonning and Dartmoor bodies, which are also enriched in Ta, as well as concentration in reworking of granitic and acid volcanic material in early Permian sediments. Fluoride water highs are sourced in these Li-F rich granites, younger F vein mineralisation as well as forming a broad high in mid-Devon, spatially related to the occurrence of lamprophyres and the late Permian Littleham Mudstone Formation

Caesium, although high in granites, is particularly enriched in the aureoles of these granites, notably in meta-basic rocks. These enrichments are evidence for the passage of Cs-rich fluids through the aureoles. Fluoride in water does not in general exceed World Health Organisation guidelines, with the exception of limited mineralised areas in west Cornwall and on Lundy Island.

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Introduction

Caesium and Fluorine are known to be enriched in some late stage granites in SW England (Bowler, 1958; Fuge and Power, 1969; Fuge *et al.*, 1992), as is caesium in early Permian sediments (Merefield 1981). Merefield (1986) further proposed that caesium could be used as an indicator of the source and diagenesis of Permo-Triassic sediments. There are limited data on the distribution of the elements in the surface environment of SW England; Fuge and Andrews (1988) showed that F is enriched in soils and waters of the china clay areas of Cornwall and Devon as did Fuge *et al.* (1992) for Cs in the St Austell area.

The limited data on the spatial distribution of the two elements was significantly supplemented in 2014 with the release of the TellusSW geochemical data set (TellusSW, 2014). The aim of this contribution is to discuss the spatial distribution of these elements from these new data and examine their distribution in relation to the evolution of late stage granites, their associated mineralisation and their distribution within Permo-Triassic sediments using mainly soil, stream sediment and water samples.

The two elements are chosen for discussion because of their association with lithium-rich granites. Tantalum and niobium are also known to be enriched in these granites but their distribution in TellusSW stream sediments has been previously discussed in Moon (2015), so is not covered in detail here. Also Ta and Nb are largely contained in relatively insoluble minerals (Scott *et al.*, 1998) and would not be expected to disperse far from their source in the secondary environment. No fluorine analyses are available for soils and stream sediments due to cost considerations detailed below but available fluoride in water is discussed. This will not reflect all fluorine in rock (Boyle, 1982) but will reflect some of its distribution as demonstrated by Fuge and Andrews (1988).

General geochemistry

Caesium is the heaviest of the stable alkali metals and has a large ionic radius, rendering it incompatible with most rock forming minerals. It can make limited substitution for K in K-feldspar and mica. Caesium forms few minerals of which it is an essential component. These minerals mainly result from late-stage volatile activity, particularly in lithium-caesium-tantalum pegmatites (London, 2005, 2008). The most important Cs mineral is pollucite. Although natural caesium is not recorded as a pollutant, its artificial isotopes ^{134}Cs and ^{137}Cs, derived from nuclear fission, are. Their presence from nuclear bombs tests as well as the Chernobyl and Fukushima incidents has led to very detailed studies of Cs mobility (Qin *et al.*, 2012). These studies showed that Cs is fixed in interlayer sites in clay minerals in the fine grained portion of mineral soils but Cs is much more mobile in organic peaty soils (Staunton *et al.*, 2002).

Fluorine is the lightest of the halogen elements and forms a number of common minerals such as fluorite and topaz as well as substituting for OH in apatite, muscovite and a range of other micas and amphiboles (Wedepohl, 1978).Fluorine is released as fluoride during weathering but its solubility is limited by the formation of fluorite, so its concentration is often inversely proportional to that of Ca^{2+} (Ander *et al.*, 2005).

Caesium has not been routinely determined in geochemical surveys due to its low abundance (upper crust average ~ 2.6 ppm) and relatively high detection limit (often 4 ppm by XRF before 1995). However improved XRF methodology as well as routine adoption of ICP-MS methodology has led to its determination in multi-element suites. Flourine is also underrepresented in multi-element databases as it is not possible to determine background level F in soils or stream sediments by XRF or ICP-MS. Most routine determinations are undertaken using an ion selective electrode after sample fusion, which is a relatively expensive method. However, fluoride determination in waters is relatively straightforward, either by ion selective electrode or by ion chromatography, and has been widely applied.

TellusSW and GBase Geochemical Data

Results from the TellusSW soils and stream sediment samples were released to complement those of the TellusSW airborne geophysical survey (TellusSW, 2014). Gbase stream sediment data are also available for the rest of Great Britain from the British Geological Survey (BGS), including the rest of SW England (Gbase, 2017).

Stream sediment, water and soil geochemistry were obtained using samples collected and analysed using standard GBase protocols of BGS (Johnson, 2005). Stream sediment and soil samples were analysed using X-ray fluorescence on pressed pellets. TellusSW stream sediment samples have also been analysed by a lithium metaborate fusion ICP-MS method by Acme Analytical (now Bureau Veritas); elements determined by this method include Cs (AcmeLab, 2017). Water samples were analysed by a variety of methods; trace elements were determined by ICP-MS, major elements and some other trace elements, including F by ion chromatography (Rawlins *et al.*, 2003).

Soil data were used as point locations but stream sediment data and waters for the TellusSW area were plotted as drainage catchments derived from point data kindly provided by BGS. These catchment plots are much more indicative of the overburden sources of the sediments than plotting as points or contouring as used in the TellusSW website (Moon, 1999). Catchments were generated using Bluesky 5 m resolution DTMs (Bluesky, 2014) using the Hydrology functions of ArcGIS 10.2 and manually checked for consistency before linking to the TellusSW attribute geochemical data.

Water data for the TellusSW survey were collected in two campaigns: 2002 and 2012/3. These have very different background chemistries due to the very different weather conditions. In order to compare them the two sets were levelled using the method of Daneshfar and Cameron (1998). The whole of the Tamar catchment north of 70500N was compared with an area within a box for the remainder of the survey bounded by 120000 N and 200000 and 265000E. The 2002 set was then regressed against the 2012/13 data using 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95 percentiles, which ignored outlying data. The overall water data used was thus 2002 data levelled to, and appended to 2012/13 data.

Caesium Distribution

Wide-spaced data from the FOREGS survey of Western Europe show that SW England is one of the most enriched areas in Cs in Europe (Salminen, 2005). Enrichment in soils (up to 47 ppm Cs relative to median 3.7 ppm; total extraction, ICP-MS) in common with other media (stream sediments and waters) also occurs in areas underlain by Variscan granites, such as NW Iberia, the Massif Central and Erzgebirge, and in Permian sediments.

Partial data are available at a more detailed scale for Britain. Stream sediment samples collected for the British Geological Survey's Gbase programme (which includes TellusSW samples) have been analysed for Cs by XRF since ~1995. Compilation of available data (16527 samples) for eastern and southern England (Table 1, Fig. 1) shows the strong enrichment of Cs in SW England, discussed in detail below, with moderate enrichment in the Cretaceous Wealden Beds and the Jurassic Kellaways and Oxford Clay formations.

Plots of TellusSW stream sediment, soil and water samples for Cs (Figs 2–4) show the enrichment of Cs in areas overlying granite and early Permian sediments, notably in the Crediton Trough. These areas are further discussed in turn below. Both fusion ICP-ES and XRF stream sediment data for the TellusSW samples were examined. Results are similar but XRF results are shown in Fig. 2 as these are slightly more comprehensive.

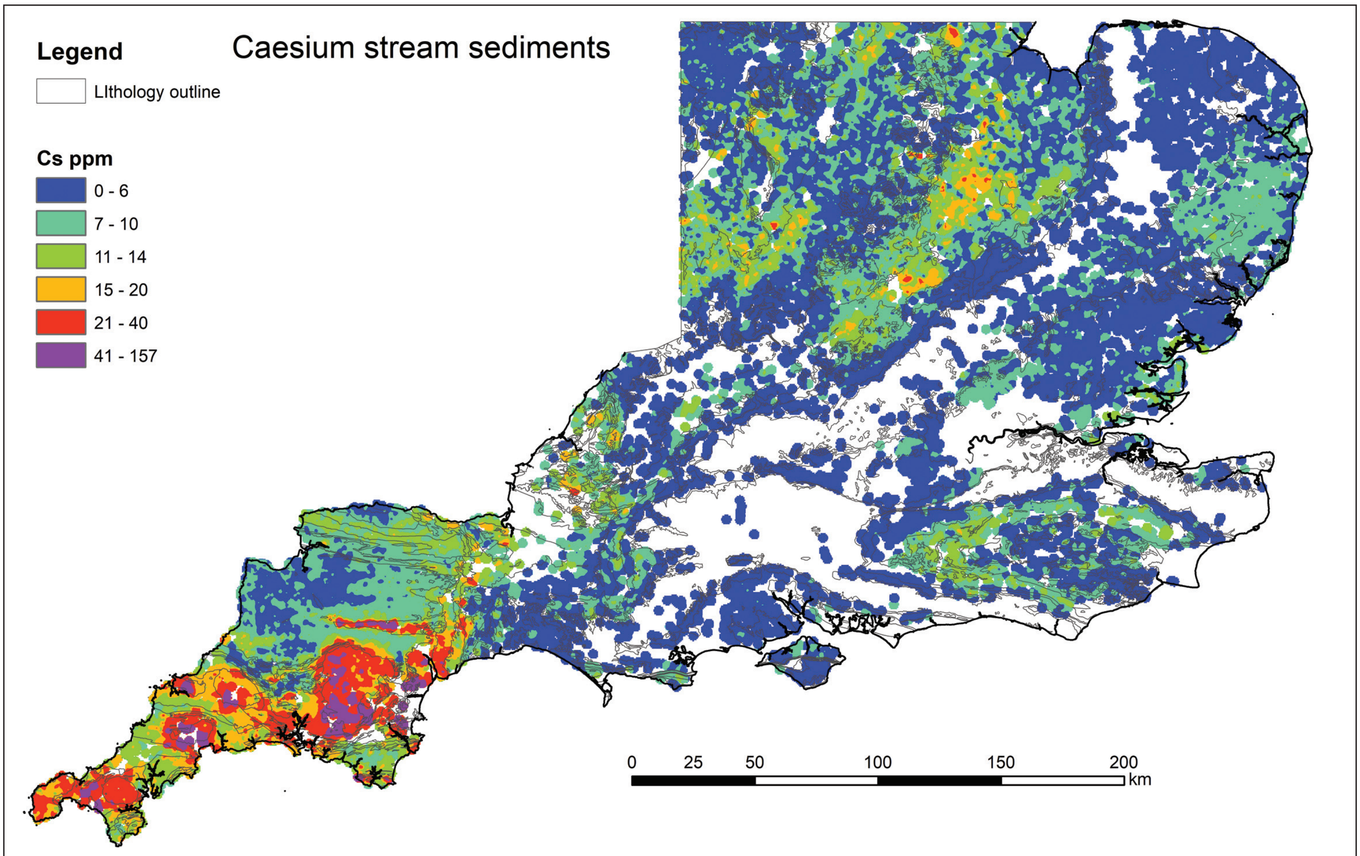

Figure 1. *Regional stream sediment geochemistry caesium. Geological outlines from BGS 1:250 000 mapping. Grid size 500 m, search radius 2000 m, inverse distance weighting. Number of samples 16527.*

	Number	Min	Max	mean	median	X_{25}	X_{75}	X_{90}	X_{95}	X_{99}
All Gbase stream sediments Cs ppm	16527	<1 (0.1)	166	7.9	6	3.4	9.5	14	20	40
TellusSW stream sediments Cs ppm	3765	<1 (0.1)	166	14.3	10	6	17	28	39	70
TellusSW soils Cs ppm	1149	2	240	15.1	10	7	17	29	38	74
TellusSW Waters Cs ng/ml	3769	<.001	11.4	0.27	.071	.018	0.261	0.65	1.08	3.28
TellusSW Waters F ng/ml	3769	<5	2007	57	29	46	68	99	129	204

Table 1. *Summary statistics of TellusSW Cs stream sediments, soils and waters and F waters as well as all Gbase Cs determinations. X_{25} is 25 percentile.*

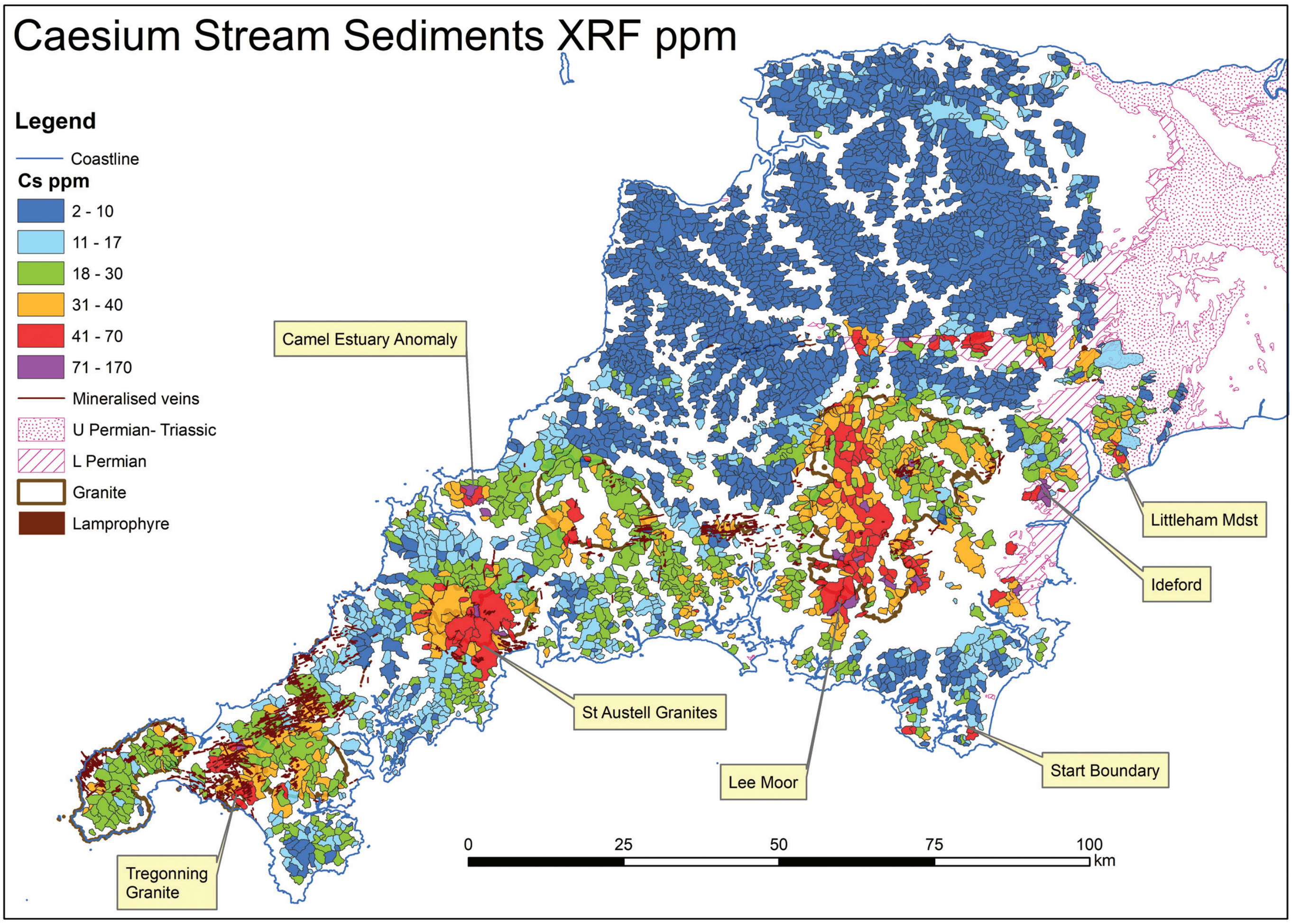

Figure 2. *Stream sediment caesium: TellusSW. Geological outlines from BGS 1:50 000 mapping. Sources: TellusSW(2014) and Digimap (2017).*

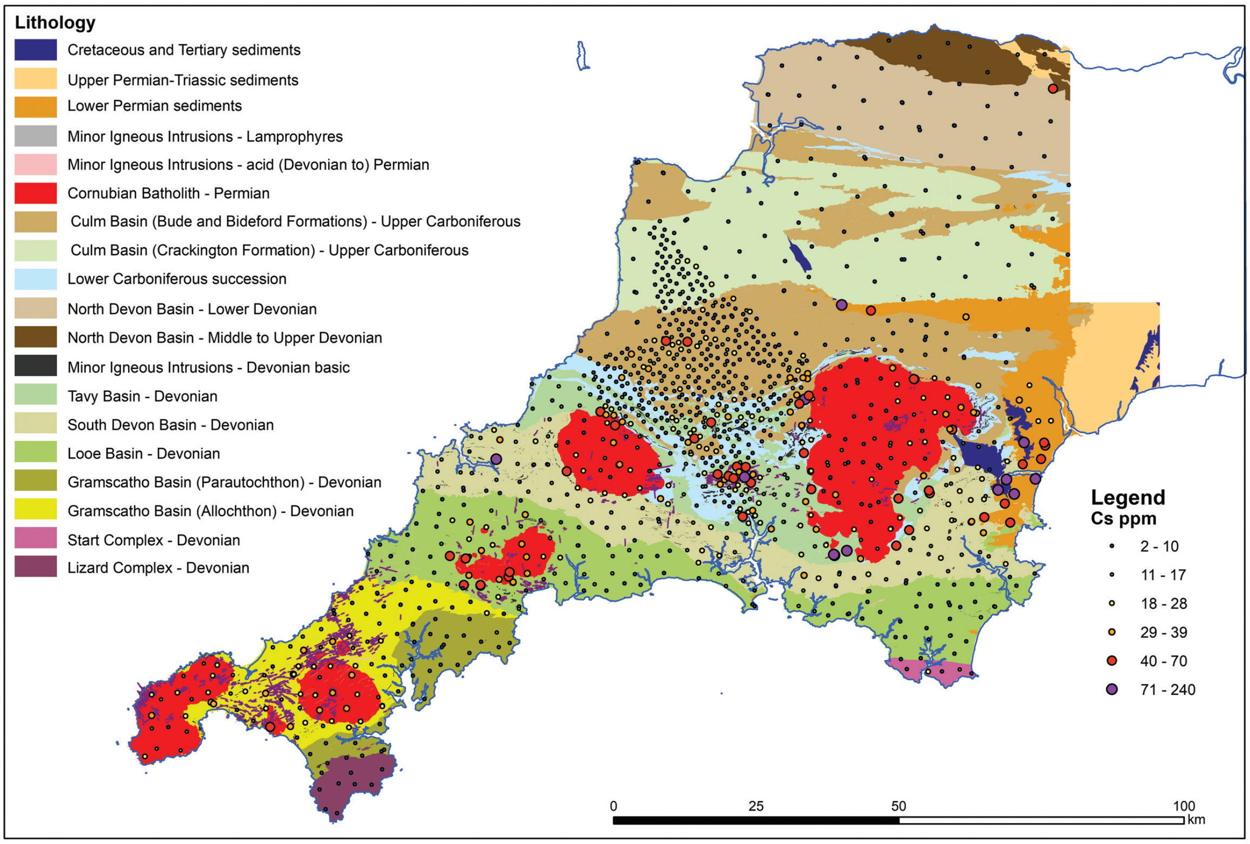

Figure 3. *Soil caesium TellusSW. Geological domains modified from Kirkwood* et al. *(2016). Other sources: TellusSW(2014) and Digimap (2017).*

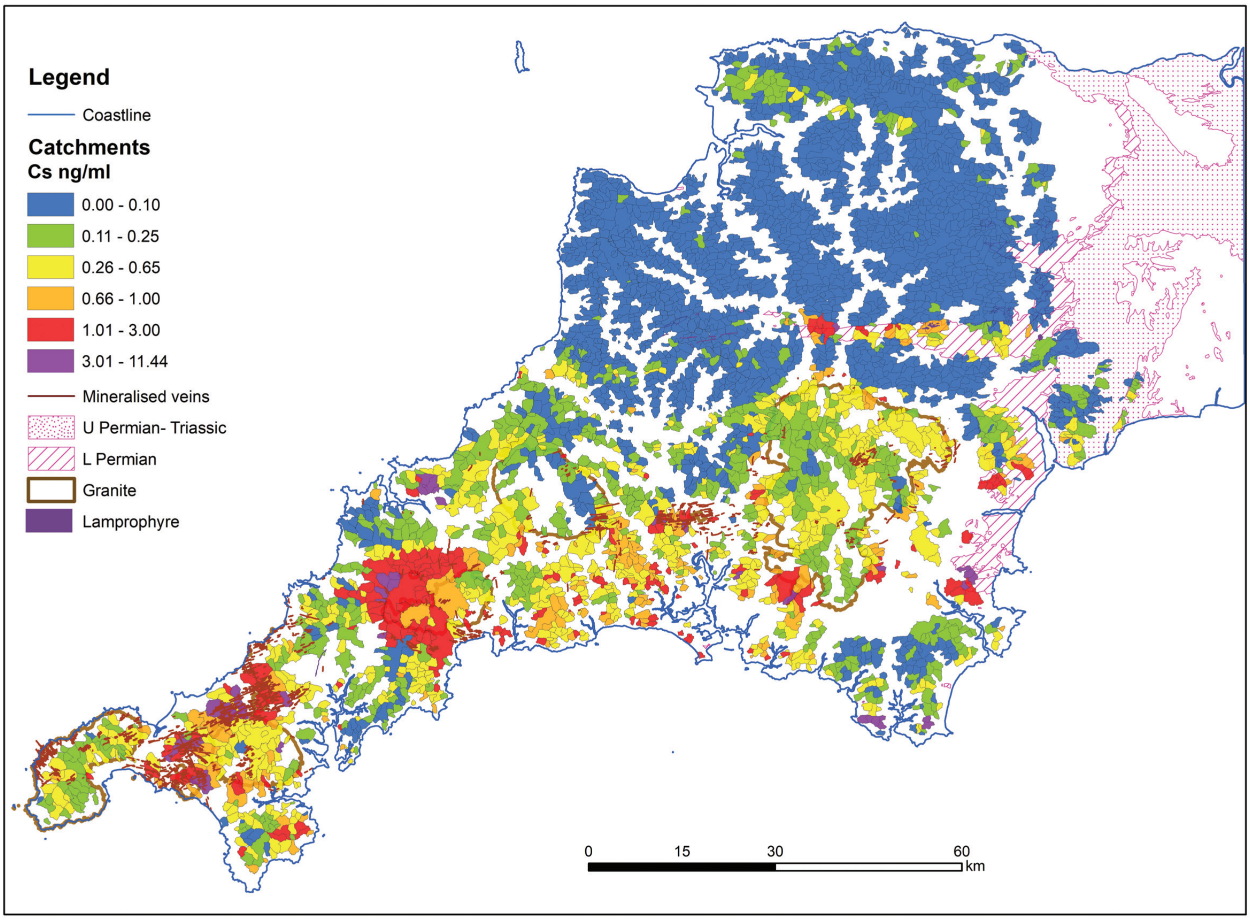

Figure 4. *Water caesium: TellusSW. Data are levelled to 2012/13 data (see text). Geological outlines from BGS 1:50 000 mapping. Sources: TellusSW (2014) and Digimap (2017).*

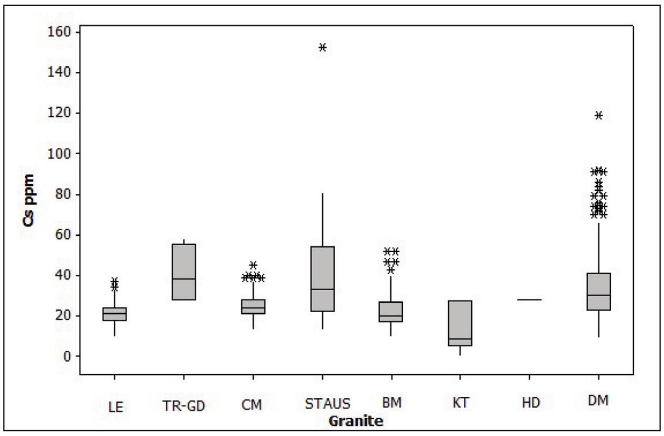

Figure 5. *Boxplot of Cs versus granite pluton, stream sediments. LE = Land's End Granite, TR-GD = Tregonning Godolphin Granite, CM = Carnmenellis Granite, STAUS = St Austell Granite, BM = Bodmin Moor Granite, KT = Kit Hill Granite, HD = Hingston Down Granite, DM = Dartmoor Granite.*

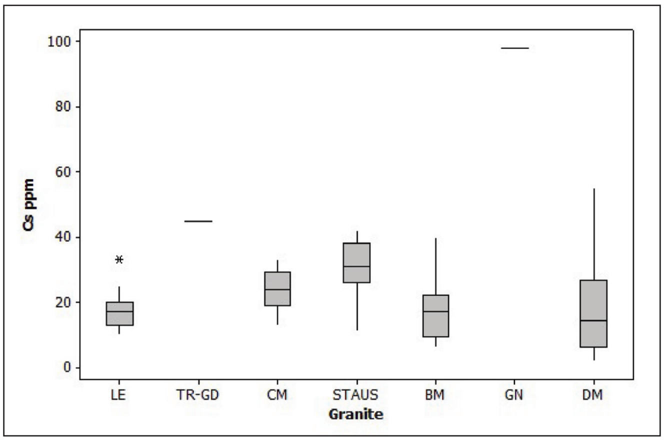

Figure 6. *Boxplot of Cs versus granite pluton, soils. LE = Land's End Granite, TR-GD = Tregonning Godolphin Granite, CM = Carnmenellis Granite, STAUS = St Austell Granite, BM = Bodmin Moor Granite, GN = Gunnislake Granite, DM = Dartmoor Granite.*

SW England Granites

Although all granites appear to be enriched in Cs (previous rock data shown in Table 2) there is aconsiderable variation between them and between sample media. These data were compared with the texture maps of Dangerfield and Hawkes (1981) and airborne geophysical data of TellusSW (Moon, 2015). Extraction of stream sediment data sourced from within individual granites using the Intersect function of ArcGIS (corrected for small slivers) shows (Fig. 5) that the younger granites (Land's End, Tregonning, St Austell, (?)Hingston Down, Dartmoor) of Chesley *et al*. (1993), Chen *et al*. (1993) and Stone (2000) are enriched relative to the older granites (Carnmenellis, Bodmin Moor, Kit Hill). The Dartmoor Granite appears particularly enriched. Similar plots for soil are shown in Figure 6

Dartmoor Granite and Aureole

There is a distinct contrast between soil and stream sediment results. The latter shows a clear division into the west and SE parts which are enriched and a less enriched in the NE part. The Cs stream sediment enriched parts of the granite correlate with the poorly megacrystic and fine-grained granites of Hawkes (1982). This area has a moderate enrichment in Ta (5–10 ppm) in stream sediments but appears distinct from the higher enrichment in Ta (12–80 ppm) associated with the topaz-granite Lee Moor area of Knox and Jackson (1990). In contrast, the soil sample results are lower in the western part of the granite probably reflecting Cs mobility in peaty soils. The limited Cs rock data of Chappell and Hine (2006) confirm Cs enrichment (69–93 ppm Cs) in the western part of Dartmoor although they observed considerable inhomogeneity in this area of the granite.

Dartmoor Granite Aureole and Meldon Aplite

Pegmatitic veins in the Meldon aplite are known to contain the only occurrence in the UK of the main economic Cs mineral, pollucite (von Knorring and Condliffe, 1984). It occurs together with petalite, columbite-tantalite, microlite, fluorite as well as orthoclase and quartz. Merefield (1981) reports a whole rock analysis of 223 ppm Cs in the aplite from Exeley and Stone (1982). According to Edmonds *et al*. (1968) the aplite is only mappable for a strike length of ~350 m and has a thickness of ~20 m although Worth (1920) claimed the dyke could be

Granite and # determ-inations	Dart moor Granite 7	Bodm-in Moor Granite 3	St Austell: Biotite granite 2	St Austell: Lithium mica-Tourmaline granite 11	St Austell: Topaz granite 3	Carnm enellis Granite 7	Tregon ning Granite 2	Land's End Granite 7	Overall mean published 25(Cs), 11 (F)
Caesium: Range ppm	28-93	40-78	32-52			38-52	121-183	28-52	
Caesium: Mean ppm	53	53	42			44	152	40	50
Fluorine: Range %	0.06-0.26	0.28-0.39	0.24-0.25	0.26-0.98	0.59-1.45	0.22-0.27	1.28-1.57	0.16-0.62	
Fluorine: Mean %	0.18	0.32	0.25	0.63	1.03	0.25	1.43	0.29	0.25

Table 2. *Selection of caesium and fluorine determinations by granite. From Chapell and Hine (2006), except St Austell non-biotite granites from Manning* et al. *(1996) and Tregonning Granite from Stone (1992). Overall means are from a compilation of Chappell and Hine (2006) and refer to pre-2006 analyses.*

mapped SW to Sourton, 3 km SW. The main aplite has not been sampled by the TellusSW surveys, although its extension in the Sourton area has a moderate Cs anomaly in stream sediments (30 ppm Cs) as well as 3 soil samples of 36–38 ppm Cs along strike (Fig. 7). Further along strike, 5 km SW, a soil sample reports 95 ppm Nb and 6 ppm Ta overlying a mapped chert band suggesting presence of undetected Nb-Ta rich aplitic material.

Surprisingly the Meldon Aplite area is not as strongly anomalous in Cs as other areas in the Dartmoor Granite aureole. Although this pattern is difficult to discern in the stream sediment data, as many catchments contain both granite and aureole rocks, Cs distribution is clear in the limited soil samples. A cluster of 3 samples south of Meldon, over a strike length of 3 km immediately NE of Lydford report 62–79 ppm Cs and are spatially associated with calc silicate derived by contact metamorphism of basic rocks. A similar bedrock control is apparent in the most enriched area of the Dartmoor aureole, 0.6–2.6 km E of the Hemerdon Granite (Fig. 7) where soil samples vary from 129–240 ppm Cs. Three enriched soil samples (52–64 ppm Cs) occur on the SE aureole and also appear associated with meta-basic bedrock.

Gunnislake, Hingston Down, Kit Hill Granites

The area underlying these granites is not well sampled by stream sediments although there is some enrichment of the areas draining northwards (Fig. 2). Soil sampling is more systematic and shows enrichment from 40 to maximum of 98 ppm Cs overlying the Gunnislake Granite. Some of these samples are also enriched in Ta, notably up to 18 ppm near Devon Great Consols mine.

Bodmin Moor Granite

Although Bodmin Moor is not fully sampled by stream sediments, there is limited enrichment in the SW and NE of the pluton. The NE of the granite is also high in soil samples although not the SW, perhaps because Cs has been leached from peaty soils in a comparable manner to West Dartmoor.

St Austell Granite and Aureole

The western part of the St Austell Granite is enriched in Cs in all media. Soil samples from TellusSW report 30–40 ppm Cs over the granite which are comparable with those reported in whole soil samples by Fuge *et al.* (1992) although lower than those in the clay-sized fraction (up to 169 ppm Cs}. The western granite is known to be composite from the work of Manning *et al.* (1996), who differentiate topaz granite, lithium-mica granite and three types of tourmaline granite. Caesium appears to be particularly enriched in the lithium granites from the data of

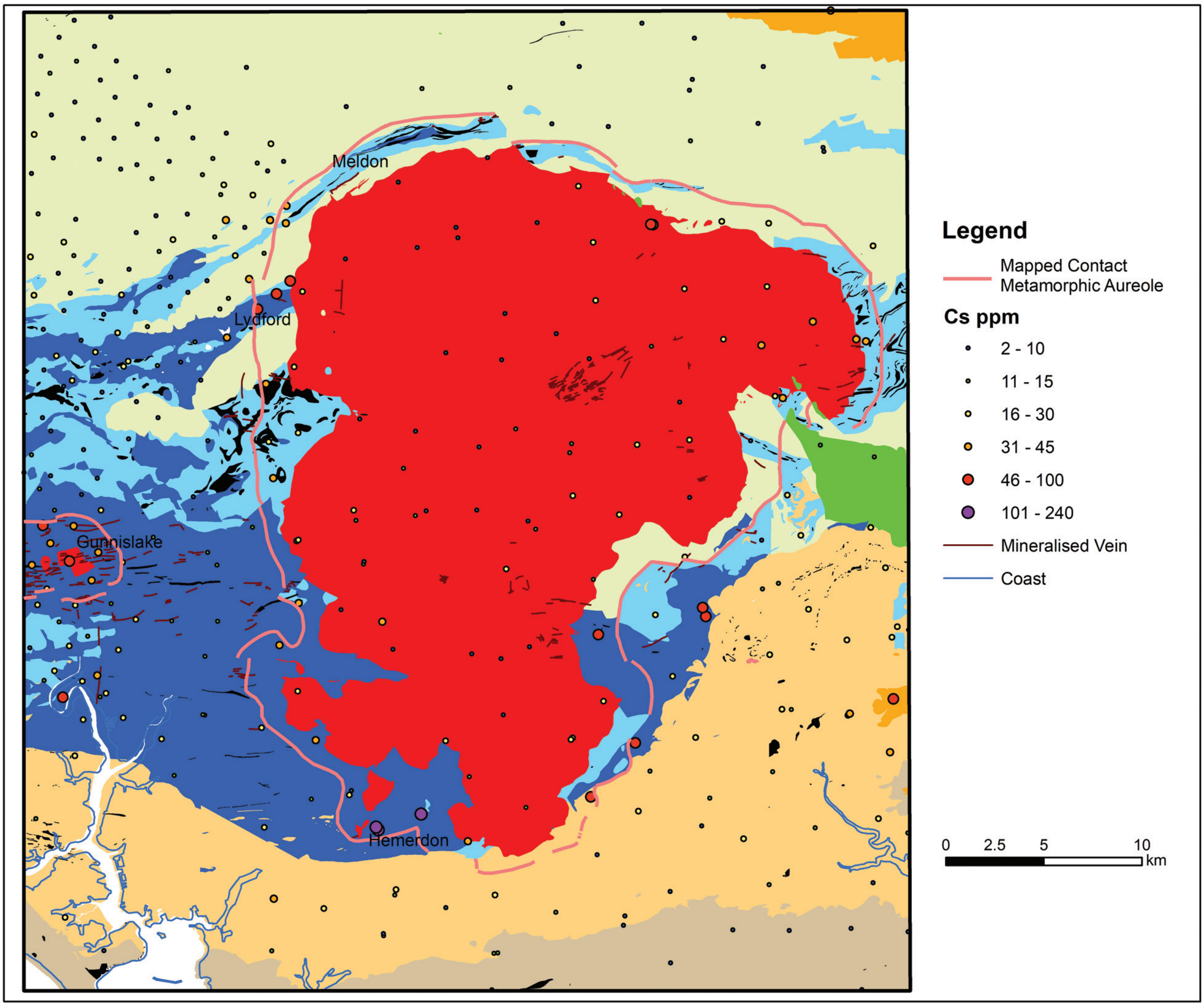

Figure 7. *Detail of Dartmoor Granite and Aureole Soils. Geological domains modified from Kirkwood* et al., *2016. Key in Figure 4. Other sources: TellusSW (2014) and Digimap (2017).*

Fuge et al. (1992) although they did not break down their granite analyses by type and did not sample the topaz granites. The TellusSW stream sediment samples also do not use small enough catchments to allow subdivision by granite type.

Soils from both TellusSW soils and the data of Fuge *et al.* (1992) show strong but inhomogenous enrichment in the aureole to the S and W of the granite. TellusSW waters also show strong enrichment in the St Austell Granite aureole but particularly to the NW of the granite. These catchments include the Treliver area where some of the extensive drilling of 2013–2014 in search for Sn were analysed for Cs amongst other elements using a Na_2O_2 digestion and ICP-ES/MS analytical finish. Analysis of the 564 samples (mainly reverse circulation chips) show a strong correlation of Cs with Mg (Fig. 8) as well as K, Rb, Tl and Li. From geological logs Cs is mainly concentrated in amphibole rich calc-silicate lithologies probably representing metamorphosed impure tuffs or limestones; These are within 350 vertical metres of the granite contact (Treliver Minerals, 2015).

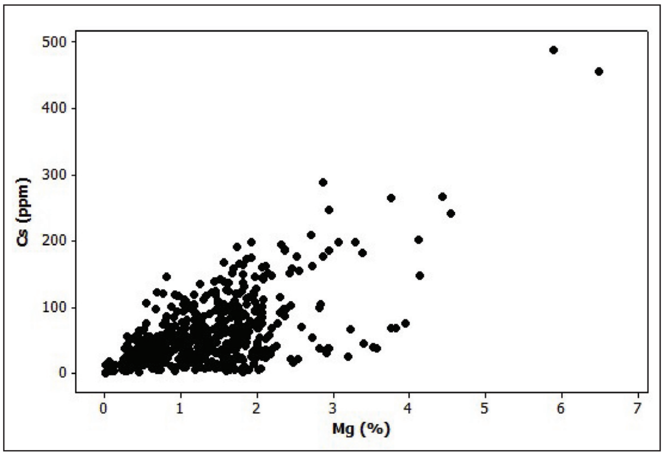

Figure 8. *Scatterplot of magnesium vs caesium, Treliver drill samples. Source: Treliver Minerals (2015).*

West Cornwall

Caesium is less enriched in stream sediments and soils than in Dartmoor or St Austell, with the exception of catchments draining the Tregonning (Li-rich) Granite, and the area running SW from Carn Brea to the buried Bosworgy Granite. The latter granite has a mean Cs content of 89 ppm (Ball *et al.*, 1998).

Camel Estuary

The area to the east of the Camel Estuary is enriched in Cs in all media (Figs 2–4). These anomalies are coherent, reaching 101 ppm Cs in stream sediments and 6.9 $ngml^{-1}$ in waters 2 km east of St Minver. Soil samples in the area reach 77pm Cs in the TellusSW dataset and 104 ppm Cs for another sample taken independently by Knight (2015) using the Gbase protocol. Although the anomaly is confirmed by Knight's samples, follow-up has found no obvious source. The catchments mainly drain pink siltstones of the Polzeath Formation which are intruded by altered dolerites and dykes mapped as elvans (BGS, 1994). These are cut by an unmapped N–S feature which appears to correlate with a deep SE–NW major fracture on the airborne magnetic survey of TellusSW (TellusSW, 2014). Field checking with a portable XRF used Rb as a proxy for Cs was un-calibrated on the instrument. Analysis of a representative shale returned ~200 ppm Rb and < 100 ppm Rb in the altered dolerite whereas a chemical analysis of the nearby elvan was 12 ppm Cs and 178 ppm Rb. A further possible explanation is an eroded, but unrecognised, Permian outlier.

Permo-Triassic Sediments

Stream sediment sampling of areas underlain by Permo-Triassic sediments is patchy due to lack of surface drainage. However, the Crediton Trough is clearly distinctly enriched relative to the surrounding Carboniferous sediments. Areas underlain by early Permian Exeter Group sediments in the Torbay area are also high in Cs, in particular, an area immediately N of the Teign Estuary. Soil sampling in these latter two areas is more systematic and confirms Cs contents of 52–80 ppm S of the Teign Estuary dropping to ~40 ppm Cs N of the estuary, with the exception of a spot high of 166 ppm Cs, 2 km E of Ideford. Soil samples in the Crediton Trough show strong enrichment two samples in the W of the structure with a maximum of 148 ppm Cs, 1 km E of the Sticklepath Fault. These are generally comparable to the whole rock samples of Merefield (1981) although he reported a maximum of 181 ppm Cs in the Ness Beds (Teignmouth Breciia). Caesium is lower in areas overlying upper Permian-Triassic sediments with the exception of areas overlying the Littleham Mudstone which have Cs contents of 30-50 ppm Cs. This pattern extends NE of the TellusSW data and is shown in Figure 1.

Start Boundary

Stream sediment Cs shows 48–60 ppm overlying and S of the Start Boundary Fault. These could represent recently removed Permian sedimentary rocks as suggested slightly further north by Leake *et al.* (1992).

Fluoride Data

TellusSW Fluoride Distribution

The TellusSW data (levelled to 2002) show (Fig. 9) trends that reflectbedrock geology although there appears to be some influence of topography and proximity to the sea, similarly to trends observed in the Gbase F water data for Wales (BGS, 1999). Rawlins *et al.* (2003) found a correlation of F with Na and Cl in the 2002 results, linking to this to the influence of sea spray. This observation appears unduly influenced by an outlying data point but there is some limited evidence of this in the overall (2002 and 2012/3) data. In these, higher concentrations of F (~100 ng ml^{-1}) are present in the west facing coasts, notably in Penwith, and these do correlate with Na and Cl highs. Calcium concentrations are generally low (< 200 ng ml^{-1}) and there does not appear to be re-precipitation of fluorite in these surface waters as discussed by Ander *et al.* (2006).

The highest F concentrations (> 200 ng ml^{-1}) reflect bedrock of topaz-bearing granites of St Austell and Lee Moor as well as the lithium-rich Tregonning Granite. Other mineralised areas with granite bedrock reflected in this class are in St. Just, Camborne-Redruth, the Caradon area of Bodmin Moor and the Kit Hill-Hingston Down area, all known to carry fluorite (Carruthers and Pocock, 1922). Two areas known to contain cross-courses mineralised in fluorite are delineated in the Menheniot and Bere Alston areas (south of Gunnislake on Fig.10). Other catchments with >200 ng ml^{-1} occur on the S and W of the Crediton Trough in contrast to lower F concentrations that are more typical of other areas underlying other Carboniferous sediments. These enriched catchments are spatially associated with the outcrop of lamprophyre dykes east of the Tamar River, although these dykes are not known along strike of the anomaly W of the Tamar River. This arc of higher concentrations continues to the E of the Exe estuary where bedrock is the Littleham Mudstone Formation. The early Permian sedimentary rocks appear generally low in F,in contrast to the later Permian-Triassic sediments which are higher, similar to the higher concentrations observed in the Gbase water data for Wales (BGS, 1999).

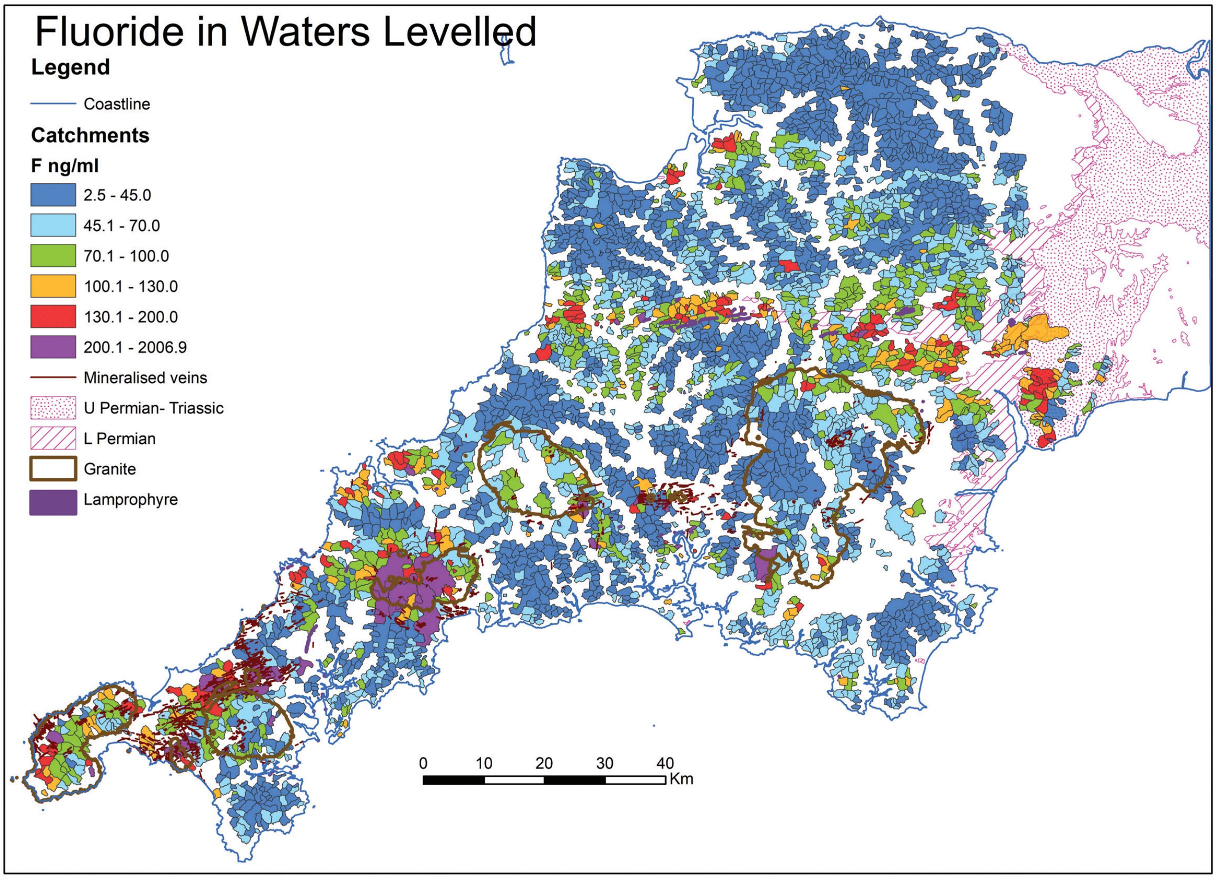

Figure 9. *Water fluoride: TellusSW. Data are levelled to 2012/13 data (see text). Geological outlines from BGS 1:50 000 mapping. Sources: TellusSW (2014) and Digimap (2017).*

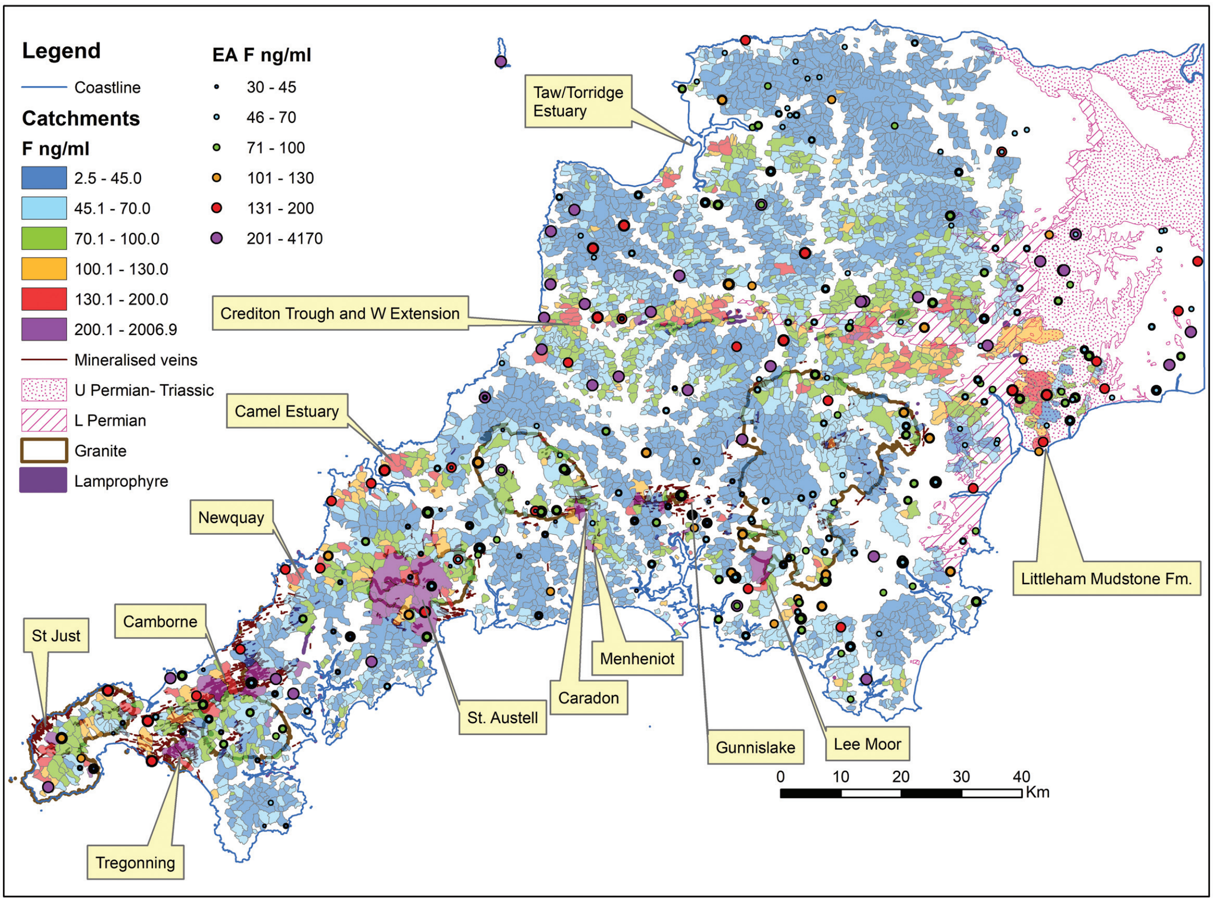

Figure 10. *Water fluoride: TellusSW and Environment Agency Monitoring Data as points. TellusSW data are levelled to 2012/13 data (see text). Geological outlines from BGS 1:50 000 mapping. Sources: TellusSW (2014) and Digimap (2017).*

Environment Agency Fluoride Data

The Environment Agency conduct sampling for water quality at a number of sites in Devon and Cornwall on a routine basis. Figure 10 shows a summary of 7615 samples collected from 2000–2017 typically on a six monthly basis. Although there is considerable temporal variation and samples represent both groundwater and surface water, the overall pattern can be used to compare with the TellusSW results and is general similar. In Devon, high F concentrations are found overlying Permo-Triassic sediments E of Exeter as well as in a broad belt paralleling the Crediton Trough. In addition, the SW area of the Dartmoor Granite, as well as rivers draining the W of the St. Austell Granite, mineralised areas of Camborne-Redruth including the Carnon River, are all high in F. Coastal areas of west Cornwall, as far N as the Camel, have moderate enrichment in F. The overall pattern is thus similar to that of the TellusSW F data with the exception of large rivers with large composite catchments.

Discussion

Lamprophyres and Fluoride

The F water anomaly largely hosted in Carboniferous sediments to the S of, and parallel to the Crediton Trough is previously unreported. It spatially correlates with the mapped extent of lamprophyre dykes. Although these dykes and associated volcanics of the Exeter Group have been geochemically investigated (Leat *et al.*, 1986; Edwards and Scrivener, 1999), F has rarely been quantified. Leat *et al.* (1986) mention F concentrations of >0.5% and >0.9% F from two potassic lava samples but other chemical data are lacking. The only other study is anelectron microprobe investigation of Jones and Smith (1985) who reported concentrations of 2–5% F from mica and 3.5–4.8% F from apatites in minettes. It is thus clear that lamprophyres have significant F content and could explain these F in water anomalies, although further work is required to confirm this.

Granites

The TellusSW data confirm the association of Cs and F with late stage granites in Devon and Cornwall. High caesium is particularly associated with the known lithium-rich younger granites of St Austell, Tregonning and SW Dartmoor, termed tourmaline (lithium) or topaz granites (Hawkes *et al.*, 1987; Floyd *et al.*, 1993; Manning, 1998; Simons *et al.*, 2017). Lithium was not determined on the TellusSW samples although a coarse map for comparison can be found in Webb *et al.* (1978). Tourmaline granites appear to be co-genetic with the biotite granites (Manning, 1998) but there is debate whether topaz granites are directly related to biotite granites depending on the postulated source of F and trace alkalis. Stone (1992) favoured remelting of biotite granite whereas Manning and Hill (1990) favoured re-melting of the biotite granite source. Tantalum is another element which appears to delineate fractionated and lithium-rich granites and is useful for comparisonwith Cs and F because tantalum's immobility in the surface environment restrict its dispersion.

The TellusSW data show Cs (and Ta) is also enriched in the west part of Dartmoor reflecting the occurrence of poorly megacrystic and fine grained granites. Chappell and Hine (2006) sampled this latter granite phase and confirmed the higher Cs, Li and Ta. They further suggested that these are more fractionated and a distinct phase from east Dartmoor and coarse granites in west Dartmoor. This is contrast to Hawkes (1982) who regards them as one phase based on field mapping, but is in accord with the earlier work of Brammall and Harwood (1932). Both Cs and F detect the topaz granites of Knox and Jackson (1990) even though these have limited outcrop in the SW Lee Moor area.

The Kit Hill, Hingston Down and Gunnislake Granites are enriched in Cs and partly in F and Ta indicating they are more similar to west Dartmoor than Bodmin Moor, although there is indication of Ta as well as F enrichment on the Caradon area of the latter granite.

Both the St Austell and Tregonning Granite are enriched in Cs and F which reflect known mapped lithium and topaz granites. The Carnmenellis Granite is generally low in Cs and F although a zone on the NW of the granite which SW extends to the buried Bosworgy Granite is enriched, suggesting that this is a separate intrusive phase. The limited data from Tregonning are in agreement with a recent study of Breiter *et al.* (2018) of the coastal section of the Tregonning Granite which showed a strong correlation of Cs (~200 ppm Cs) with Li and F in leucogranitic and aplitic sheets.

Granite Aureole

Highest Cs concentrations in the TellusSW surveys are found in granite aureoles.This is in accord with the studies of Bowler (1957) and Ball *et al.* (1998). Bowler concluded that Cs (together with F) invariably increased in traverses from unaltered country rock towards a granite contact. He found that Cs was hosted in biotite in the aureole, in contrast to a feldspar host in granite. Stone and Awad (1988) showed enrichment at the granite contact but found it limited to ~1 min the Tregonning Granite and 4 m in the Porthmeor area in Penwith. Ball *et al.* (1998) discussed longer traverses at Redmoor, Hemerdon and Bosworgy. They found that Cs (and Rb) increased from background at 300–500m from the granite toward the granite contact. However, this increase was erratic depending on the nature of the pelite and they recommended using K/Cs and K/Rb ratios to smooth the trend. They also reported very high concentrations of Cs in greenstones within 200 m of the granite contact at Hemerdon. The TellusSW data highlight the concentration of Cs in meta-basic lithologies. The detailed analyses from Treliver show a correlation of Cs with Mg suggesting the Cs is hosted in mica or amphibole, although further work is required on this. The nature of transport of Cs (and other ions) was discussed by Ball *et al.* (1998), who suggested that micro-fracturing was most favourable pathway although they also suggest diffusion was possible. Observation on drill-cores at Treliver supports the micro-fracturing theory as fluids appear to have moved along a major fault into micro-fractures which cut the metapelites and basites. These fractures also appear to have permitted the transport of boron and tin-rich fluids.

Mineralisation

Caesium highs appear to mainly reflect lithologies and meta-basic lithologies rather than mineralisation whereas some F highs reflects vein mineralisation. This signature seems to be ofboth higher temperature mineralisation in Camborne–Redruth as well lower temperature type in Menheniot and Bere Alston. This latter cross-course vein type often has local shale metal sources so it is not unlikely that F is mobilised from F-rich lithologies such as in Bere Alston where the F-rich vein is adjacent to a lamprophyre.

Permo-Triassic Sediments

The TellusSW data show that Cs is enriched in the early Permian sediments of the areas from Ideford south to Brixham, as well as the Crediton Trough, confirming the observations of Merefield (1981). In addition, the Littleham Mudstone Formation and area of the Start Boundary fault were also identified as enriched in Cs. Merefield (1981) found high concentrations in acid volcanic clasts within the early Permian sediments and took this as the most likely source of Cs for the sediments as his Dartmoor Granite samples were low in Cs (22 ppm). The TellusSW data indicate another potential source of the Cs enriched fine-grained western part of the Dartmoor

Granite, although acid volcanics originally overlying the Dartmoor Granite would still most likely provide the major source. There is however no evidence for general Cs enrichment in Devonian sediments as suggested by Merefield (1981). This distinctive enrichment in Cs overlying Permian sediments would be useful in identifying areas where these lower Permian sediments have been removed by erosion as in the Start Bay area. A preliminary investigation shows a close correlation with the distinctive hummocky geomorphological expression of these sediments on the Lidar images and in the field. The enrichment of Cs and F in the Littleham Mudstone Formation is of unknown host and requires further work although the unit is known to be enriched in metals, notably U, V and Cu (Carter, 1931; Bateson, 1987).

Fluoride highs over Permo-Triassic sediments appear to reflect mudstones as the Sherwood Sandstone is low (BGS, 1999; Bearcock and Smedley, 2012).

Environmental Implications

There is considerable debate as to whether F is an essential element for human health but it is clear that moderate concentrations of F of ~1 mgl^{-1} prevent dental caries and a guideline of 1.5 mg l^{-1} has been set by the World Health Organisation above which the occurrence of Fluorosis should be monitored. This guideline is only exceeded in the Camborne–Redruth area for the TellusSW data and in the Environment Agency data for the River Carnon in Cornwall and on Lundy Island for Devon. This latter anomaly reflects a F-rich Tertiary granite. Ander *et al.* (2016) reported an excess of F in three private water supply samples of undisclosed location in Cornwall.

Conclusions

The TellusSW surveys have provided considerable new data on the distribution of Cs and F in Cornwall and Devon. Fluoride forms an E-W anomaly across Devon which appears to mark the sub-crop of lamprophyric intrusions. Caesium is concentrated in later granite phases, both lithium-tourmaline and topaz rich, and is correlated with Li and to some degree with Ta. However unlike Ta, Cs is released from the granite into their aureoles and can be concentrated in meta-basic rocks in these aureoles, probably as a result of fluid movement along micro-fractures and then being captured in biotite or amphibole. Fluoride in stream water detects known fluorine-rich granites and also some vein mineralisation, notably in Camborne–Redruth, Menheniot and Bere Alston.

Caesium is concentrated in early Permian sediments in the area between Brixham and the Teign Estuary as well as the western Crediton Trough, as a result of reworking of granitic or acid volcanic material, derived from Dartmoor or volcanic rocks originally overlying Dartmoor.

Caesium and fluoride have few environmental implications, with the exception of limited surface waters in intensely mineralised areas of west Cornwall and on Lundy Island.

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