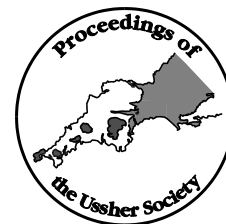# Baseline geochemistry of Devonian low-grade metasedimentary rocks in Cornwall: preliminary data and environmental significance

P.W. Scott[1], K.S. Reid[1], R.K. Shail[1] and R.C. Scrivener[2]

Geochemical baseline data provide information on the state of the environment before modification by mining and other anthropogenic activities. A summary of the analyses of 41 elements on 100 samples from Devonian metasedimentary rocks away from areas of mineralization and granite intrusions in Cornwall are presented. The data show a remarkable consistency. Differences in major elements can be related largely to changes in mineral proportion expected from grain size variations within the sedimentary rocks. The trace element data indicate that similar types of sediment accumulated in the Gramscatho, Looe and Trevone basins and that subsequent metamorphism has not significantly re-distributed elements. Compared with an average UK Lower Palaeozoic shale and the North American Shale Composite, the Devonian metasedimentary rocks of Cornwall appear to be marginally depleted in many trace elements. Values for As, Ni and Cr frequently exceed published soil guideline values, especially in mudstones, which brings into question the issue of the identification of land, which is considered to be polluted.

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INTRODUCTION

Baseline geochemical information is extremely important in a region such as Cornwall, where there has been extensive polymetallic mineralization (e.g. Sn, W, As, Cu, Pb, Zn), largely related to magmatic-hydrothermal veins associated with Variscan granite plutons. In addition to the natural geochemical anomalies resulting from the interaction of these ore deposits with the surface environment, over 2000 years of mining and mineral processing has led to a re-distribution of many elements at and near the present-day land surface. Geochemical baseline data enable the unmodified state of the surface environment to be documented, and they provide a datum against which any changes can be measured (Darnley, 1997). They also provide guidance to those policy makers who are concerned with environmental issues and educate those groups who have an interest in establishing an understanding of what constitutes pollution.

This work presents preliminary results from an ongoing study to establish a geochemical baseline for the Devonian low-grade metasedimentary rocks in Cornwall. It has been achieved by sampling and analysing Devonian successions that, as far as possible, are remote from the effects of metasomatism and magmatic-hydrothermal mineralization adjacent to the granites and elvans. As such it is primarily an assessment of how sediment provenance, diagenesis and low-grade regional metamorphism determine the lithogeochemistry of these successions. Work is also in progress to assess the extent to which contact metamorphism, metasomatism and magmatic-hydrothermal mineralization subsequently modified the lithogeochemistry in areas adjacent to the granites. Collectively, these processes are expected to account for most of the natural variation within the Devonian successions of Cornwall; *in situ* weathering will also be locally significant. Anthropogenic effects are not considered. The data presented in this study are compared with an average UK Lower Palaeozoic shale (Jones and Plant, 1989) and the North American Shale Composite (Gromet *et al.*, 1984), and a commentary on the environmental significance of the data is given.

PREVIOUS WORK

A number of previous studies have focussed upon the contact metamorphic, metasomatic and magmatic-hydrothermal processes affecting the distribution of a limited number of elements in the low-grade metasedimentary rocks immediately adjacent to the Cornubian batholith, e.g. Bowler (1958), Floyd (1967), Mitropoulos (1982), Beer and Ball (1986), Stone and Aswad (1988), Ball *et al.* (1998), Ball *et al.* (2000) and Ball *et al.* (2002). In contrast, few studies have addressed the more general variations in lithogeochemistry. Henley (1974), in a pioneering study, presented a summary of 96 chemical analyses, for 10 major and 25 trace elements, of Devonian metasedimentary rocks sampled across the boundary between the Gramscatho and Looe basins in the Perranporth area. At least 12 geological factors were considered to potentially influence the geochemical
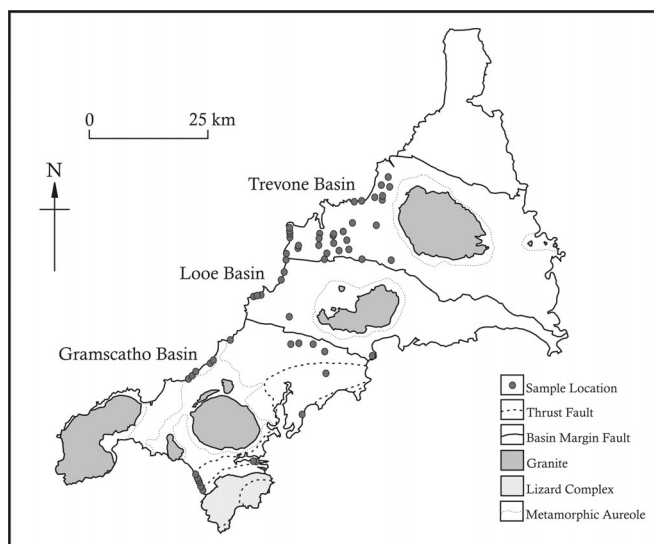

Figure 1. Simplified geological map of Cornwall and sample locations.

composition, but contact metasomatism and mineralization accounted for some of the variation due to the proximity of the study area to the granite. The role of provenance in determining the lithogeochemistry of Gramscatho Basin sandstones in areas remote from the granites has been evaluated by Floyd and Leveridge (1987) and Shail and Floyd (1988); however, mudstones and some elements of environmental significance such as As were not analysed.

GEOLOGY

The geochemical data presented in this work are from analyses of lithostratigraphical units within the Devonian Looe, Gramscatho, and Trevone basins (Isaac *et al.*, 1998; Leveridge *et al.*, 2002) (Figure 1). The Looe Basin contains the Lower Devonian Dartmouth and Meadfoot groups; these are dominated by mudstones and sandstones that were deposited in alluvial, lacustrine and shallow marine environments and are associated with penecontemporaneous volcanic rocks. Collectively these record the early stages of continental rifting (Leveridge *et al.*, 2002). The Gramscatho Basin also initiated during Lower-Middle Devonian rifting, but the majority of the succession of deep marine mudstones, sandstones, conglomerates and volcanic rocks accumulated during renewed Upper Devonian rifting and the subsequent early stages of Variscan convergence (Isaac *et al.*, 1998). The Trevone Basin initiated during Middle-Devonian rifting and continued to develop through subsequent Upper Devonian and earliest Tournaisian rift episodes (Isaac *et al.*, 1998; Selwood *et al.*, 1998). It comprises a deep marine mudstone-dominated succession with some volcanic rocks. It has recently been proposed, on the basis of re-mapping in the Plymouth area, that the Trevone Basin comprises two separate basins: the South Devon Basin and the Tavy Basin (Leveridge *et al.*, 2002).

All of these sequences underwent low-grade regional metamorphism and deformation as a consequence of Variscan convergence during the Carboniferous and the areas sampled include rocks of both anchizone and epizone (Warr *et al.*, 1991; Andrews *et al.*, 1998). Granite emplacement during the Early Permian (Chen *et al.*, 1993) brought about contact metamorphism, metasomatism and widespread magmatic-hydrothermal mineralization (Scrivener and Shepherd, 1998). Some epizone rocks outside of the mapped contact aureoles probably achieved this grade due to contact metamorphism and fluid advection above granite at depth.

SAMPLING, ANALYTICAL PROCEDURE AND QUALITY CONTROL

100 2-3 kg samples of low-grade metasedimentary rocks, categorised as sandstone, siltstone, or mudstone, were collected from locations in the three Devonian sedimentary basins that were, as far as possible, remote from mapped contact aureoles and magmatic-hydrothermal mineralization. Whilst every effort was made to collect the freshest possible material, all samples had undergone minor weathering. Samples were cleaned to remove obvious weathered parts, crushed and pulverised using a chrome steel mill before analysis by ICP-MS at Acme Analytical Laboratories in Vancouver, Canada using a 4-acid digestion process. The major minerals present in the samples were determined using a Siemens D5000 powder X-ray diffractometer.

The geochemical analytical procedure involves the digestion of 0.25 g of sample powder by a solution of 18:10:3:6 HCl-HF-HClO$_4$-HNO$_3$, heated to fuming on a hot plate and taken to dryness (Acme Analytical Laboratories, 2002). The residue is dissolved in dilute (15%) aqua regia of 2:2:2 HCl-HNO$_3$-H$_2$O heated in a boiling water (>95° C) bath for 30 minutes. Acme's quality assessment / quality control protocol requires simultaneous digestion of two regent blanks randomly inserted in each batch. The sample solutions are aspirated into a Perkin Elmer Elan 6000 ICP mass spectrometer to determine 41 elements: Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hf, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Sn, Sr, Ta, Th, Ti, U, V, W, Y, Zn, Zr. Further quality control samples in the form of duplicates, local standards and reference samples were submitted along with the sample batches. One duplicate, standard and reference sample per fifty samples was submitted. The reference sample (SDO-01) was sourced from the USGS, originating from the Huron Member of the Ohio Shale near Morehead, Kentucky (Kane *et al.*, 1990).
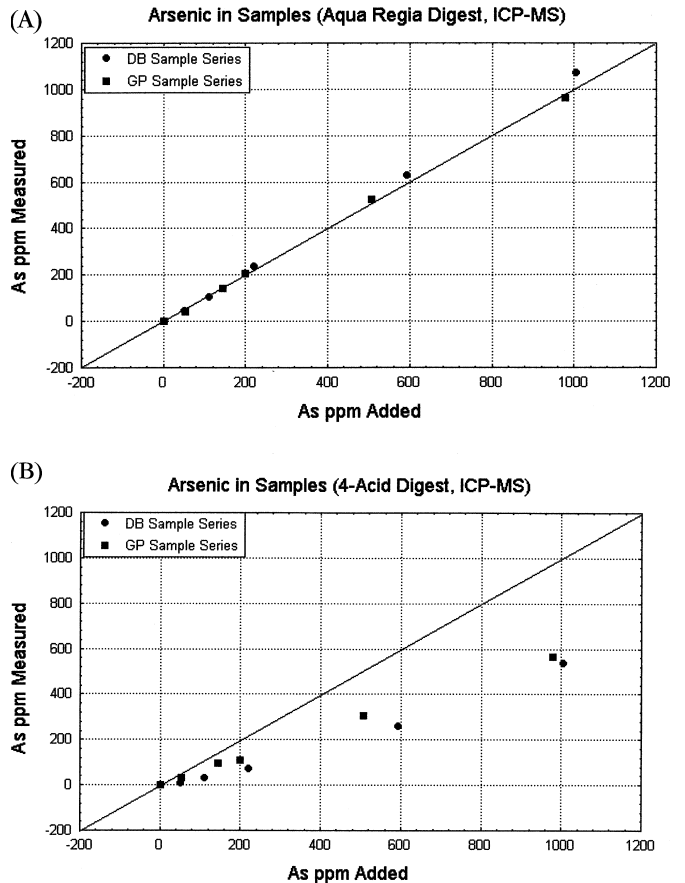

Figure 2. Arsenic data for samples of Delabole slate (DB) and Grampound Grit (GP) spiked with successively greater amounts of arsenopyrite and measured by (A) aqua regia and (B) 4-acid digestion processes.

The data for all measured elements for the reference sample were within the range of accepted analytical error quoted for the reference (Kane *et al.*, 1990), except for As and Ba. For these two elements the analytical results from an initial batch of samples showed under-reporting in the reference sample, compared with the published USGS data (Kane *et al.*, 1990). For arsenic, the problem is in the 4-acid digestion process where the element has a tendency to volatilise during fuming. In order to determine the amount of arsenic lost in this process, five samples each of Delabole Slate and Grampound Formation sandstone were spiked with varying amounts of arsenic from arsenopyrite, then submitted for ICP-MS analysis by 4-acid (total) and aqua regia (partial) digest. The latter procedure is known to digest As within minerals, and no fuming stage is required before determination by ICP-MS. It is not as sufficiently aggressive to digest completely many other elements compared with the 4-acid process. Thus is not suitable for universal adoption. The comparative data for the spiked samples are show in Figure 2. A good correlation between the amount of As added and the aqua regia digestion data is found. It appears that a systematic under-reporting by around 30-40% in As occurs with the 4-acid digestion process. Although the reported results below for As are those measured (i.e. not adjusted), it should be recognised that the true values should be elevated by around 30-40%.

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Ba showed consistent under-reporting for the reference sample (SDO-01) using both the 4-acid and aqua regia digestion process (34±1 ppm measured, against the certified 397±38 ppm for the reference). This suggests that the reference sample contained barite which is known to be insoluble with the 4-acid digestion process. Measured amounts of Ba for the Cornwall Devonian metasedimentary rocks using the 4-acid digestion process are around 400-650 ppm suggesting that the element is located in minerals other than barite, probably feldspar, although the presence of further insoluble barite cannot be discounted.

The measured levels and ranges of Ni and Cr are identical to those found in further, as yet unpublished, data of the authors for sandstones, siltstones and mudstones from the Devonian metasediments in Cornwall determined by the same analytical procedure, but using a tungsten carbide mill for sample grinding. Thus, any addition of Ni and Cr by contamination through the use of the chrome steel mill is considered to be negligible.

	Gramscatho mudstone	Gramscatho siltstone	Gramscatho sandstone	Looe mudstone	Looe siltstone	Trevone mudstone	Trevone siltstone
No.	16	14	3	3	5	48	3
	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD
TiO_2	0.53±0.16	0.31±0.04	0.50±0.18	0.30±0.08	0.30±0.07	0.39±0.13	0.45±0.02
Al_2O_3	15.26±1.23	12.18±1.85	12.22±0.77	16.36±0.23	12.94±2.31	16.09±1.02	16.26±0.73
Fe_2O_3	7.59±1.11	5.41±1.33	4.92±0.22	7.55±0.25	6.10±1.63	7.79±1.04	6.81±0.26
MnO	0.10±0.06	0.06±0.03	0.08±0.01	0.13±0.07	0.14±0.05	0.11±0.06	0.09±0.01
MgO	2.27±0.83	1.34±0.48	2.57±0.92	2.66±0.80	2.32±0.41	2.03±0.24	2.35±0.14
CaO	0.19±0.15	0.15±0.12	1.62±1.29	2.01±3.22	0.43±0.51	0.36±0.64	6.49±2.16
Na_2O	1.51±0.75	0.91±0.94	3.31±0.50	0.78±0.28	0.96±0.58	0.51±0.25	0.65±0.08
K_2O	3.86±0.85	2.62±0.67	1.80±0.45	3.80±0.48	3.07±0.77	4.05±0.35	3.61±0.18
P_2O_5	0.14±0.04	0.12±0.06	0.17±0.02	0.14±0.02	0.12±0.04	0.13±0.06	0.13±0.03
S	0.06±0.02	0.06±0.04	0.05±0.00	0.07±0.03	0.05±0.00	0.09±0.07	0.30±0.10
As	15.3±7.7	10.4±4.6	7.0±1.0	24.3±7.2	15.4±8.9	18.6±10.6	11.0±1.7
Ba	651.2±90.2	461.4±92.7	514.3±156.9	466.0±9.8	453.4±126.6	459.5±67.7	407.7±9.5
Be	2.9±0.8	1.7±0.7	1.7±1.1	3.3±0.6	2.4±1.1	2.9±0.7	2.3±0.6
Bi	0.3±0.1	0.2±0.1	0.1±0.0	0.4±0.1	0.2±0.1	0.3±0.1	0.4±0.1
Ce	37.3±9.9	50.6±11.7	42.7±4.9	51.3±17.8	53.8±23.8	28.0±15.1	56.0±5.2
Cd	0.1±0.0	0.1±0.1	< 0.1	< 0.1	< 0.1	0.1±0.1	< 0.1
Co	19.7±4.9	12.5±5.2	13.0±6.2	18.0±3.6	20.2±6.3	20.8±5.7	18.0±0.0
Cr	123.4±25.9	80.8±21.9	155.4±63.6	115.7±19.3	129.6±14.1	106.6±12.2	101.2±3.5
Cu	36.8±12.2	25.3±17.0	18.63±2.6	29.9±4.5	18.6±9.4	28.2±9.4	28.8±1.6
Hf	3.4±0.3	3.2±0.7	2.1±0.2	3.9±0.4	3.5±0.2	3.7±0.4	3.1±0.2
La	17.0±5.0	23.9±6.1	24.0±4.6	25.3±11.6	30.5±16.4	13.2±7.6	29.9±5.3
Li	110.5±46.1	97.2±48.0	42.6±6.4	150.6±24.9	132.8±36.0	146.6±28.2	106.1±15.5
Mo	0.7±0.7	0.8±0.7	0.7±0.3	0.5±0.2	0.4±0.2	0.5±0.5	0.5±0.1
Ni	57.3±11.7	39.4±12.7	59.4±17.6	65.9±10.9	68.4±18.9	64.8±10.0	64.1±4.5
Nb	9.9±1.6	7.2±0.8	7.2±1.8	6.8±2.3	6.8±1.5	9.0±3.2	11.2±0.3
Pb	21.7±12.0	13.8±6.2	15.0±1.6	19.1±7.0	16.1±10.1	16.0±9.6	22.8±2.5
Rb	115.3±27.1	95.4±27.5	47.3±15.9	124.1±21.2	105.7±19.0	93.6±27.4	141.8±28.3
Sb	1.1±0.6	0.6±0.3	0.7±0.3	1.6±1.3	0.6±0.2	2.5±2.4	0.7+0.4
Sc	11.9±1.9	7.9±1.9	10.0±3.6	14.3±2.1	8.8±1.6	12.1±1.3	11.3±0.6
Sn	3.4±0.5	2.3±0.7	1.4±0.4	2.9±0.6	2.4±0.8	3.1±0.5	3.5±0.2
Sr	74.4±19.2	68.2±29.3	261.7±113.2	82.7±33.9	53.0±17.7	66.5±28.7	283.7±57.1
Ta	0.5±0.1	0.4±0.1	0.4±0.1	0.5±0.3	0.3±0.1	0.7±0.2	0.5±0.1
Th	7.4±1.5	8.4±1.5	7.1±0.3	8.9±2.0	8.4±2.8	5.5±2.2	10.1±1.4
U	2.4±0.4	2.0±0.6	1.9±0.1	2.4±0.3	2.0±0.3	2.5±0.4	2.1±0.1
V	163.2±40.3	87.7±22.5	108.0±23.3	152.3±18.2	103.2±31.9	148.7±15.8	148.3±3.5
W	1.5±1.2	1.1±0.4	1.3±0.3	1.3±0.7	3.9±2.5	1.27±1.3	1.2±0.1
Y	11.7±7.9	9.0±3.3	17.6±1.4	10.8±4.7	13.3±9.7	6.4±3.3	14.8±1.1
Zn	110.8±15.6	86.4±29.5	63.3±5.9	104.7±13.7	91.4±18.0	116.8±25.0	116.0±13.5
Zr	99.5±7.9	94.5±17.4	62.5±8.4	113.0±9.6	102.9±5.3	112.0±12.1	93.6±4.1

***Table 1.** Major, minor and trace element geochemistry of Devonian metasedimentary rocks from the Gramscatho, Looe and Trevone basins. All oxides and S as wt%, others as ppm. SD = Standard Deviation.*

RESULTS

The data are summarised in Table 1, subdivided according to lithology and sedimentary basin. Analyses where one or more trace elements have considerably anomalous values from the mean are not included in calculating the mean, even though data for the other elements are not significantly elevated or depressed. This is to remove any likelihood of the dataset being biased by the effects of hydrothermal mineralization. The outlier values for these excluded samples include: Pb 348 ppm, As 67 ppm and Mo 7.4 ppm, single element anomalous values in three Trevone mudstones: Ni 269 ppm and MnO 0.22% in a Gramscatho Basin sandstone; W 35 ppm in a Gramscatho Basin mudstone; and Zn 293 ppm and Ba 880 ppm in a Gramscatho Basin mudstone. Data for Ag and Au are not presented as values are below the detection limit of the analytical technique. The X-ray diffraction data for all samples show the main mineral phases in varying proportions to be quartz, chlorite, mica/illite, plagioclase, K-feldspar, calcite and hematite.

The unequal distribution of the numbers of samples between the different lithologies and basins within the dataset limits the degree of interpretation possible. However, taken as a whole, the data are remarkably consistent. The major elements (Table 1) show the variations to be expected between mudstones, siltstones and sandstones, Al_2O_3, Fe_2O_3 and K_2O reducing as the grain size of the primary sediment increases. MgO, however, remains at similar levels in the mudstones, siltstones and sandstones probably reflecting the levels of chlorite in all of the samples. CaO is elevated in Trevone Basin siltstones, reflecting a relatively high carbonate component. The trace element data show no major feature of difference between levels in the different basins, which would imply that similar types of sediment accumulated in the different basins and that subsequent metamorphism has not re-distributed elements selectively within basins. Only relatively minor differences occur between mudstones, siltstones and sandstones within each basin.

The range of values for most elements are similar to the data from Henley (1974) and Shail and Floyd (1988). The most significant difference is in Zr. This element is reported at higher levels by both Henley (1974) (median values of 165-256 ppm) and Shail and Floyd (1988) (192-242 ppm). This may be accounted for by the different analytical procedure, and possibly by the incomplete digestion of zircon in the present samples, since Henley (1974) and Shail and Floyd (1988) used X-ray fluorescence spectrometry. Other differences are found between the present data set (Table 1) and that of Henley (1974) who had
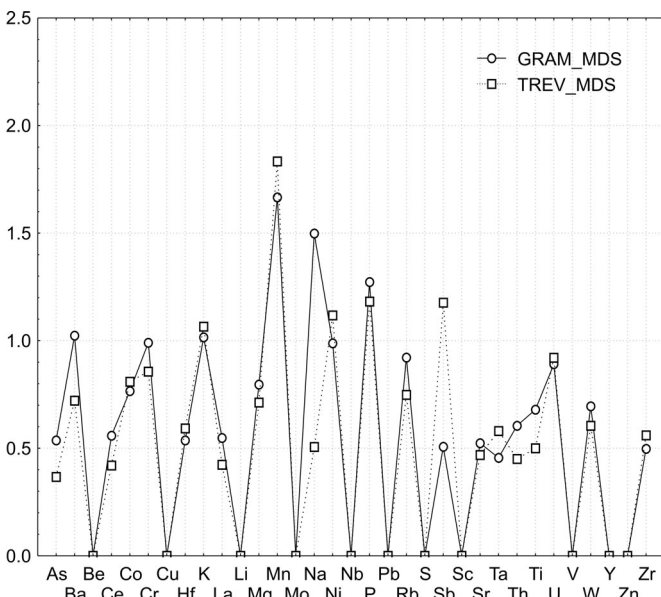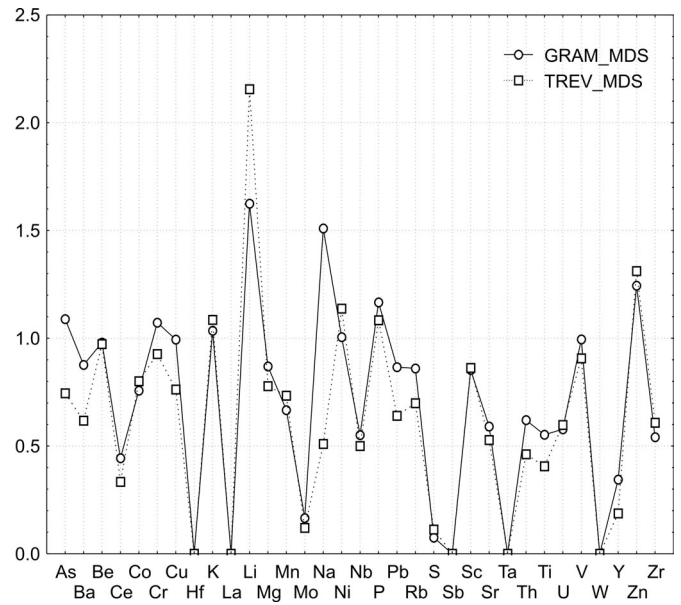

Figure 4. *Geochemistry of Gramscatho and Trevone mudstones normalised to Lower Palaeozoic shale average (Jones and Plant, 1989).*

higher overall values of Sn (median values for different stratigraphic units are 13-22 ppm), Ce (112-133 ppm), Ba (1040-1407 ppm), Pb (43-78 ppm) and Th (27-41 ppm). It is considered that the differences in Sn, Ba and Pb can be accounted for by the effect of mineralization on Henley's samples.

The data for the Gramscatho and Trevone basin mudstones are compared with the North American Shale Composite (NASC) (Gromet *et al.*, 1984), and an average UK Lower Palaeozoic shale (Jones and Plant, 1989) in Figures 3 and 4, respectively. Although all of the differences between the Cornish mudstones and these composite samples are within a narrow range (note the scale is linear), the dominant feature is one of depletion in minor and trace elements. Ce, Mo, S and Y are especially depleted relative to the average Lower Palaeozoic shale. Li is enriched relative to the Lower Palaeozoic shale. Relative to NASC, Mn is enhanced, although there is a discrepancy in the NASC data for this element (Gromet *et al.*, 1984). Major differences between the mean compositions of the two mudstones only appear in Li, Na and Sb, although for all three elements the standard deviations for the data are high.

ENVIRONMENTAL SIGNIFICANCE

The range of the lithogeochemical data for As, Pb, Ni and Cr are shown in Figures 5-9, separated according to grainsize
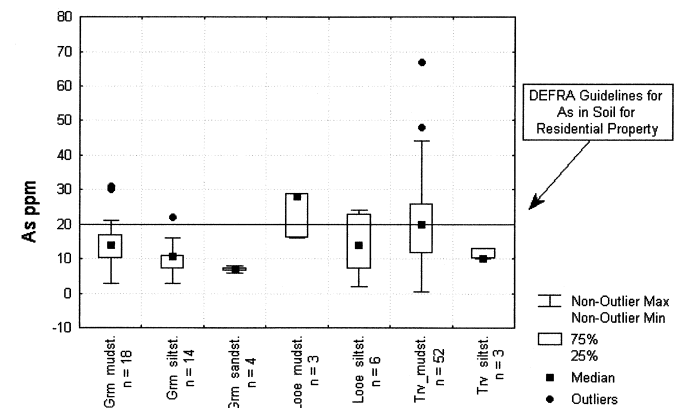

Figure 3. *Geochemistry of Gramscatho and Trevone mudstones normalised to North American Shale Composite (Gromet et al., 1984).*

Figure 5. *Range of arsenic values for samples from Gramscatho (Grm), Looe and Trevone (Trv) basins, showing also SGV for As in residential land with plant uptake.*

(sandstone, siltstone, mudstone) and sedimentary basin. Arsenic in mudstones within the Trevone Basin is further subdivided by formation. The soil guideline values (SGVs) for each element in soil for residential property with plant uptake are also shown (Department for Environment, Food and Rural Affairs, and the Environment Agency, 2002a-e). SGVs are considered a screening tool in the assessment of land affected by contamination. They can be used to assess the risks posed to human health from exposure to soil contamination, and represent 'intervention values' (Department for Environment, Food and Rural Affairs, and the Environment Agency, 2002a-e). To an assessor of contaminated soil, they indicate that concentrations above this level might present an unacceptable risk to the health of site-users (e.g. residents) and that further investigation and/or remediation is required. Although different values for SGVs sometimes apply to other types of land use (allotments, residential without plant uptake, and commercial), those for residential sites with plant uptake are taken here as the most appropriate for rural areas in Cornwall. SGVs supersede earlier guideline data (ICRCL, 1987) which have recently been withdrawn (DEFRA, 2002), although fewer elements are included.

The lithogeochemical data for As show that the SGV is often exceeded, especially in mudstones (Figure 5). Values above the threshold of 20 ppm are found particularly in the Jacket's Point, Tredorn Slate, Trevose Slate and Bedruthan formations of North Cornwall (Figure 6), all samples being taken from sites well away from known mineralization; and, given that the As data are estimated at 30-40% lower than the true values, more samples would exceed the threshold if this correction is applied. The range of data for Pb are wholly below the thresholds, even including extreme values (Figures 7). Many values of Ni, especially in mudstones, and some of the data for Cr exceed the threshold
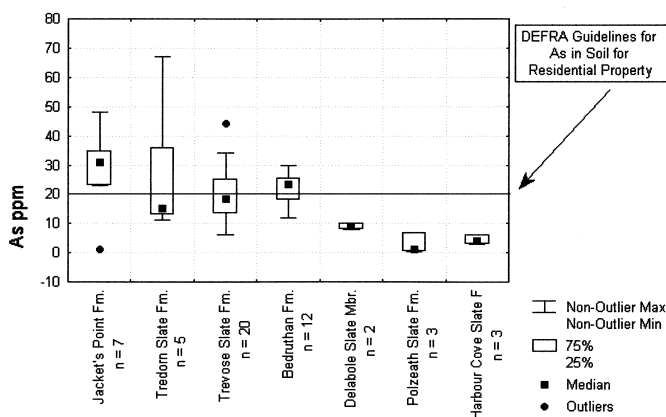

Figure 8. Range of nickel values for samples from Gramscatho (Grm), Looe and Trevone (Trv) basins, showing also SGV for Ni in residential land with plant uptake.

Figure 9. Range of chromium values for samples from Gramscatho (Grm), Looe and Trevone (Trv) basins, showing also SGV for Cr in residential land with plant uptake.

(Ni, 50 ppm; Cr, 130 ppm) (Figures 8 and 9). All measured values for Cd are well below SGVs at all pH levels (pH 6, SGV = 1; pH 7, SGV = 2; pH 8, SGV = 8) (Department for Environment, Food and Rural Affairs, and the Environment Agency, 2002b). Cu and Zn values are significantly lower throughout, compared with the threshold levels (Cu, 130 ppm; Zn, 300 ppm) set by ICRCL (1987).

SGVs are thresholds to indicate soil affected by contamination, and applying such values to lithogeochemistry to indicate contamination in an area is not directly valid. The processes of soil formation can lead to significant depletion of elements, such that some elements above the SGV in the bedrock may be significantly reduced in the soil. However, enrichment may also occur depending on the soil-forming process. Ultimately, only data on the bioavailability of elements can give reliable information about possible health or environmental risks. The present data show that some of the Devonian strata in Cornwall and particularly mudstones in the Trevone Basin of North Cornwall, have a natural enrichment in As and Ni, and to a lesser extent Cr. This brings into question the appropriateness of using set levels of SGVs within Cornwall unless further qualifying criteria are also applied, or if the SGVs are applied rigorously, the present data show the potential for a significant degree of natural contamination within the county. Arsenic in NASC (28.4 ppm) (Gromet *et al.*, 1984) also exceeds the threshold, as does Ni in both NASC (58 ppm) and the average Lower Palaeozoic shale (57 ppm) (Jones and Plant, 1989). Arsenic in the average Lower Palaeozoic shale (15 ppm) is below the threshold. Cr is only marginally below the threshold in NASC (124.5 ppm) and the average Lower Palaeozoic shale (115 ppm). Thus, it appears that the SGVs for these elements are set at inappropriate levels, which are within the range of values typically found in mudrocks.

Figure 6. Range of arsenic values for samples from Trevone Basin mudstones, showing also SGV for As in residential land with plant uptake.
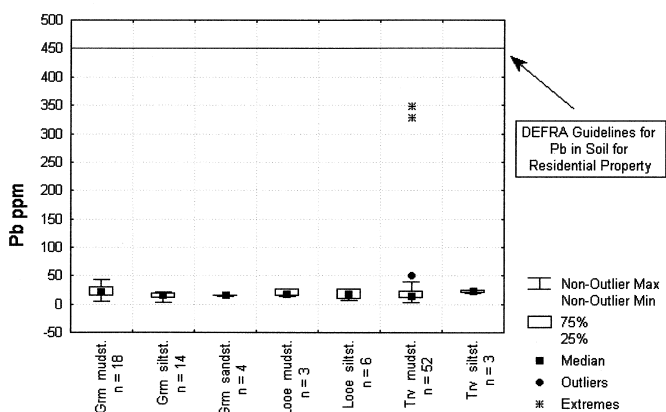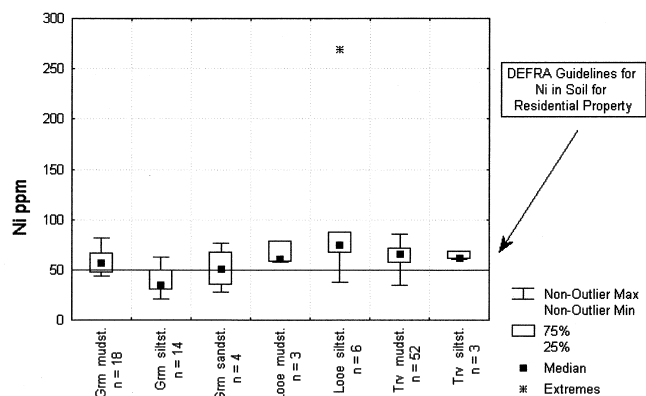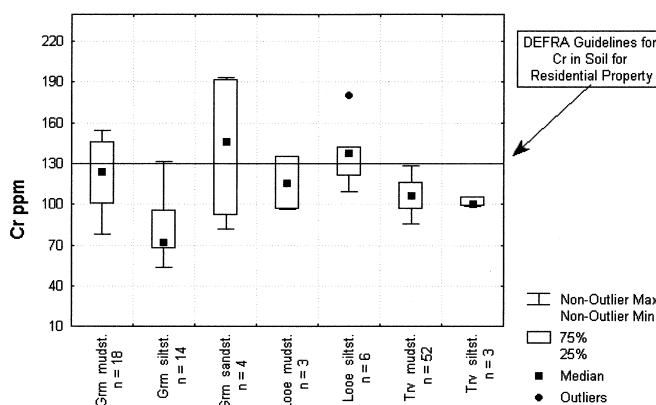

Figure 7. Range of lead values for samples from Gramscatho (Grm), Looe and Trevone (Trv) basins, showing also SGV for Pb in residential land with plant uptake.

CONCLUSIONS

The lithogeochemical data are quite consistent with no wide variations apparent. There are differences between samples, which would be expected to be associated with changes in mineralogy in the different sizes of the primary sediment. No major geochemical differences appear between the sediments from the Gramscatho, Looe and Trevone basins. The trace element data from the mudstones overall show a minor depletion of many minor and trace elements compared with some other averaged shales. Soil guideline threshold values for As, Ni and Cr, used to indicate contaminated land, are often exceeded. This brings the suitability of SGVs set at present levels as a measure for assessing contamination into question.

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