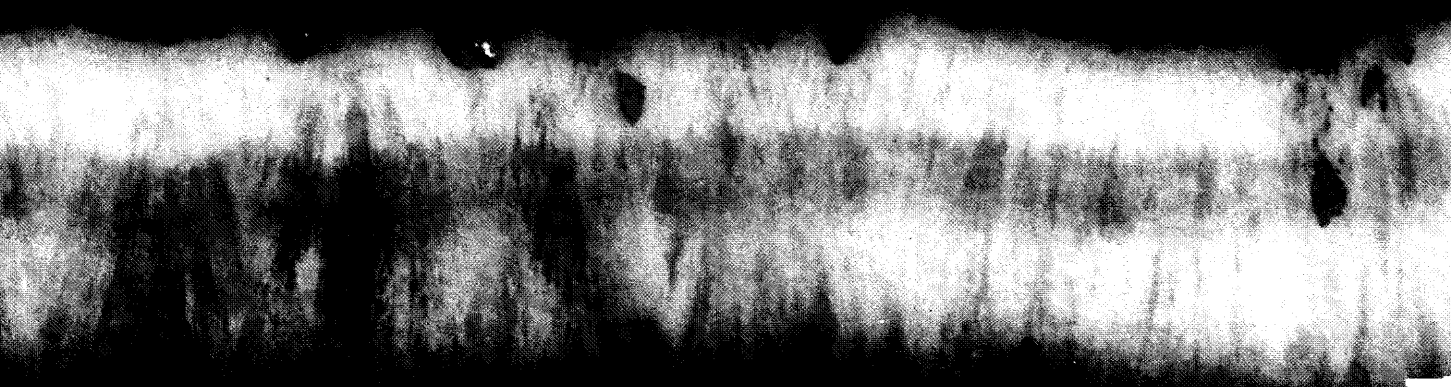
British Geological Survey

MINERAL RECONNAISSANCE PROGRAMME

Report No.89

Geochemical and geophysical investigations of Permian sediments (Littleham Mudstone) of part of Devon



Department of Trade and Industry

BRITISH GEOLOGICAL SURVEY
Natural Environment Research Council

Mineral Reconnaissance Programme

Report No. 89

Geochemical and geophysical investigations of the Permian (Littleham Mudstone) sediments of part of Devon

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CONTENTS

DATA PACKAGE

Detail of the geophysical and geochemical investigations and additonal data may be purchased as a data package (see below) on application to either:

Dr D. J. Fettes, Programme Manager, Mineral Reconnaissance Programme, BGS, Murchison House, West Main Road, Edinburgh, or J. H. Bateson, BGS, Keyworth, Nottingham.

The information package contains:

1 Borehole location/Geology map of area.
2 Detailed lithological logs of all three boreholes.
3 Simplified graphic lithological logs of the boreholes with possible correlation.
4 a Pit profiles with sample points.
  b Chemical values of the Littleham Mudstones from the pits.
  c Chemical values of soils overlying the subcrop of the Littleham (Aylesbeare Group) Mudstones.
5 Paper copy of analyses of Littleham Mudstones from each of the boreholes with summary statistics.
6 Paper copy of the following geophysical logs:

	Black Hill	Withycombe	Venn Ottery
Neutron Combination Log	—	/	/
Neutron-neutron Log	/	/	—
E.Log SP/SPR	/	/	/
E.Log 16–64″ Resistivity	/	/	/
Formation Density Log	/	/	/
Focused Electric Log	/	—	/
Compensated Sonic Velocity	—	/	—

7 Gamma Log of part of Black Hill borehole.
8 Distribution and amplitude of anomalies in gamma-ray log for all boreholes.
9 Geophysical logs of part of Black Hill borehole.
10 Mineralogy and Petrology Report No. 85/12; Vanadiferous nodules from the Littleham Marls near Budleigh Salterton, Devon. P. H. A. Nancarrow.
11 Selected useful bibliography.
12 Access to core material.

SUMMARY

New geophysical and geochemical data from three deep cored boreholes drilled through the Littleham Mudstone sequence (Permian), are presented together with chemical data from the investigation of a number of uraniferous nodules. This investigation provides new chemical data on the host sediments (mudstones) that contain the nodules. The nodules themselves are scattered throughout the mudstones and have long been known to be enriched in a variety of metals in addition to U and V.The information from the holes provides new data on the geophysical characteristics of these sediments in an area where there are few alternate sources of this information.

Additional detailed information,data,examination of available core material and consultation with appropriate staff may be purchased on application.

INTRODUCTION

Investigation into the occurrence of vanadium and uranium within the sequence of dominantly 'red-beds' of the south-west of Britain commenced in the 1930s with the work of Carter (1931) who examined the radioactivity associated with nodular concretions found in parts of the sedimentary succession.

Subsequently more detailed investigations have been conducted on the chemistry and mineralogy of these nodules by Perutz (1939), Ponsford (1955),Durrance and George (1976), Durrance and others (1980), Durrance (1984) and Harrison (1962, 1975). A regional investigation into the occurrence of uranium in the Aylesbeare Group Mudstones was undertaken by Tandy (1973) as a part of a Uranium reconnaissance programme that extended over a number of areas of the United Kingdom.

From these sources it was apparent that it was advisable to investigate the levels of U, V and other associated metals in the Permian sediments of the south-west province.

OUTLINE OF THE GEOLOGY

The Permo-Triassic rocks of the study area crop out in an approximately north-south zone on either side of the Exe Estuary; they rest upon the Carboniferous with marked unconformity. The sediments on the western side are regarded as Permian in age (Henson, 1971) and comprise the Teignmouth Breccia at the base succeeded by the Dawlish Sandstone and a further breccia deposit-the Exe Breccia (Fig.1). The Permian sediments cropping out on the eastern side of the Exe are dominantly a mudstone sequence- the Aylesbeare Mudstones (Bristow and others, 1985) which, as indicated by recently completed mapping of the area (Edwards, 1984a, b), can be subdivided to the south of Aylesbeare into two mappable units,the lower Exmouth Mudstone and Sandstone and the Littleham Mudstone above. The division between the two is made at the highest lenticular sandstone. Farther north this lithological distinction cannot be made. Overlying the mudstones are the Budleigh Salterton Pebble Beds. The argillaceous sediments of the Littleham mudstone lack sufficient carbonate to justify their former classification as 'marls'; they vary from siltstones to mudstones and clays with occasional thin sandstones. Available information (Henson, 1973) on the clay mineralogy of the Aylesbeare Group Mudstone indicates deposition in a fluvio-lacustrine environment. The heavy mineral studies demonstrate that detrital material was derived from the denudation of the Carboniferous landmass to the west that gradually unroofed the granite beneath.

The mudstone sequences are generally dark red in colour with reduced bands and zones of pale green colour and ubiquitous reduction spots of variable size. Durrance and Laming (1982) record that the red- beds contain upto 9.1% Fe_2O_3 mainly as haematite which is lacking in the paler coloured beds. The mudstones are of interest as they contain radio-active nodules with concentrations of a variety of metallic elements.

The strata dip with little variation at 5 degrees or less to the east.

INVESTIGATIONS

1 Uranium and base metals in water and stream sediments

The uranium exploration programme of 1971/72 in this area investigated the occurence of this element together with Cu and Zn in surface waters and Pb and Ni in stream sediments. The results of this investigation are recorded in two reports (Tandy, 1973, 1974) in which the distribution of high U values was thought to indicate a number of continuous zones within the sedimentary sequence that might carry higher than normal values of U and V.

Apart from resampling a few of the stream waters that carried high values to confirm these concentrations no further investigations have been undertaken.

2 Soil and soil profiles

Surface and deep soil samples were collected from an east – west traverse (see Fig.1) approximately 1.5 km in length across the outcrop of the Littleham Mudstone,the most easterly of the sites being situated close to the Littleham Mudstone/Budleigh Salterton Pebble Bed junction and the most westerly just on the Exmouth Mudstone and Sandstone.

Two samples were collected from each of 16 sites, one from beneath the humus layer(at approx. 0.20 m) and the other from a depth of 1.80 – 2.00 m at which depth each hole had penetrated into recognisable bedrock. The deepest of the samples, therefore, represents the top part of the weathered bedrock. The same sites were also used to measure the content of radon in the soil gas.

The levels of the elements in the soils and deeper samples together with the radon values are shown graphically in Figure 2 and indicate relatively high values of Ba, Rn, Mn and V associated with the surface soils. Lead (Pb), vanadium and to a lesser extent manganese show enrichment in the deeper profile levels particularly in relation to a known nodule-bearing horizon.

As part of the investigation into the behaviour of the various elements in the soil profile 3 pits were dug along the northern bank of the Coombe Stream to depths of 0.9, 1.0 and 1.4 m respectively. By means of hand auger these holes were sampled to depths of 1.4, 1.65 and 2.25 m in addition to being regularly channel sampled at approximately 0.20 m intervals.

The histograms in Figure 3 show the gain/loss plots for the four profile horizons in relation to the bedrock values.

3 Radon gas in soil

The auger holes used to obtain the soil samples (see above) were also used to measure the quantity of Radon gas. The measurement of Rn took place in each hole after

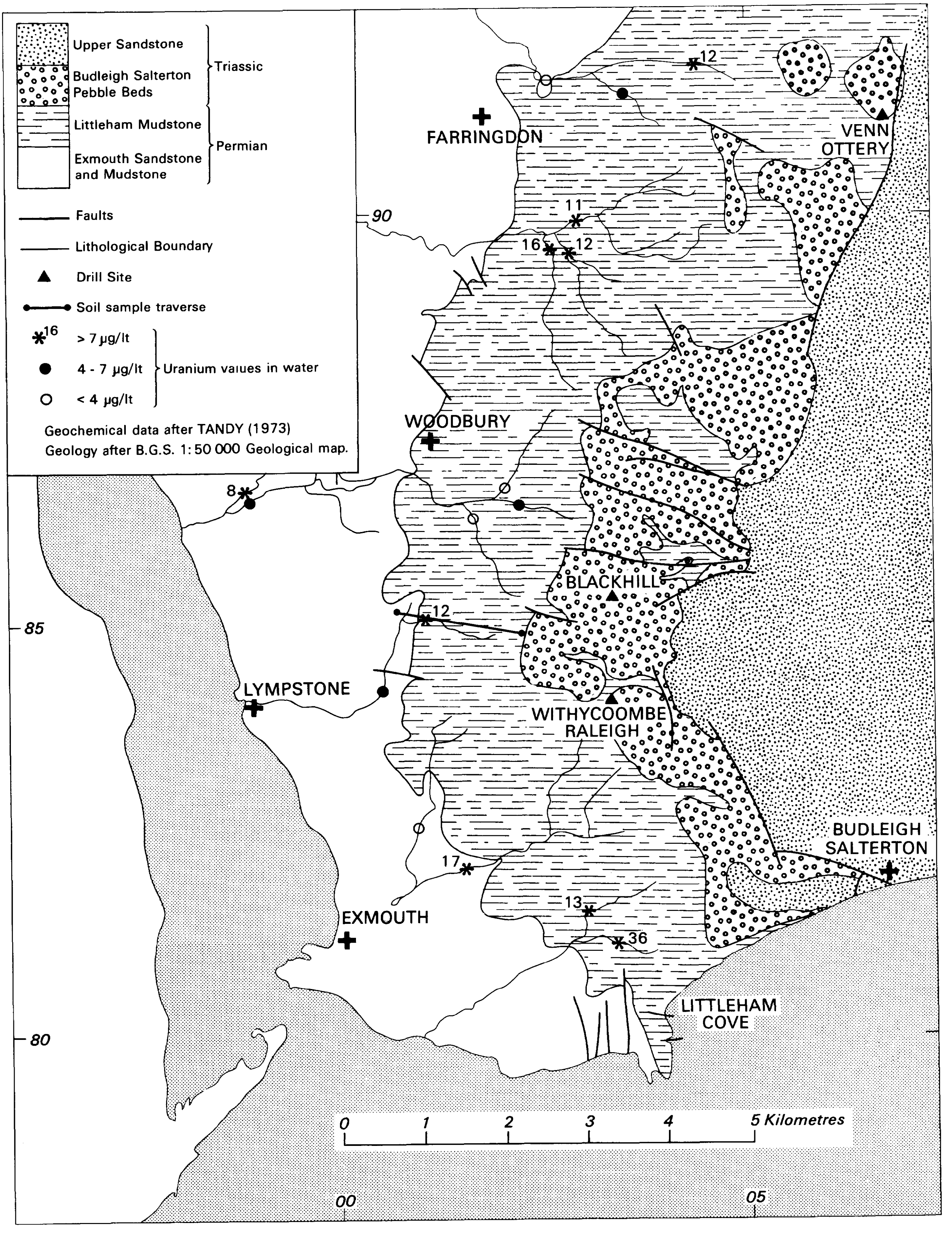

Fig. 1. Geology of the Woodbury area of Devon.

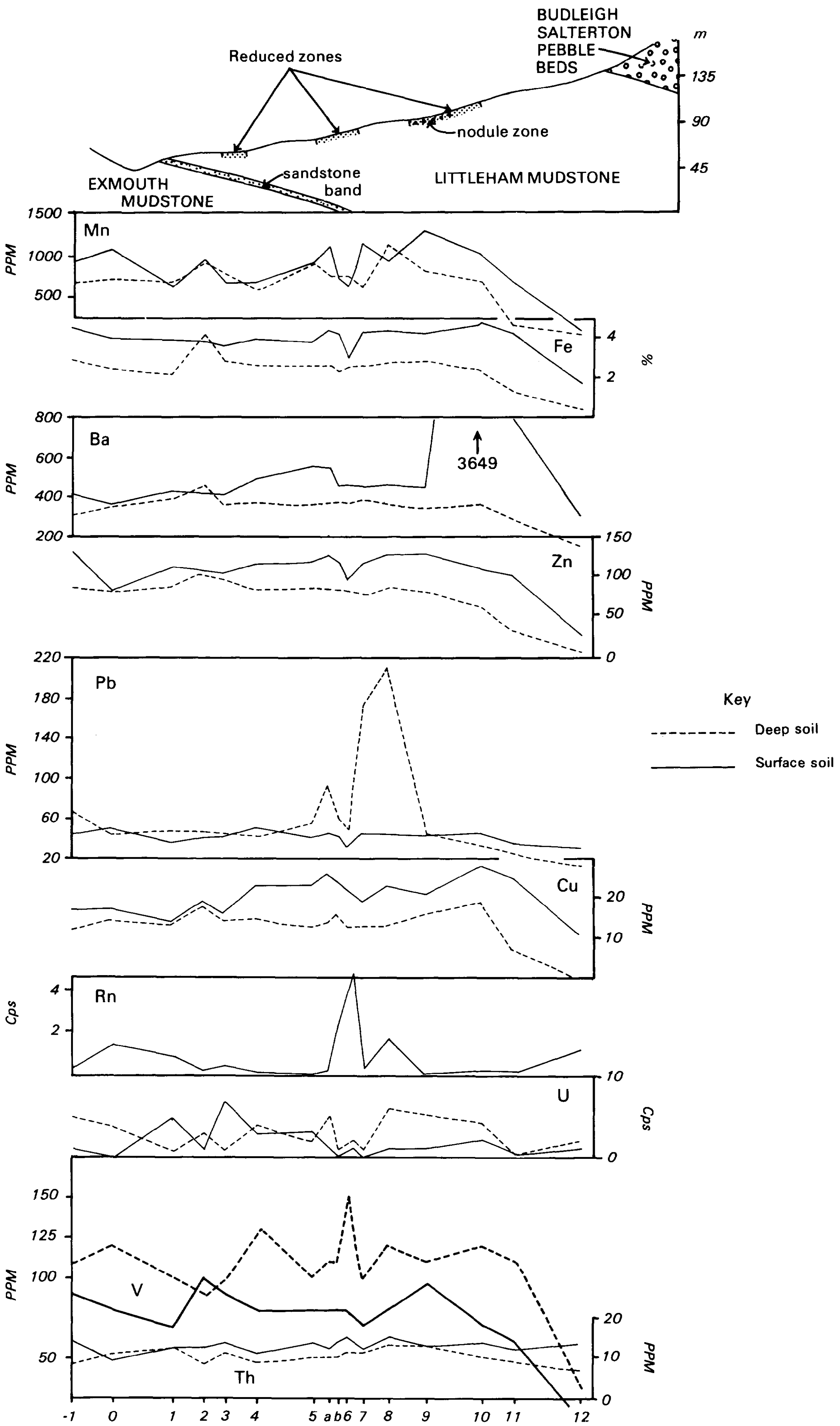

Fig 2. Distribution of elements in soil and auger samples.

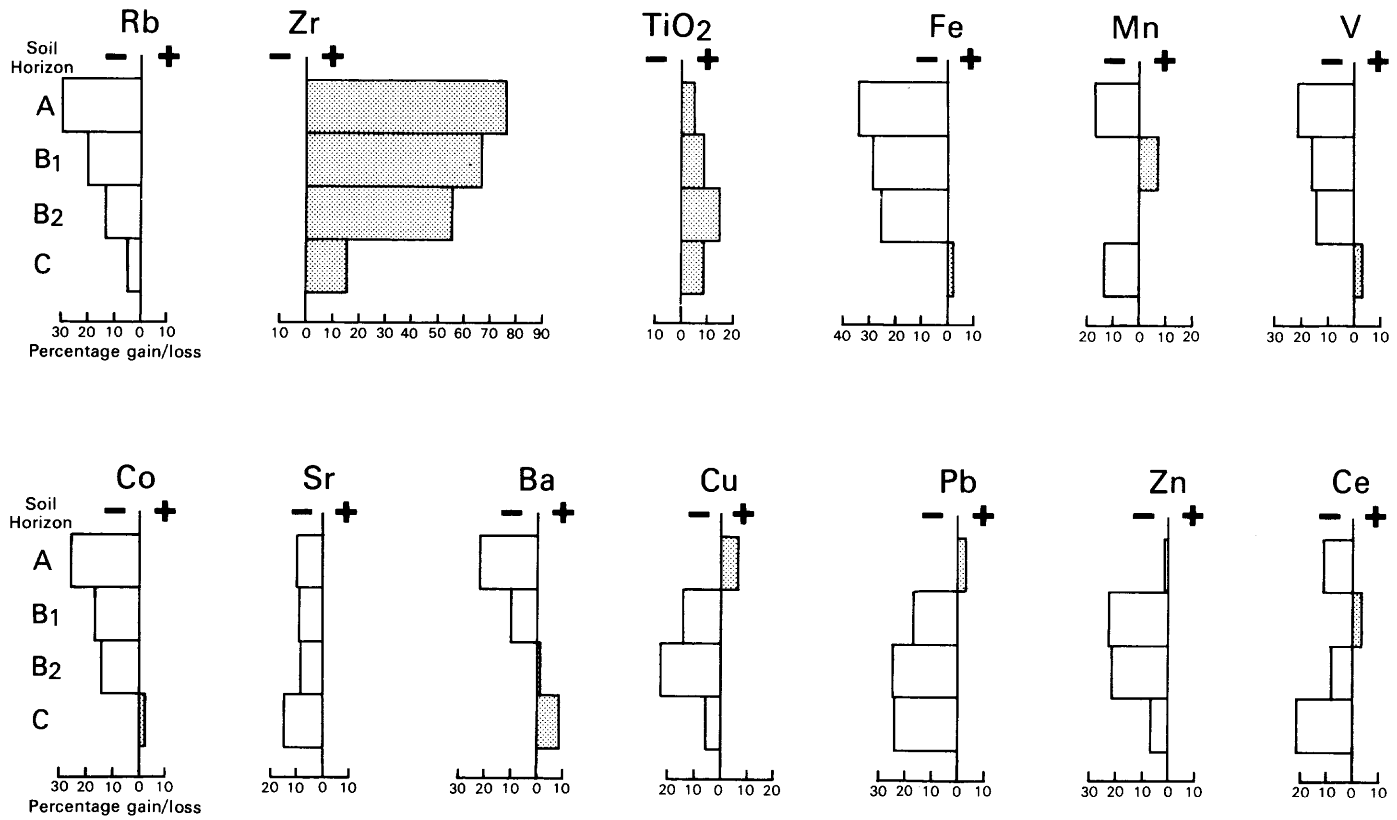

Fig. 3: Gain/loss percentages for the common metals in the Littleham Mudstone soil profiles in comparison to values found in bedrock.

a rest period of approximately 5 minutes following the initial pumping out of the hole.The values for Rn (in cps.)are given in Fig 2.

4 Borehole data

In order to be able to assess the geochemical characteristics of the Littleham Mudstone it was necessary to obtain fresh,unweathered material to supplement the data obtainable from surface exposure. To this end three cored boreholes were drilled not only to provide the samples for analysis but also to provide further information on the stratigraphy of the mudstones and in particular to identify possible lateral facies variation and changes in thickness.

The locations of the holes (see Fig 1)were selected where it seemed probable that a complete succession of the entire thickness of the Littleham Mudstone could be cored.The sites were located in working or disused quarries (where the operation would have minimal environmental impact) and drilling commenced at the bottom of the Budleigh Salterton Pebble Bed;it was the intention to drill to the highest of the sandstones in the Exmouth Mudstone and Sandstone sequence.

A total of 877.99 m were drilled and cored by Drilling and Prospecting International Ltd; the hole at Withycombe Raleigh reached 280.20 m, that at Blackhill 287.89 and 309.88 m were cored at Venn Ottery. Each hole was surveyed for a number of geophysical parameters by Robertson Research Engineering Services Ltd. (see section 6, below).

The main elemental values for the Littleham succession in the boreholes are given in Table 1.

Table 1 Mean chemical values in the Littleham mudstone succession in the boreholes

Elements (ppm)	Blackhill	Withycombe Raleigh	Venn Ottery	Mean value	Average in shale
Mo	20.0	11.5	—	—	3.0
V	138.5	155.0	154.0	146.3	130.0
Co	18.0	32.0	34.0	25.5	20.0
Al	8.0	6.7	—	7.6	10.45
Fe%	4.0	4.0	4.5	4.1	3.33
Ca%	2.0	32.0	2.5	2.5	2.21
Mn	625.5	89.4	9.6	765.3	850.0
Cu	29.0	32.0	62.0	38.0	50.0
Pb	31.0	48.0	34.0	36.0	20.0
Ni	41.0	56.0	33.5	43.2	70.0
Zn	114.0	118.0	157.0	125.8	100.0
Cr	73.0	74.0	68.0	72.0	100.0
Rb	168.0	165.0	159.0	165.0	140.0
Ba	504.0	493.0	471.0	493.0	700.0
Ce	80.0	79.0	86.0	81.3	50.0
Ti	0.9	0.8	0.9	0.9	0.46
Zr	197.0	194.5	197.0	196.4	160.0
Y	4.0	43.0	38.0	42.3	25.0
Sr	134.0	150.0	252.0	167.5	300.0

Note: Average values from Levinson, 1974, except for Al. from Vinogradov, 1956, Fe and Ca from Turekian and Wedepohl, 1961

5 Nodules from the Littleham Mudstone

During the course of this investigation a number of nodules of various sizes were collected for examination and analysis.Examples were obtained from the 'classic' location in the inter-tidal zone at Littleham Cove as well as from a number of localities inland (Fig. 4). Some of these were analysed for major oxides and minor elements- the data from which are presented, together with some earlier published data, in Table 2. A number of nodules have been examined using XRF, Electron micro probe, XRD and Evolved gas analysis (Nancarrow, 1985) from which it was noted that while there are some similarities with material described earlier in the literature these tend to be chiefly in the gross geochemical and textural characteristics. There are significant differences; the total lack of native copper in the new samples compared with the earlier examined specimens, and also the less common occurrence of sulphides, arsenides and V oxides. The samples examined by Nancarrow (1985) fall into two distinct groups:-

a Dark zoned nodules with a strongly zoned matrix but without a distinct nucleus,
b Nodules with a small but distinct nucleus.

The former are rich in sulphides, arsenides and V oxides with minor clausthalite and native silver. In the second group the distinct nucleus is rich in Pb, Cu (with or without Se) but with little evidence of other mineralisation outside the nucleus apart from V oxide enrichment. The physical form of the nodules varies from spherical to ellipsoidal (the flattening being approximately parallel to the bedding). Harrison (1975) suggested that the flattening was due to post depositional compression of the sediments implying that the nodules could on the basis of their shape be defined as either pre- or post-depositional. The available geochemical data neither supports nor refutes this thesis.

6 Geophysical investigations

Borehole logging: objectives

In order to maximise the range of data obtained from the drilling programme, a suite of logs was recorded in each of the boreholes. Since the boreholes were cored throughout, the value of the geophysical data is proportional to the degree of departure from a simple correlation between geophysical response and lithology, indicating more subtle changes than inspection of the core could reveal. Furthermore, the known presence of nodules, of which some are radioactive, in the Littleham Mudstone indicated that the gamma-ray logs for each hole would be of particular interest. In this respect it would have been valuable to record a Gamma ray Spectrometer log, but unfortunately this could not be offered by the majority of logging contractors.

Logging procedures

Each borehole was logged as soon as possible after completion of drilling, so that in each case the drilling rods had been pulled at the end of the shift about 15 hours previously. Logging operations took 12–15 hours at Black Hill and Withycombe Raleigh, but were spread over two days at Venn Ottery. At Black Hill Quarry and Venn Ottery the logs were run from the drilled depth of the borehole up to surface, but at Withycombe Raleigh, squeezing formations in the lower part of the borehole prevented the geophysical tools from reaching the drilled depth by 20 m (50 m for the Sonic log). The logs run in each borehole were as follows:

Black Hill
1 Formation density
2 Natural gamma ray
3 Caliper
4 16" and 64" Normal resistivity
5 Spontaneous potential
6 Single point resistance
7 Focussed electric
8 Neutron-neutron

Withycombe Raleigh

As for Black Hill Quarry, but without a Focussed electric log (due to instrument failure), but with in addition a Compensated sonic velocity log.

Venn Ottery

As for Black Hill Quarry,but with an additional Natural gamma ray log recorded with the Neutron-neutron log,using the Sidewall neutron combination tool.

Table 2 Analyses of nodules

	Dark Zone	Light Zone	HB 1	HB 2	HB 5	HBR 8009 Dark Zone	HBR 8018 Dark Zone	Knowle Bore Vanadium-rich		
Si_2O_2	51.86	59.05	42.50	53.90	49.60	0.00	0.00	6.46	8.34	3.28
TiO_2	0.71	0.88	0.64	0.54	0.80	0.61	0.65			
Al_2O_3	14.16	15.14	15.00	13.30	13.50			1.82	3.64	4.29
Fe_2O_3	2.32	2.82	1.92	1.56	2.19	3.10	2.26	0.36	0.34	
Na_2O	0.56	0.88	2.90	3.10	3.40					
K_2O	4.60	4.86	5.70	5.60	5.30			0.74	1.25	0.68
CaO	0.70	3.06	3.72	5.86	2.13	0.80	2.42	0.56	6.80	25.17
MgO	2.85	2.47	3.10	1.90	2.50					
Mn	tr					0.07	0.08			
S	0.08									
V*	7.80	1.07	4.21	1.48	4.23	1.87	0.17	44.27	31.16	3.98
CO*	0.14	0.05	0.27	0.01	0.09	0.004	0.09			
Ni*			0.12	0.01	0.04	0.005	0.08			
L.O.I.	8.52	8.52	8.80	8.60	7.30					

Source: Perutz, 1939. BGS Laboratories, 1985. Harrison and others, 1983.

Note: Fe_2O_3 values may be high in samples with high V valkues recalculated from oxides indicated*

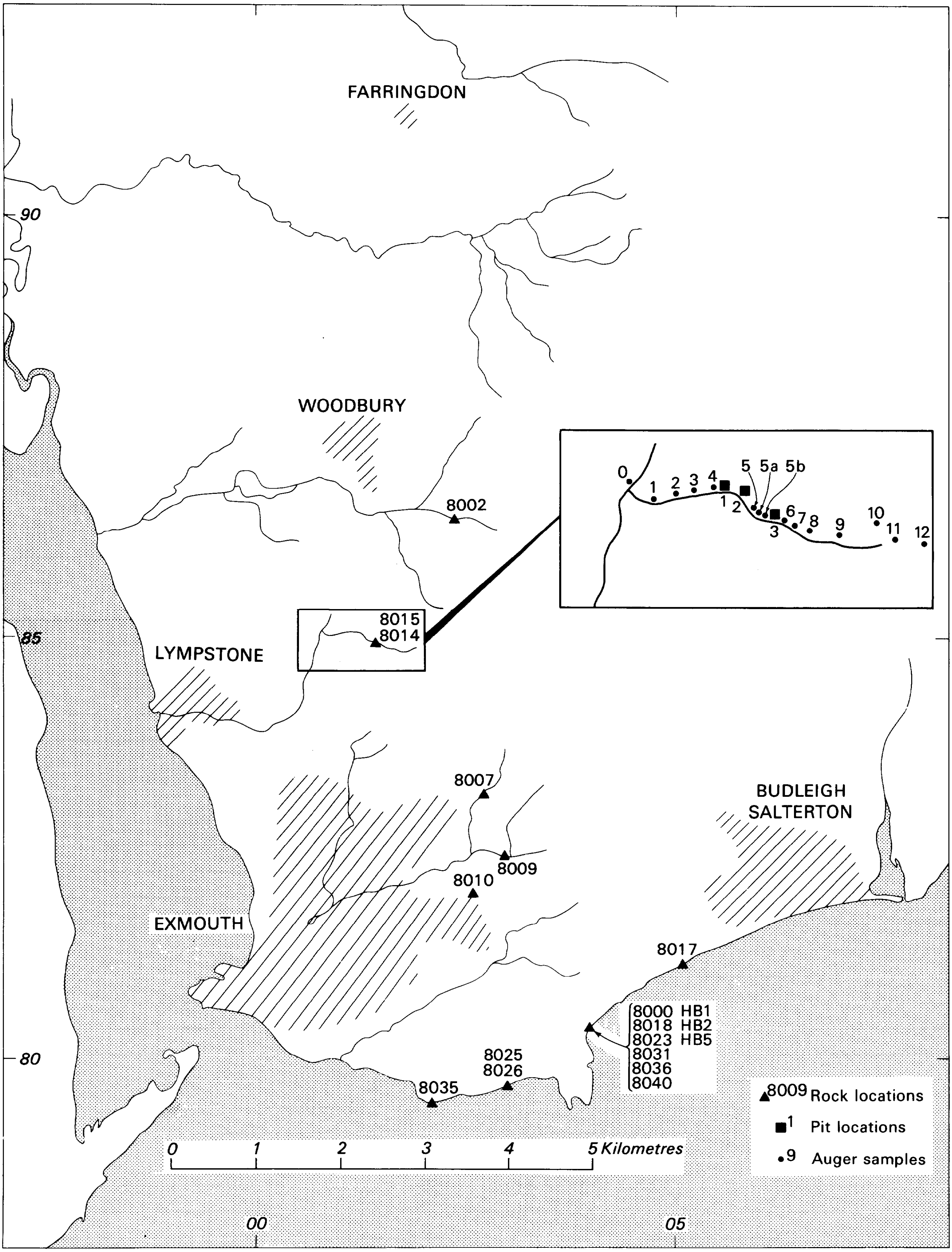

Fig. 4: Location, Rock, Soil and Pit samples.

CONCLUSION

The information obtained from this study indicates that there is little evidence of general enrichment of metals in the enclosing sediments but it does provide a useful data base of chemical signatures.The geophysical information, however, adds significantly to the data currently available on the characteristics of these sediments. The lithological logs also add information that is significant in the better understanding of the environment in which these sediments were accumulated.

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