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Reduction and related phenomena in the New Red Sandstone of south-west England

J H Bateson and C C Johnson

BRITISH GEOLOGICAL SURVEY

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SUMMARY

This report gives an account of the geological setting of reduction features in New Red Sandstone sediments from the area around Exmouth and Budleigh Salterton in south-west England, along with a review of the state of research and investigation into these phenomena. The abundance and significance of the commonest reduction phenomena (green spherical spots) are assessed, together with geochemical and mineralogical data from recent investigations on nodule material. The lack of identifiable fossil material within the Aylesbeare Mudstone suggests that the hypothesis that the formation of reduction spots and nodules is dependent upon the presence of organic matter is neither adequate nor appropriate for the occurrences in this area. Earlier investigations had identified in some of the nodules, carbon-containing substances, the origin of which was not clear; the possible relationship of this material to the formation of the reduction features is considered.

INTRODUCTION

The Permo-Triassic rocks of England comprise a variety of lithologies, many of which are characteristically red and/or brown in colour. This colour indicates the oxidation state of the iron oxides, reflecting the arid landscapes from which the detritus was eroded. The red colour is not, however, ubiquitous, for most sequences contain grey to green bands and lenses and a variety of small green to grey-green spots. Such reduction features are not confined to rocks of this age or to this region (Manning, 1975), and there has been much investigation into the conditions of their formation. The reduction features in the Littleham Mudstone Member of the Aylesbeare Mudstone Formation in Devon have attracted attention mainly because of associated nodules.

Investigation of the nodules in south-west England commenced with Carter (1931), who showed that they contain abnormally high levels of radioactive minerals. The investigations of Perutz (1939), Ponsford (1955), Durrance and George (1976), Durrance et al. (1978, 1980), and Harrison (1962, 1975) added considerably to the bank of information on these structures, particularly in the identification of the mineral species that are present. Tandy (1973, 1974) produced data on their geographical and geological distribution. However, little chemical information was available on the surrounding paler haloes or the host rocks.

The information presented here has been obtained during investigations (on behalf of the Department of Trade and Industry) into the distribution of uranium and vanadium in the host mudstones as well as the reduction features.

REVIEW OF EARLIER INVESTIGATIONS

The identification of radioactivity associated with the nodules from Littleham Bay led to the analysis of this material for uranium and other radioactive elements. Carter (1931) demonstrated the association of the pale haloes with the nodules and the ubiquitous occurrence of very small reduction spots throughout the sequence of the host mudstone.

Perutz (1939) reported the content of uranium in the nodules to be in the range 0.3–0.5 volume percent. Durrance and George (1976), following the suggestion of Harrison (1962), confirmed the presence of coffinite ($USiO_4$) and metatyuyamunite ($Ca(UO_2)_2VO_4)_2.3.5H_2O$) in the nodules. The coffinite, it was suggested, had been stabilised in a reducing environment caused by decaying organic debris. Further investigations by Durrance et al. (1978) into the state of the iron compounds within the Littleham Mudstone concluded that ferric oxide formation was inhibited by the presence of organic remains and resulted in the haloes of pale sediment. They concluded that the red colour of the rocks was due to the progressive change of iron-bearing minerals to hydrous ferric oxides, and subsequent conversion to hematite after deposition. The formation of the nodules was thought to be related to the redistribution of uranium salts from migrating ground water, under reducing conditions around organic matter.

Henson (1972, 1973) researched the palaeogeography of the depositional basin. The earlier paper interpreted seismic data to support the thesis that deposition took place on a pediment east of a mountain range cored by the Dartmoor granite. This work also estimated the probable thicknesses of the Permo-Triassic sedimentary units preserved in this basin.

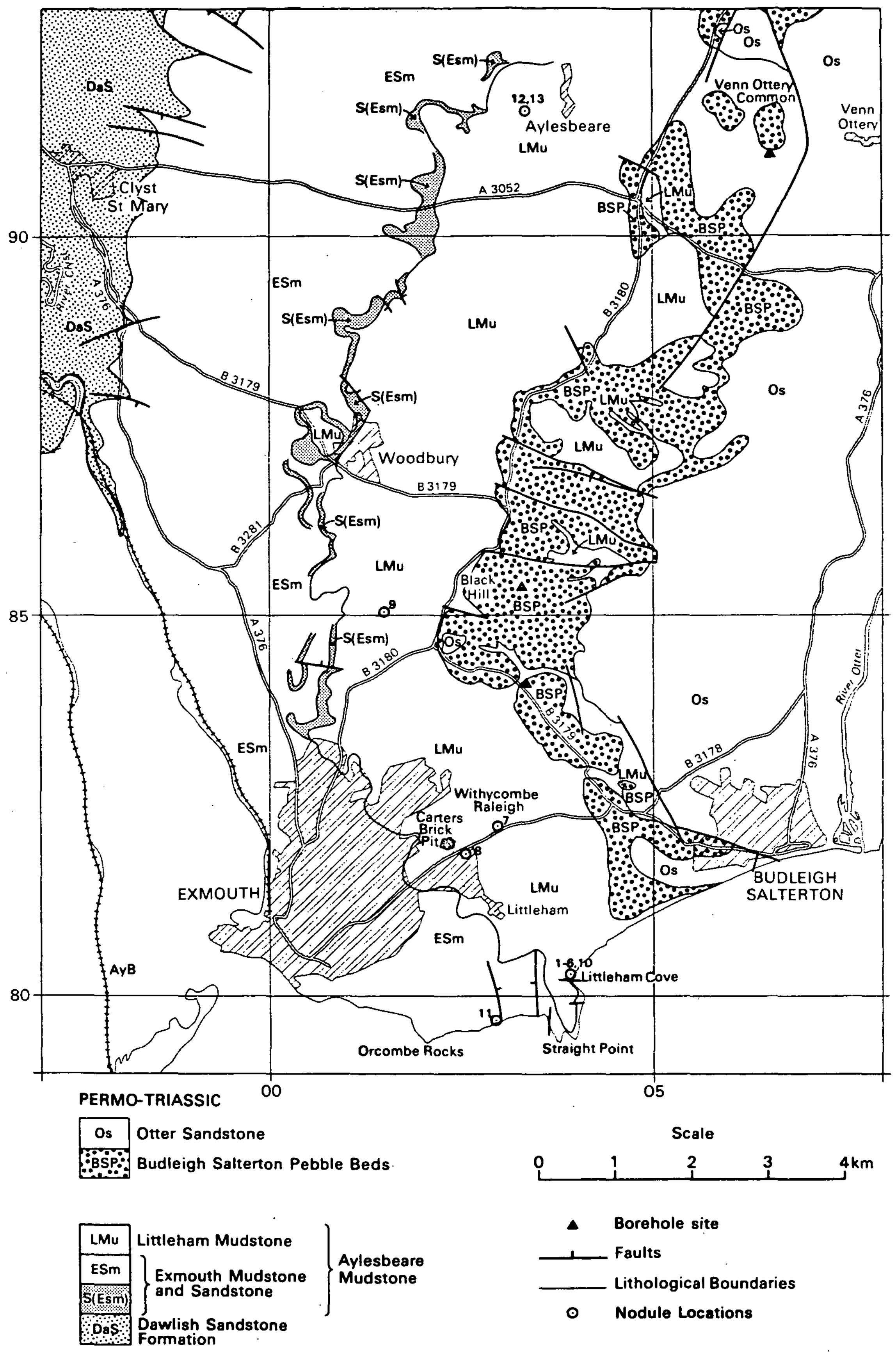

Figure 1 Geology of the Exmouth-Aylesbeare area (after Bristow et al., 1985) and location of boreholes

A study of the clay mineralogy of these sediments (Henson, 1973) showed the main assemblage of illite, kaolinite and chlorite to be consistent with derivation from the west. The sandstone units beneath the Littleham Mudstone were considered to represent material deposited as alluvial fans, while silts were thought to represent overbank deposits and the mudstones deposits on a flood plain. The occurrence of euhedral crystalline calcite, dolomite and gypsum indicated that a depositional environment approaching supersaline conditions existed during the evaporation of temporary lakes.

Tandy (1973, 1974) demonstrated the widespread occurrence of dissolved uranium salts in surface waters, and showed that the distribution of nodules was wider than had previously been known. He also suggested that the reduction features might be of use as stratigraphic indicators. This view is not confirmed by the present work, which suggests that the distribution of reduction features is controlled by other factors in addition to the stratigraphic horizon.

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 with a marked unconformity upon Carboniferous rocks (Figure 1). The sediments on the eastern side of the Exe belong to the Aylesbeare Mudstone. Bristow et al. (1985) indicate that this formation is divisible south of the Aylesbeare district into two members, the Exmouth Mudstone and Sandstone below, and the Littleham Mudstone above. Farther north, this lithological division has not been recognised.

The Aylesbeare Mudstone is well exposed in the coastal sections between the Exe estuary and Budleigh Salterton where it dips eastward at approximately 5^{o}. Exposure inland is poor, confined to small streams and a few old clay pits.

Faults, both parallel and perpendicular to the strike, affect the Aylesbeare Mudstone and are most obvious where they displace sandstone beds.

The Littleham Mudstone comprises silts, mudstones, and clays with some thin sandstones; the mudstones lack sufficient carbonate to be classified as 'marls' as in older nomenclature. The thickness of the Littleham Mudstone had been estimated by Henson (1972), using seismic profiling data, as 88 m; the estimate of 275 m quoted in Selwood et al. (1984) is, however, consistent with borehole data reported by Bateson et al. (1987).

Henson (1971), in a study of the Permo-Triassic rocks of south-west England, deduced from palaeoccurrent information in the more arenaceous lithologies that the material had been derived from the south-west and deposited as flood-plain sediments. Durrance and Laming (1982) interpreted the palaeocurrent information as indicating that the climate of the period was basically semi-arid, with periodic (?seasonal) rains to account for the accumulation of the flood deposits. The environment of derivation and deposition is pertinent to this study, particularly as it provides evidence on whether the land mass was vegetated or not. This part of the Permo-Triassic sequence in Devon generally lacks plant remains, although similar successions in other areas have yielded such material (Durrance and Laming, 1982; Warrington 1971). It is suggested that the climate was too arid to support any substantial plant population (Durrance and Laming, 1982, page 171).

GEOCHEMISTRY OF THE LITTLEHAM MUDSTONES

Previous investigations were concerned almost exclusively with research on the vanadiferous and uraniferous nodules. Little information has been published relating to the chemical characteristics of the host rocks, the Littleham Mudstone. Consequently, three cored boreholes were sunk in the area to investigate the stratigraphy and lithological variations through the Littleham Mudstone and to provide fresh samples for analysis. In addition to the geochemical information from the core material, analyses were obtained from surface material (Nancarrow, 1985).

The three boreholes (Figure 2) at Blackhill, Withycombe Raleigh and Venn Ottery cored respectively 288 m, 280 m and 310 m of sediments; of which 230 m and 200 m at Blackhill and

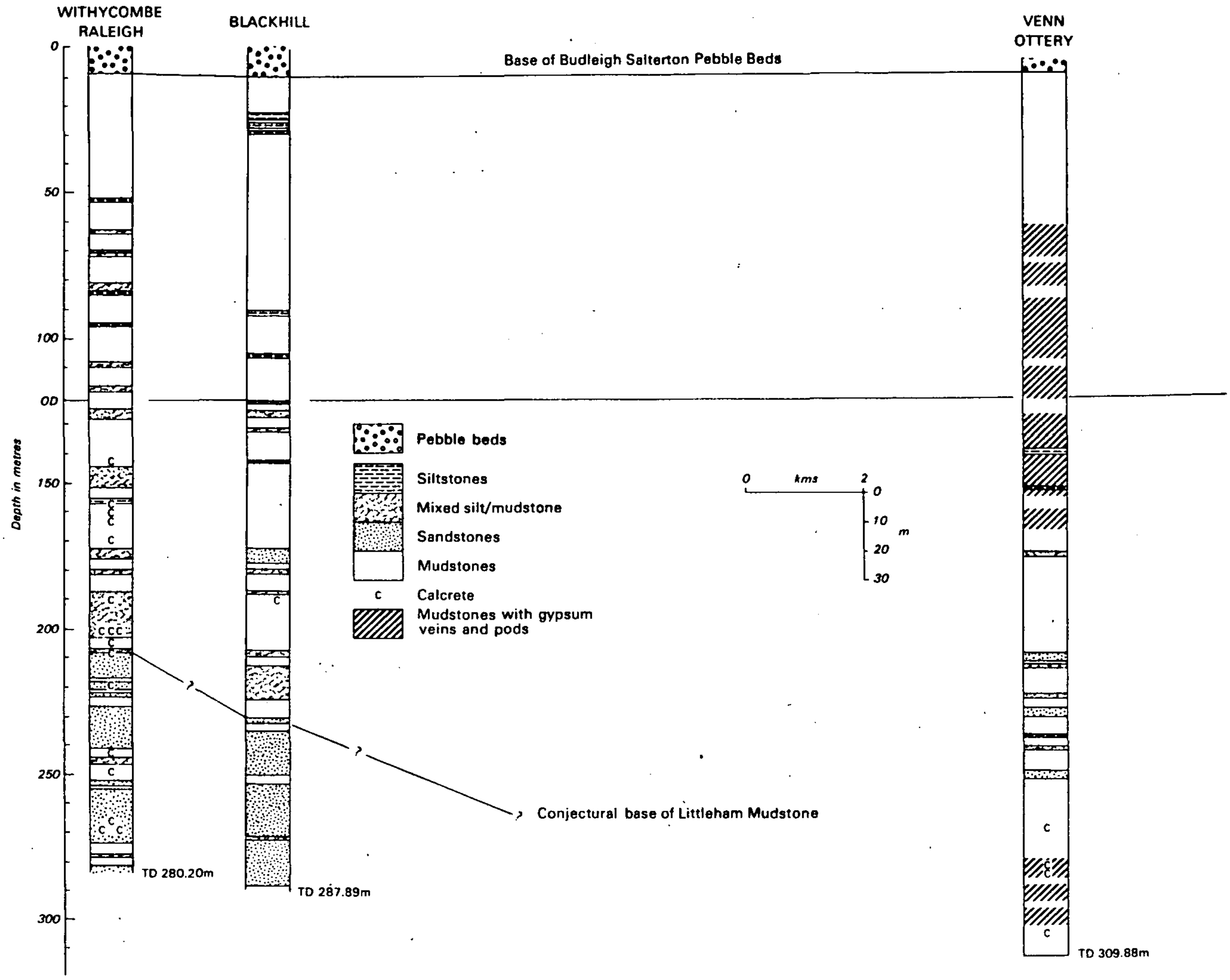

Figure 2 Simplified lithological subdivisions in the boreholes

Withycombe are considered to be Littleham Mudstone. The borehole drilled at Venn Ottery, some 5 km north of Blackhill, although deeper than the other two, did not encounter any sandstones that could be positively correlated with sandstone units in the lower part of the succession at the other sites, and which are taken as the uppermost part of the Exmouth Mudstone and Sandstone. The Littleham Mudstone at Venn Ottery may, therefore, be over 300 m thick; or the lower part of the cored succession could be a lateral non-arenaceous equivalent of the Exmouth Mudstone and Sandstone. In addition, the sequence at Venn Ottery shows an abundance of small veinlets and pods of gypsum.

Table 1 gives the mean concentrations of a number of elements in 200 samples of the Littleham Mudstones. They are plotted as normalised multi-element diagrams (Haslam and Plant, 1990) in Figure 3. Figure 3a (average elemental concentrations normalised to average shale values: Levinson, 1974), shows that many of the elements have values close to those of average shale. Figure 3b presents the elemental data for each hole normalised against the internal averages. Broadly speaking for most elements, there is little variation from the norm with the exception of Mn and Al which are somewhat reduced in the Venn Ottery material while Cu and Sr show some enrichment in the same core. The most dramatic variable is the greatly enhanced Ca value obtained in the Withycombe Raleigh material.

Between ca 150 m and 250 m in the Withycombe Raleigh borehole the lithologies (see Figure 2) show a record of calcareous nodules and bands associated with the mudstones, and these are reflected in the higher Ca values.

Table 1 Mean chemical values for 200 samples of the Littleham Mudstone from the Blackhill (97 samples), Withycombe Raleigh (48) and Venn Ottery (55) boreholes

	Blackhill	*Withycombe Raleigh*	*Venn Ottery*	*Mean*	*Average 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	44.0	43.0	38.0	42.3	25.0
Sr	134.0	150.0	252.0	167.5	300.0

Average shale values from Levinson (1974) except Al from Vinogradov (1956), Fe and Ca from Turekian and Wedepohl (1961)

All concentrations in ppm, except Fe, Ca, Ti and Al in %

DISTRIBUTION OF REDUCTION PHENOMENA

Reduction features, identified by their green and grey-green colouration, may be referred to four main types: (1) bands and discontinuous beds and zones; (2) green spherical spots with no apparent nucleus; (3) nodules of grey/black colour and smaller varieties called fish-eyes that are surrounded by a halo of pale green reduced material; and (4) diffuse patches of reduced material.

Bands, beds and zones

These structures are particularly obvious in the sea cliff exposures of the Littleham Mudstone between Budleigh Salterton and Littleham Cove. In general, the boundary between the green reduced bands and the surrounding rocks is sharp and commonly coincides with a change in lithology from mudstone to siltstone or sandstone. Examples occur, however, where the boundary is neither sharp nor accompanied by marked lithological change. Some joints and other planar features also exhibit reduction features which suggests that this development may be related to the passage of fluids along these open structures.

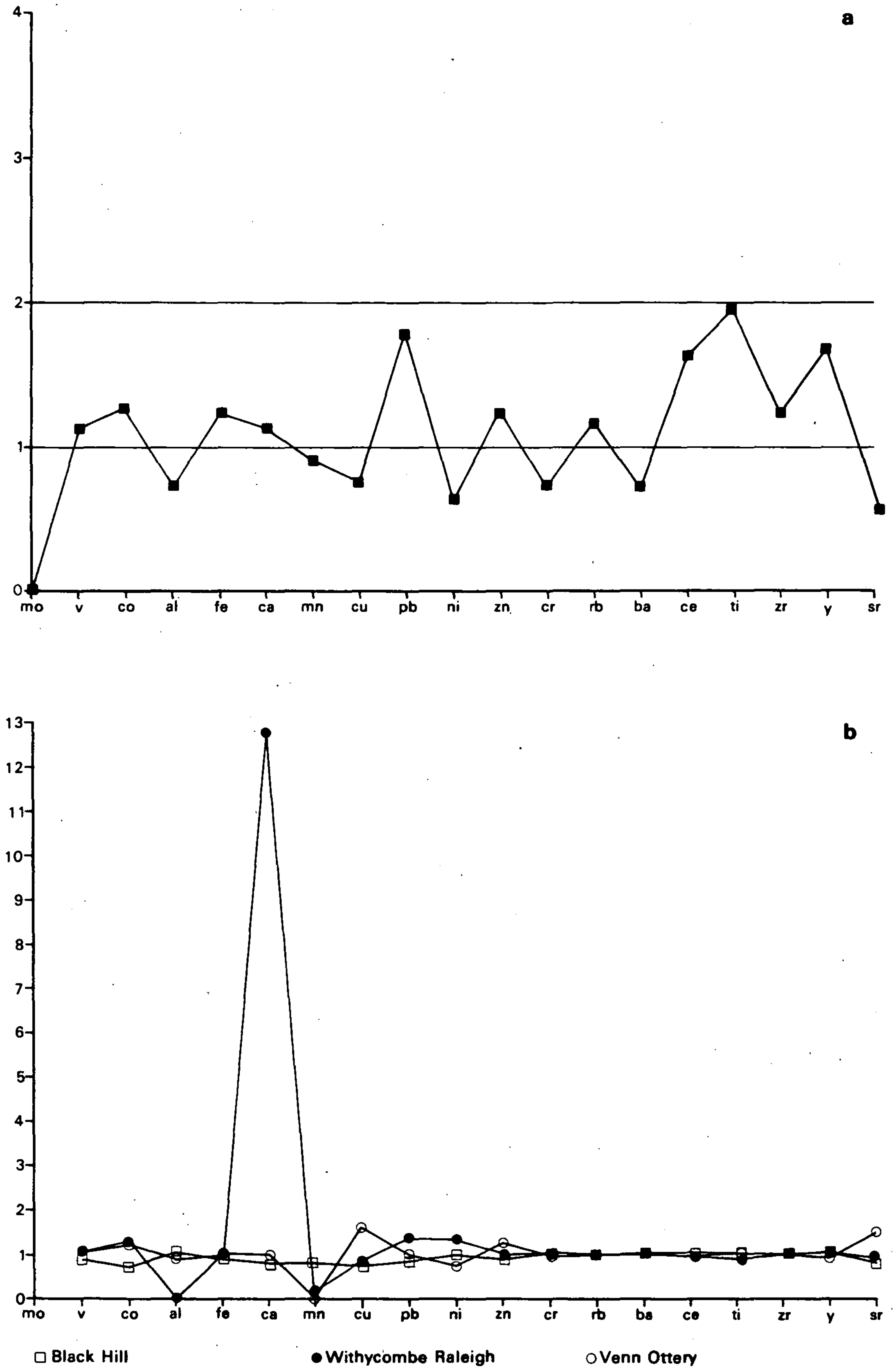

Figure 3 Normalised multi-element diagrams for borehole samples: (a) mean values for 200 samples (from all boreholes), normalised to average shale; (b) mean values for each borehole (97 samples from Blackhill, 48 from Withycombe Raleigh and 55 from Venn Ottery) normalised to averages for the sample set

Table 2 Number of spots in each size classification, Blackhill borehole

Depth in metres	*Diameter of spots, mm*					
	0–2	*2–4*	*4–6*	*6–8*	*8–10*	*>10*
26.4–28.0	293	95	10	1	4	2
43.5–45.0	224	68	12	1	1	2
58.7–60.4	1222	116	10	2	–	–
73.3–74.7	1867	77	30	2	1	1
87.8–89.3	387	21	2	–	1	1
102.2–103.7	85	2	1	–	–	–
116.9–118.3	133	38	2	1	–	–
131.6–133.1	1468	137	29	4	–	–
146.2–147.7	1094	105	9	1	1	–
160.9–162.4	810	109	33	4	1	–
175.6–177.1	301	16	5	–	–	1
190.0–191.6	769	85	14	3	1	7
204.7–206.2	1868	261	68	13	2	2
219.3–220.8	501	53	7	1	1	2
Totals	9839	1183	199	33	13	18

Green spots

These are developed in almost every outcrop of the Littleham Mudstone. They appear, in two dimensional section, as round or slightly ellipsoidal spots set in a matrix of red mudstone. The boundary with the surrounding mudstone is sharp. Spots may coalesce to produce a complex mass of overlapping spots. They do not typically show evidence of identifiable core material (examples that do contain a dark nucleus are traditionally referred to as 'fish-eyes'—see below), and may be characterised as follows:

1 Usually spherical, but some examples are flattened parallel to lithological boundaries

2 Lithologically indistinguishable from the host material.

Material obtained from the boreholes confirmed that spotting is a ubiquitous feature in these rocks and is not a weathering phenomenon.

Figure 4 shows the distribution of spots of different sizes as measured on the surface of the core at different depths down the borehole (see Table 2). The smaller spots (0–4 mm) are the more abundant throughout the succession; larger spots generally follow the distribution pattern of the smaller ones, with similar peaks and troughs. These variations do not correlate with lithological variations (see Figure 2).

Nodules

The nodules are found in a variety of sizes, ranging from from less than 1 cm to 15 cm in diameter. They are generally spherical, but also occur flattened, stellate and with distinct ribs (Harrison, 1975). They are, in the unweathered state, harder than the enclosing

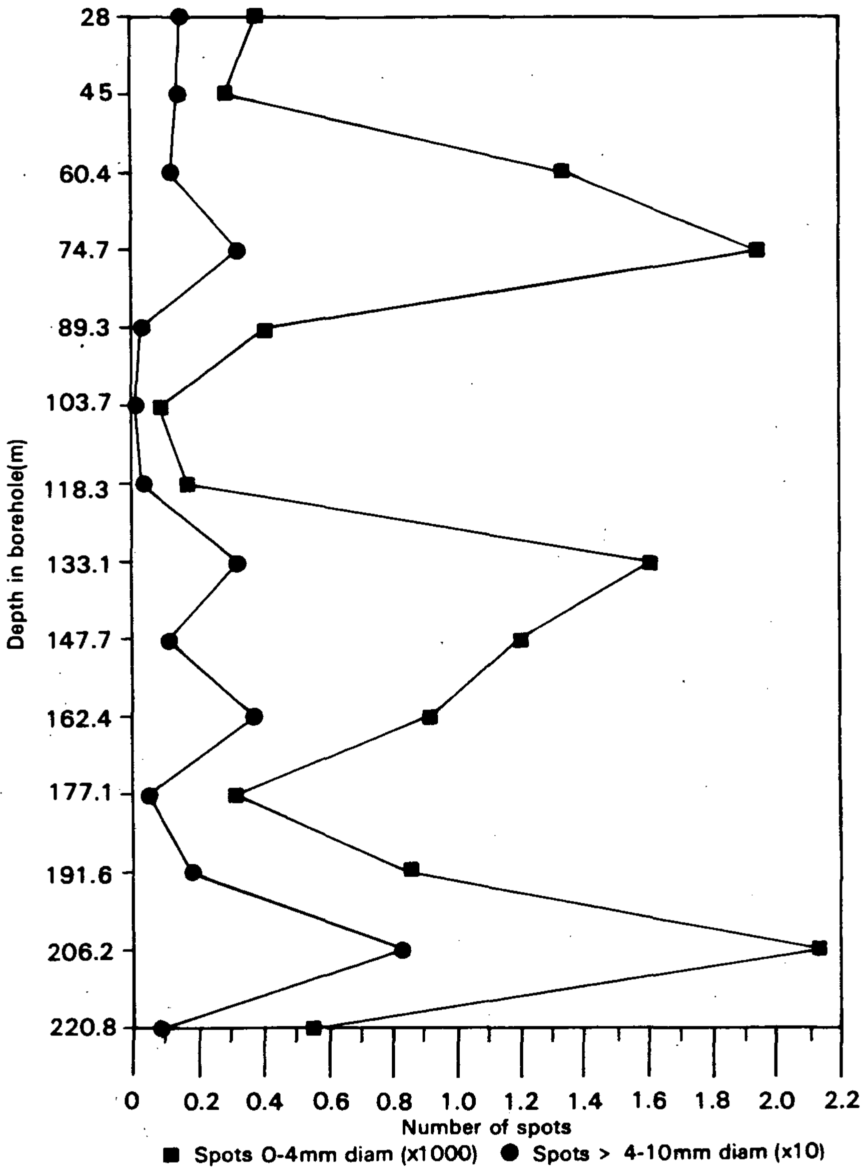

Figure 4 Size distribution of reduction spots in the Blackhill borehole

sediments and are surrounded by pronounced haloes, of varied width. These haloes consist of pale-coloured sediment, contrasting with the dark grey or black colouration of the nodules themselves.

Investigations into the chemistry and mineralogy of the nodules are well recorded. Further work on 13 samples from several localities in the area is reported here. The most extensive accumulation of in situ nodules is recorded from the foreshore at Littleham Cove, and formerly from the now infilled Carter's Brickpit (see Figure 1).

Tandy (1973, 1974), examined several small stream sections crossing the outcrop of the Littleham Mudstone and showed the nodules to be geographically widespread, occurring at various stratigraphical levels in addition to the lower horizons exposed at Littleham Cove, although it is in these horizons that they are most abundant.

Physically smaller, but possibly closely related, are 'fish-eyes'. These are small green spots that have a pronounced dark nucleus similar to the much larger mass that forms the dense part of a nodule. The physical conditions that control the development of the nodules and the 'fish-eyes' are unknown.

In Littleham Cove the nodule-rich zone lies close to the plane of a significant strike fault that can be traced inland for a number of kilometres, but there is no record of a similar fault structure controlling nodule develpment at Carter's Brickpit. There is also little to suggest that at either locality the occurrence of the nodules is lithologically controlled. Dines (1942) concluded that the occurrence at Carter's Brickpit is at a different stratigraphical level from that at the coast.

Reduced patches

A less common form of reduction phenomenon is the diffuse patch of reduced material. These are of varied size and consist of large patches of reduced grey-green material with diffuse and indistinct margins, which may occupy almost the whole of the sedimentary unit, giving it a mottled appearance. Such patches may enclose irregularly distributed and shaped lamellae of dark, dense material similar in aspect to the dark central material of the nodules.

In the coastal section between Orcombe Rocks and Straight Point, in the stratigraphically lower and more arenaceous sediments of the Exmouth Mudstones and Sandstones, the presence of reduction spots is confined to intercalated argillaceous beds.

The data used in this study are all from core and outcrop material of the Littleham Mudstone.

CHEMISTRY OF THE NODULES

The chemical analyses (by XRF) of 13 nodules (Table 3) are semi-quantitative. The nodules for analysis were selected and individually identified from a number of locations (see Figure 1). The green halo material where it remained adhered to the central nodule was removed manually and the complete nodule processed for analysis. The scatter plots (Figure 5) show the relationships between selected elements in individual, numbered nodules. The figure shows that in most instances, the elements define two identifiable groups of nodules particularly clearly seen in the relationship Co/As. Nancarrow (1985) suggested, on the basis of mineralogical studies, that the nodules seem to allow classification into two types:

Type 1 nodules (samples 1, 3, 4, 5 and 6) are '...dark, dense nodules with strong colour zoning in the matrix...geometric centre but no distinct compositional nucleus...rich in sulphides, arsenides and vanadium oxides'.

Type 2 nodules (samples 2, 7, 8, 9, 10, 11 and 12) have a distinct nucleus (which may be small) and colour zoning, but have little evidence of mineralisation. Nodules 7 and 13, on the basis of the plots in Figure 5, may also be considered as part of this group. All the plots in Figure 5 demonstrate the clear subdivision into two groups, confirming the classification proposed by Nancarrow (1985). The correlation matrix for element concentrations in the nodules (Table 4) demonstrates high correlations between the pairs of elements Co-As, Co-Cu, Co-U, Cu-Pb, Cu-As, Cu-Se, Cu-U, Rb-Sr, As-U, Se-As and V-Se.

Data from these two types of nodule are compared in Figure 6a. The host sediment is compared with average shale in the histogram of Figure 6b. Figure 6a shows a marked chemical enrichment in U, As, Se, Cu and Co for Type 1 nodules relative to Type 2. The distinctive groupings are well illustrated by the U v V plot (Figure 5). Sample 4 has certain element concentrations that are not typical of Type 1 (lower Se and Cu), and sample 2 has a U concentration similar to that of Type 1. There is greater variability in results from Type 2 nodules. This may be because they come from diverse locations (see Figure 1). Those nodules mineralogically and chemically classified as Type 1 are all from the Littleham Cove locality, where it may be suggested that their exotic composition was enabled by the passage of mineralising solutions (rich in U, As, Se, Cu and Co) moving relatively easily via the adjacent fault structure. Figure 6b shows the relatively small enrichment of certain elements in the Littleham Mudstone compared with average shale. Of the elements determined, all except Sr and Cu are enriched in comparison with the average shale.

Table 3 Summary of chemical data for nodules

		Y	Sr	U	Rb	Th	Pb	As	Se	Zn	Cu	Co	V
1	8000a	630	70	7100	240	10	3000	4300	1600	390	15000	1900	36000
2	8000b	340	80	1800	260	15	15	70	10	440	970	70	16000
3	8000c	350	70	4200	230	10	3300	6100	1800	340	26000	2800	38000
4	8000d	80	100	1400	290	10	370	5000	80	380	980	1800	21000
5	8000e	130	110	1200	330	10	460	2000	1200	270	2300	1100	67000
6	8000f	160	70	1300	280	10	3200	4200	1500	1300	17000	1200	48000
7	8009	160	80	20	240	10	290	120	nd	410	740	40	11000
8	8010	10	20	30	200	10	180	20	nd	580	1100	nd	6000
9	8014	30	50	20	200	15	40	10	nd	190	190	60	7100
10	8023	40	150	4	280	20	15	15	nd	110	30	60	300
11	8026	15	60	20	220	10	110	10	nd	230	60	40	8000
12	8045	30	80	30	200	15	1600	140	10	410	810	80	15000
13	8046	760	90	80	260	5	2800	120	30	680	2500	150	24000

Data from Appendix 1, Table 1, Nancarrow (1985)

All concentrations in ppm

Table 4 Correlation matrix for chemical data, nodules

	Y	Sr	U	Rb	Th	Pb	As	Se	Zn	Cu	Co
Y	–										
Sr	0.05	–									
U	0.56	–0.06	–								
Rb	0.14	0.71	0.08	–							
Th	–0.51	0.37	–0.18	–0.09							
Pb	0.65	–0.09	0.58	0.01	–0.47	–					
As	0.24	0.04	0.71	0.31	–0.32	–0.62	–				
Se	0.09	–0.40	0.67	0.10	–0.21	0.59	0.71	–			
Zn	0.22	–0.28	0.01	0.13	–0.44	0.56	0.26	0.15	–		
Cu	0.40	–0.15	0.72	0.02	0.28	0.83	0.81	0.87	0.38	–	
Co	0.27	–0.09	0.76	0.23	–0.35	0.59	0.97	0.75	0.18	0.81	–
V	0.31	0.13	0.46	0.61	–0.44	0.53	0.61	0.73	0.36	0.55	0.61

___ indicates significant probability at 99.9% confidence level

Data from Appendix 1, Table 4a, Nancarrow (1985)

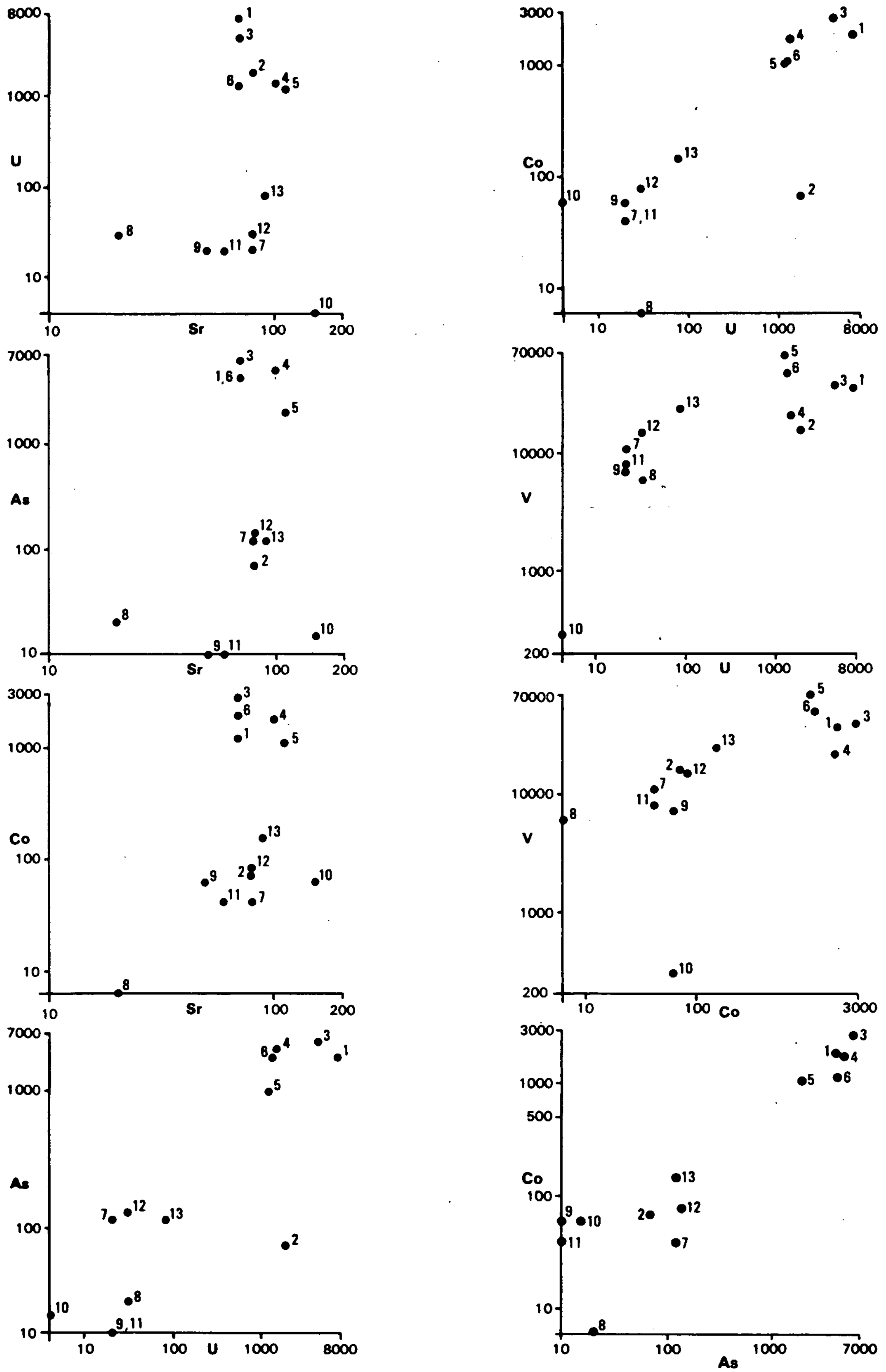

Figure 5 Scatter plots of nodule chemistry

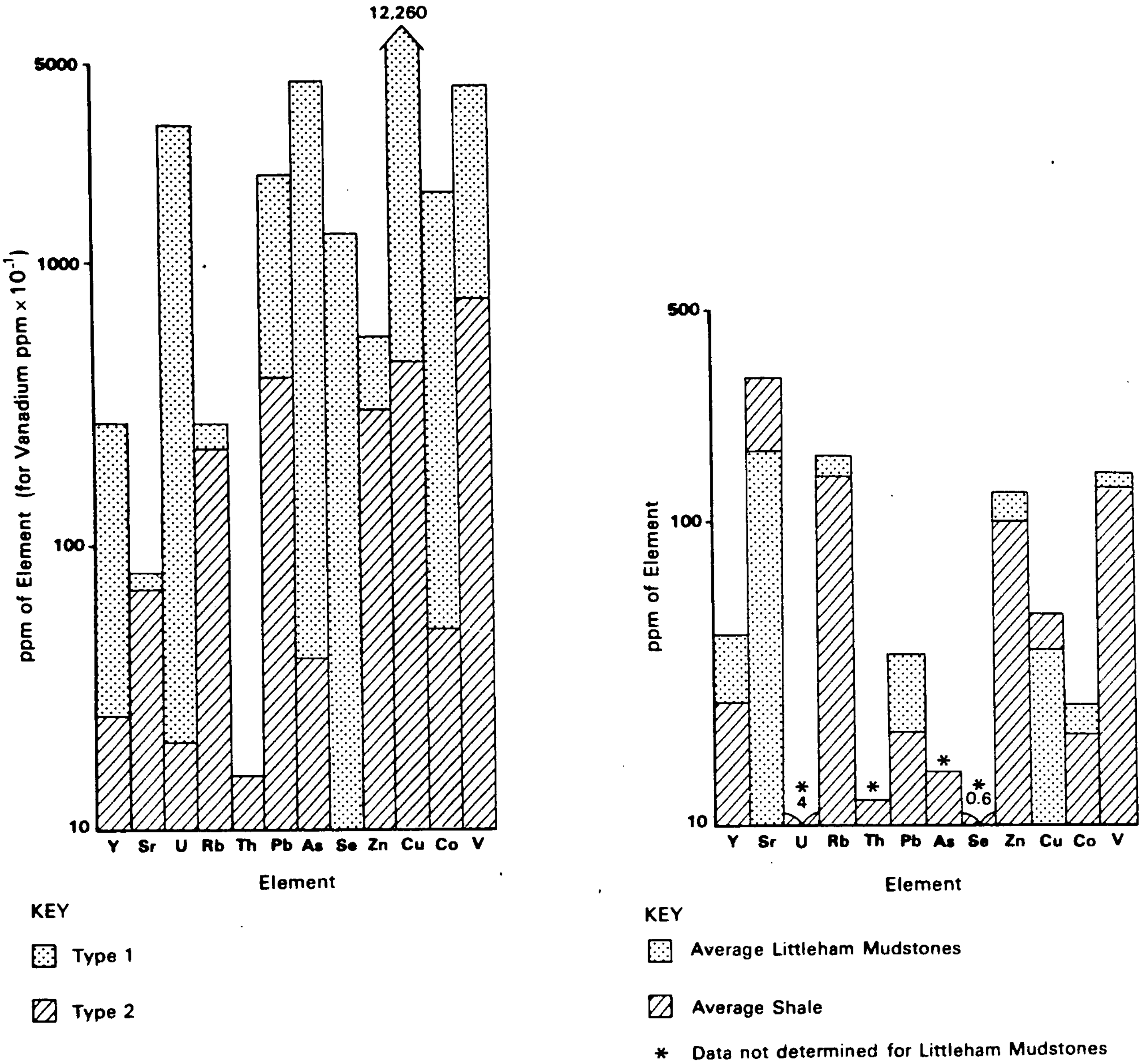

Figure 6 Comparison of chemical data: (a) Type 1 and Type 2 nodules; (b) Littleham Mudstone and average shale

ORIGIN OF THE REDUCTION FEATURES

It is generally agreed that the basic variation in the colour of the red-bed sediments between red and green varieties is an indication of changed local environmental conditions from oxidising to reducing, which is represented by the state of the iron oxides (Durrance et al., 1978). There is some debate as to whether the reduction features (green spots, haloes, patches etc) represent changes in the oxidation state of the iron 'effected during or post lithification or whether they represent relics of original material that have not been oxidised' (Durrance et al., 1978). These authors (p 1237) suggest that the reduction spots are better explained as 'areas in which oxidation . . . has been inhibited'. They suggest that the Littleham Mudstones became reddened during their burial beneath up to 1000 m of sediment, at the same time as the 'oxidation of organic remains' (p 1239)—a process which locally caused the reduction of the surrounding red ferric oxides. Similar reduction phemomena elsewhere are associated with plant-derived material (e.g. Curiale et al., 1983), but there is no evidence of plant material in the Aylesbeare Mudstones in south Devon.

Curiale et al. (1983), reporting on the uranium-rich nodules in the Permian Hennessey Group Beds in Oklahoma, discussed their origin, particularly with respect to their occurrence in a sequence devoid of identifiable plant remains. Their chemical data suggest that the nodules were formed about a nucleus of hydrocarbons (of a type that is chemically similar to hydrocarbons associated with oil formation), which have been affected by biogradation and radiation.

These nodule occurrences in the USA (Curiale et al., 1983) show some similarities to the Littleham Mudstone:

1. they occur in red silt/mudstone deposited in a near-shore environment
2. the greatest concentration of nodules occurs in proximity to fault zones
3. the nodules are always surrounded by a pale coloured halo
4. they are in proximity to known oil-bearing strata
5. the concentration of elements in the nodules is not reflected in significant changes in the chemistry of the host rocks
6. significant levels of uranium are known in the groundwater

In the absence of recognisable plant material within the Littleham Mudstone an origin similar to that proposed by Curiale et al. (1983), relating the formation of the nodules to hydrocarbons, is attractive. Although the precise nature of the dark material associated with the nodules has not been investigated, Harrison et al. (1983) record the presence of hydrocarbons in association with coffinite in a vanadiferous nodule from the Mercia Mudstone. They suggested that 'the possibility exists of abiogenic hydrocarbon associated with the metalliferous solutions', which seems to imply that the hydrocarbon material is not now readily identifiable as derived originally from either plant or animal material.

Although data about the nodules from this area are incomplete, the lack of identifiable organic debris as a nucleus suggests that an alternative genetic model must be sought. Harrison et al. (1983) suggested that the dark material in some nodules possibly derived from oil or gas evolving from lower levels in the sedimentary pile. The presence of oil and gas bearing strata in the general area (Sherwood Sandstone at Wytch Farm), lends some support to this model, and to the possibility that hydrocarbons were available and could have migrated through the sedimentary pile. During the compaction and early lithification of the sediments, the upward migration of volatile hydrocarbons would be affected by the lithology and grain size of the sediments, the more permeable arenaceous strata becoming saturated with hydrocarbons. Structural features, such as faults, would facilitate the easier passage of gases and fluids and may account for the local increase in reduction phenomena (e.g. at Littleham Cove) and the commonly observed selvage of reduced material on fault and joint planes.

In the less permeable argillaceous sediments, the upward migration of hydrocarbons would have been more likely in the gaseous state. Bubbles of gas escaping slowly upwards would not only inhibit oxidation locally but provide an environment in which reduction could actively take place. The size of such a zone would be in proportion to the size of the gas bubble.

In a recent review paper, Hofmann (1991) considers the role of wood and bitumens in the formation of reduction spheroids. According to his calculation the required volume of either of these materials in some 50% of cases is likely to exceed the volume of the spheroid, from which he concludes (p 120) that 'reduction spheroids have not formed from a pre-existing organic nucleus in the sediment'. On the basis of the currently available data, such a conclusion may well be applicable to the reduction spheres and spots described in this report, which are similarly without nuclei. Hofmann's thesis concludes that bacterial activity using dissolved reductants 'such as methane or low molecular weight organic acid anions, or inorganic compounds such as ammonia or hydrogen' are responsible for the development of these reduction phenomena. It is his contention (p 21) that the localisation of the reduction phenomena is dependant upon the presence of bacteria acting catalytically upon the reductants to enable reducing conditions to prevail.

All studies of the compositions of nodules have noted their chemical variety—adjacent nodules, for instance, frequently demonstrate considerable variability in the exotic elements. There is currently no evidence that the composition has either stratigraphic or geographic significance.

The primary source of the metallic elements in the nodules is also of interest, particularly as there is lack of constancy in the chemistry of the nodules: neither geographical provenance nor stratigraphical position seem to be reflected in the chemical composition.

The host-rock samples collected from the three boreholes were analysed for uranium (by XRF), but approximately 72% of the 196 samples of typical Littleham Mudstone analysed for uranium recorded values <5 ppm (the limit of detection from the technique used)—levels which accord with an average value in shales of 4 ppm (Levinson, 1974).

The primary source of the uranium found in some nodules may well be the granites of south-west England, which at the time of deposition of the Littleham Mudstone would have been undergoing erosion and thus could provide uranium in solution to the sediments. Basham et al. (1982), in a study of uranium-bearing accessory minerals in granites in the British Isles, conclude that 'Uraninite has been recognised as the dominant contributor of uranium to the Hercynian granites of south-west England'. Zircon, monazite and apatite also occur in the granite, but are less significant as hosts for uranium.

Alteration of the granites by either weathering or hydrothermal activity would release appreciable quantities of uranium as soluble salts and secondary minerals to the surface and groundwaters (Fischer and Stewart, 1961) and thus into the sediments in the adjacent depositional basins. Several uraniferous species have been identified in the nodules (Houstoun and Jefferies, 1982; Harrison, 1975; Nancarrow, 1985) from which it is concluded that the primary U phase was coffinite precipitated from a fluid medium, possibly as colloidal coatings on other grains. Subsequent oxidation gave rise to a suite of uraniferous salts including metatyuyamunite (Durrance and George, 1976) and tyuyamunite. The existence of hydrocarbons would provide a suitable scavenger focus for the precipitation of uranium and the other metallic species, such as vanadium.

Analyses of 200 samples from the Litleham Mudstone (Table 4) have shown that these sediments contain on average 146 ppm V, close to the mean value of 120–130 ppm for shales (Levinson, 1974). The values obtained from the nodules (expressed as elemental vanadium) vary between a low of 300 ppm and a high value of 6.7%, with the majority of the values in excess of 1%.

According to Henson (1973) the clay mineralogy of the Littleham Mudstone indicates an environment that was approaching supersaline when these fine-grained sediments were deposited, which suggests that the physico-chemical conditions were such that the potential mobility of both of these metals, from whatever source, would have been at a maximum.

Hofmann (1991) in his study concludes that the weight of evidence from a wide variety of locations, geological environments and ages, points towards a genesis for the reduction phenomena and accumulation of exotic elements that assumes a supply of porewater containing both the reductants and exotica (p 121). The localisation of of the reduction spots, according to Hofmann's hypothesis, would seem to be related to the presence of bacteria.

In the south Devon area there is no evidence of particulate organic matter but some hydrocarbon substances have been recognised in some of the spheroids (Harrison, 1975). Such complexes would enable reduction of ferric iron to ferrous iron, resulting in the formation of typically green/grey spheroids. If the complexes were in some way derived from a deeper petroliferous unit then the existence of fault masses and more porous units would assist in their migration through the sedimentary pile.

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