A

THESIS

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THE REGIONAL/GEOCHEMICAL. DISTRIBUTION OF CADMIUM IN ENGLAND AND WALES

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ABSTRACT

The use of cadmium in industry has long been recognised as a potential health hazard. Although measures for its control are strictly applied, evidence is available to suggest that environmental contamination can lead to serious intoxication and disease (such as Itai-Itai-Byo in Japan). The ability of the human body to readily accumulate cadmium and the natural concentration of the metal by biological enrichment through the food-chain, has led to world-wide concern amongst environmentalists about any possible link between sickness and environmental conditions.

This thesis is concerned with the identification and study of those localities in England and Wales in which anomalous amounts of cadmium have been detected in natural materials over a wide and persistent area. The geochemical cycle which has led to the enrichment of the metal in natural environments is described with the assistance of a detailed study of the chemical form, mineralogical associations and elemental associations of cadmium in black shale sediments in which the metal is commonly strongly enhanced. In addition, identification of form and elemental associations of cadmium in soils have been determined with regard to the availability of the metal to plants and hence to the natural food-chain. The effects of long term exposure to cadmium pollution has still to be fully assessed; indications are that long-term, low-level exposure to cadmium from environmental sources may result in its accumulation to levels at which toxic effects might result.

This study of the areas of cadmium anomaly has shown that the primary sources of cadmium to the environment are industrial emissions,

metallic sulphides and metal enriched black shales. The major source of low-level cadmium to the natural food-chain is from black shales in which cadmium is found to be 50 to 60 times the crustal abundance (0.2 ppm).

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CHAPTER I

1 INTRODUCTION TO THE PHYSICAL CHEMISTRY AND GEOCHEMISTRY OF CADMIUM

1.1 PHYSICAL PROPERTIES AND RELATED MINERALOGY

Cadmium is a bluish-white metal with an atomic weight of 112.4, a valence state of two and an electronic configuration 1-8-18-18-2. It is present in Group 2B of the Periodic Table along with zinc and mercury. The common occurrence of cadmium in zinc ores led to its discovery in 1817 by F. Stromeyer and its being named after the ancient Greek name Kalmeia (latin; Cadmia) for zinc carbonate (calamine).

Both cadmium and zinc have been detected and quantitatively determined in solar and stellar atmospheres (Rankama and Sahama, 1950). Noddack (1930) reported an average of 30.0 ppm cadmium in troilite meteorites and 8.0 ppm in nickel-iron meteorites. The highest concentration of cadmium is found in the sulphide phase of meteorites and the second highest in the metal phase. Considerably less cadmium is found in the silicate meteorites which confirms that the metal is predominantly chalcophile with a subordinate oxyphile nature.

In scientific literature the geochemical behaviour of cadmium is regarded as being analogous to that of zinc because of similar electronic structures and ionisation potentials of the two elements. Crystallochemical relations between cadmium and other elements are governed by relative sizes of the ionic radii. The ionic radius of Cd^{++} is 0.97A, quite close to that of Ca^{++} (0.99A) and Na^{+} (in octahedral co-ordination, 0.98A). Thus it would be expected that some cadmium will enter into minerals of calcium and possibly sodium in the same way that zinc, by virtue

of its similar ionic radius to iron and magnesium, is found in early magmatic oxide ores. Spectrographically detectible substitution of cadmium for calcium has been shown in bytownite feldspar of anorthosite and also in monoclinic augite phenocysts of basalts (Goldschmidt, 1958). Rankama and Sahama(1950) however, wrote that the manner of occurrence of cadmium in such igneous rocks is still unknown and that cadmium very seldom becomes enriched in igneous rocks. The abundance ratio of zinc: cadmium in igneous rocks is approximately 900:1. Goldschmidt (1958) further commented on the consequence of these size relations by showing that the crystal structures of cadmium oxide and carbonate closely resembled those of corresponding calcium compounds. In the zinc deposits of Franklin Furnace USA, he also demonstrated that cadmium could enter calcite structures in preference to manganiferous zinc oxide (zincite) and zinc ferrite (franklinite). The failure however of cadmium to enter feldspar and apatite structures in the cadmium-enriched late stages of the magmatic differentiation processes in the Skaergaard intrusion has been interpreted as a measure of the relatively stronger degree of covalency between Cd^{++} and O^{++} compared with that between Cd^{++} and Ca^{++} (Brooks and Ahrens, 1961). Vinogradov (1959) referred to the comparatively large ionic radius of Cd^{++} and wrote that cadmium probably entered into minerals of later crystallisation. According to Sandell and Goldich (1943) cadmium, like zinc, seems to be concentrated in ferro-magnesian minerals. Most of the cadmium in acidic igneous rocks is present in biotite although traces of the metal have been reported in apatite. Cadmium has a notable tendency of concentrating in the sphalerite structure (the most common zinc mineral found in nature) although other zinc minerals inevitably contain small quantities of cadmium. The corresponding cadmium compound is greenockite (cadmium sulphide) which is frequently found in nature as a yellow coating on weathering sphalerite. At low and moderate

temperatures cadmium is more chalcophile in nature than zinc; both elements are strongly enriched in hydrothermal rocks and minerals formed at a relatively low temperature. When the amount of sulphur present is insufficient to accommodate cadmium and zinc as sulphides, then cadmium will be preferentially concentrated in the sulphides (Goldschmidt, 1958). Cadmium has been reported in a galena (lead sulphide) described by Oftedal (1941) where contamination by sphalenite appeared to be excluded. Other cadmium minerals are rare in nature invariably forming as the result of weathering and oxidation of primary minerals. The most common cadmium minerals are the forementioned sulphide greenockite, which is crystallographically hexagonal in form, and the isometrically structured sulphide, hawleyite, although cadmium oxide (monteponite) and carbonate (otavite) have been reported frequently. Cadmium has been reported in the various secondary minerals formed in the oxidised zones of zinc deposits such as, manganese oxides, limonite, and forms of montmorillinite. The cadmium content of these more common minerals and those associated with igneous rocks are summarised in Table 1.1.

Eight stable isotopes of cadmium are known in nature, of which the two most common are ^{114}Cd, with an atomic mass of 113.9036 and a natural abundance of 28.86 per cent and ^{112}Cd, with an atomic mass of 111.9028 and a natural abundance of 24.07 per cent. Radioactive isotopes with mass numbers, 104, 105, 107, 109, 111, 113, 115, 117, 118 and 119 have been made artificially (Strominger et al, 1958) of which an isomer of ^{113}Cadmium has the longest half-life, 5.1 years.

1.2 CADMIUM IN THE UPPER LITHOSPHERE AND IN HYDROTHERMAL MINERAL DEPOSITS

The average cadmium content in the rocks of the upper lithosphere has been quoted as 0.5 ppm and the zinc: cadmium ratio is around 250 (Goldschmidt 1958). The ratio of zinc : cadmium for American

TABLE 1.1 CADMIUM PRESENCE IN MINERAL SPECIES

	Mineral Type and Name	Chemical Composition	Cd (ppm)
1	SULPHIDES		
	Sphalerite	ZnS	1-20,000
	Greenockite	CdS	778,000
	Hawleyite	CdS	778,000
	Chalcopyrite	Cu. FeS_2	< 0.4-110.0
	Marcasite	FeS_2	< 0.3-50.0
	Arsenopyrite	Fe. AsS	< 5.0
	Galena	PbS	< 10.0-3,000.0
	Pyrite	FeS_2	< 0.06-42.0
	Pyrrhotite	$Fe_{(1-x)}S$	Trace
	Tetrahedrite	$(Cu. Fe. Zn. Ag)_{12}-SbAs_4S_{13}$	80.0-2,000.0
2	SULPHATES		
	Anglesite	$PbSO_4$	120- 1,000+
	Barite	$BaSO_4$	<0.2
	Anhydrite/	$CaSO_4$	< 0.2
	Gypsum	$CaSO_4. 2H_2O$	
3	OXIDES		
	Magnetite	Fe_3O_4	n.d. - 0.31
	Monteponite	CdO	875,000
	Limonite	Hydrous iron oxide	< 5-1,000
	Manganese Oxide	MnO. OH/ MnO_2 etc.	< 10-1,000
4	CARBONATES		
	Otavite	$CdCO_3$	651,800
	Smithsonite	$ZnCO_3$	0.1-23,500
	Calcite	$CaCO_3$	< 1.0-23.0
5	SILICATES		
	Riebeckite	$Na_2Fe_5(Si_8O_{22})(OH)_2$	0.88-5.8
	Arfvedsonite	$Na_3(Mg. Fe)_4Al(Si_8O_{22})-(OH. F)_2$	2.2
	Olivine	$(Mg. Fe)_2(SiO_4)$	0.37
	Plagioclase	$Na-Ca(AlSi_3O_8)$	0.14-0.15
	Pyroxene	$Ca. Mg. Si_2O_6$	0.42-0.44
6	NON SPECIFIC		
	Pyromorphite	$Pb_5cl(PO_4)_3$	< 1.0-8.0
	Scorodite	$Fe. ASO_4. 2H_2O$	< 1.0-5.8
	Beudomtite	$Pb. Fe_3(ASO_4)(SO_4)(OH)_6$	100.0-1,000.0
	Apatite	$Ca_5(PO_4)_3(OH, F, Cl)$	0.14-0.15
	Bindheimite	$Pb_2. Sb_2O_6(O. OH)$	100.0-1,000.0
	Lead Selenide		300.0
	Lead Telluride		10.0
	Alabandine		180.0

magmatic rocks given by Sandell and Goldrich (1943) was found to be rather uniform, about 250:1 by weight. The average amount of cadmium in igneous rocks is 0.18 ppm and zinc 80 ppm (Sandell and Goldich, 1943).

In early magmatic sulphides the amount of zinc and cadmium present is relatively low. A study of the data of cadmium content in Norwegian sphalerites by Oftedal (1941) indicated that amounts of cadmium are highest in those sphalerites which are formed at low to medium temperatures and lowest in those that are formed at high temperatures. Goldschmidt (1958) suggested that the proportion of cadmium to zinc depends partly on the available amount of zinc sulphide and in accordance with this, sphalerites which are found to contain more than 1 per cent cadmium contain only 1 or 2 per cent iron. In addition low iron (and manganese) contents provided independent evidence of a low temperature of formation. El Shazly (1956) has studied extensively the occurrence of minor elements in syngenetic and epigenetic sphalerites and detected the elements cobalt, gallium, germanium, indium and thallium. In addition to the discovery of cadmium in galena I. and W. Noddack (1931) recorded 300 ppm cadmium in a hydrothermal lead selenide and 10 ppm cadmium in lead telluride. They also reported the presence of 180 ppm cadmium in the manganese sulphide, alabandine.

1.3 CADMIUM IN IGNEOUS AND METAMORPHIC ROCKS

Mention has already been made of the more occasions when cadmium is enriched in igneous rocks (see page 3).
The abundance of the element in igneous rocks depends greatly on the composition of the original melt. During magmatic differentiation cadmium and zinc remain largely in the residual magmas although silicate rocks formed during the main stage of differentiation contain

proportionately more zinc than cadmium. Vincent and Bilefield (1960) concluded that late stage granoplyres of basic magma revealed a fourfold increase in cadmium content in comparison with the original more mafic parental magmas. In seven dolerites, gabbros and greenstones Sandell and Goldich (1943) found an average of 0.19 ppm cadmium, whilst the average cadmium content of thirteen granites was 0.12 ppm. Some controversy, however, still exists concerning cadmium behaviour during differentiation of magmas. Preuss (1941), for example, recorded over ten times as much cadmium in granites compared with that in gabbros. Such apparent discrepancies in results can probably be explained by regional differences in metal content of magmas.

The cadmium content in metamorphic rocks is predictably very low, ranging from 0.026 ppm in eclogite to 0.16 ppm in gneiss (Brooks, 1960, 1961). For a suite of metamorphic rocks analysed by Boyle (1972) the mean cadmium presence was less than 1.0 ppm although levels as high as 5.0 ppm in hornfels and skarn were recorded.

1.4 CADMIUM IN SEDIMENTARY ROCKS

Amongst the sedimentary rocks, those of argillaceous type are considerably more enriched in cadmium than are those of the arenaceous and calcareous type. Of the argillaceous rocks black shales, deposited under reducing conditions contain highest quantities of cadmium. In the black Pierre shale of the USA where total carbon content averaged 3.5% (a figure six times greater than that of the average shale) Tourtelot (1969) reported cadmium concentrations in the range 0.5-8.4 ppm. Black shales analysed by Krauskopf (1955) have enrichment factors of 44 for lead (representing a maximum of 400 ppm) and 77 for zinc (a maximum of 1000 ppm) in comparison to his average grey shale. Concentrations of 100 - 1,000 ppm cadmium have been recorded in some parts of the Mansfield

'Kupferschiefer' (copper shale) in Germany (Cissarz, 1930). Rankama and Sahama (1950) noted that in the Mansfield copper-shale the highest concentration of cadmium and zinc in places where production of hydrogen sulphides by decaying organisms has been rather weak. Cadmium, zinc and, in addition, lead occur in zones independent to those of copper enirchment and it is known that the elements iron, nickel, cobalt and copper have a greater affinity for sulphur than do zinc or cadmium. However, greater enrichment in cadmium than in zinc, as reported from the Mansfield copper shale, indicated a precipitation of cadmium by hydrogen sulphide from inherently stagnant bottom water. Durham et al (1963) reviewed accounts in the literature concerning the sources of the metals and stressed the uniqueness of each situation with respect to the availability of metals to an environment capable of their retention.

Little is known of the presence of cadmium in the carbonate sediments although Goldschmidt (1958) argued that very small amounts of the element may replace calcium in calcite. Rarely documented analyses of limestone show an average cadmium content of less than 1.0 ppm (Wedepohl, 1966). Bowen (1966) published the results of analyses of cadmium in shales, sandstones and limestones which averaged 0.3, 0.05 and 0.035 ppm respectively. Wedepohl (1966) further reported that the average cadmium content of non-carbonaceous argillites and sandstones does not exceed 1.0 ppm.

The cadmium content of coals are highly variable. Boyle (1972) reported presences ranging from less than 1.0 to 20.0 ppm cadmium in the ash of coals and from 0.3 to 2.0 ppm in the whole coal. The work of Rankama and Sahama (1958) indicated less than 1.0 to 3.0 ppm cadmium with an average of 0.25 ppm in peats, and up to 50.0 ppm in the ash of bogs. They concluded that oxidate sediments such as manganese-rich lake and bog ores absorb significant

amounts of cadmium and zinc. However cadmium was not detected in the ash of 46 samples of crude oil from the Ukraine nor in the subsequent analyses of the oil itself. (Porfir'ev et al, 1970). In contrast a range of zero to 700 ppm cadmium was detected by the same authors in samples of oil from a site in Belorussia and the cadmium content of six ashed soil samples from the same site ranged from 1,600 to 7,000 ppm.

1.5 CADMIUM IN THE WEATHERING CYCLE AND IN SOIL FORMATION

Many elements are present in different oxidation states in the earth's crust. Their stability in a particular state depends upon the energy change necessary to cause the addition or removal of electrons. The oxidation potential, which quantitatively represents such an energy change, is related to the reference reaction:

$$H_2 = 2H^+ + 2e \qquad Eo(\text{oxidation potential}) = 0.00V$$

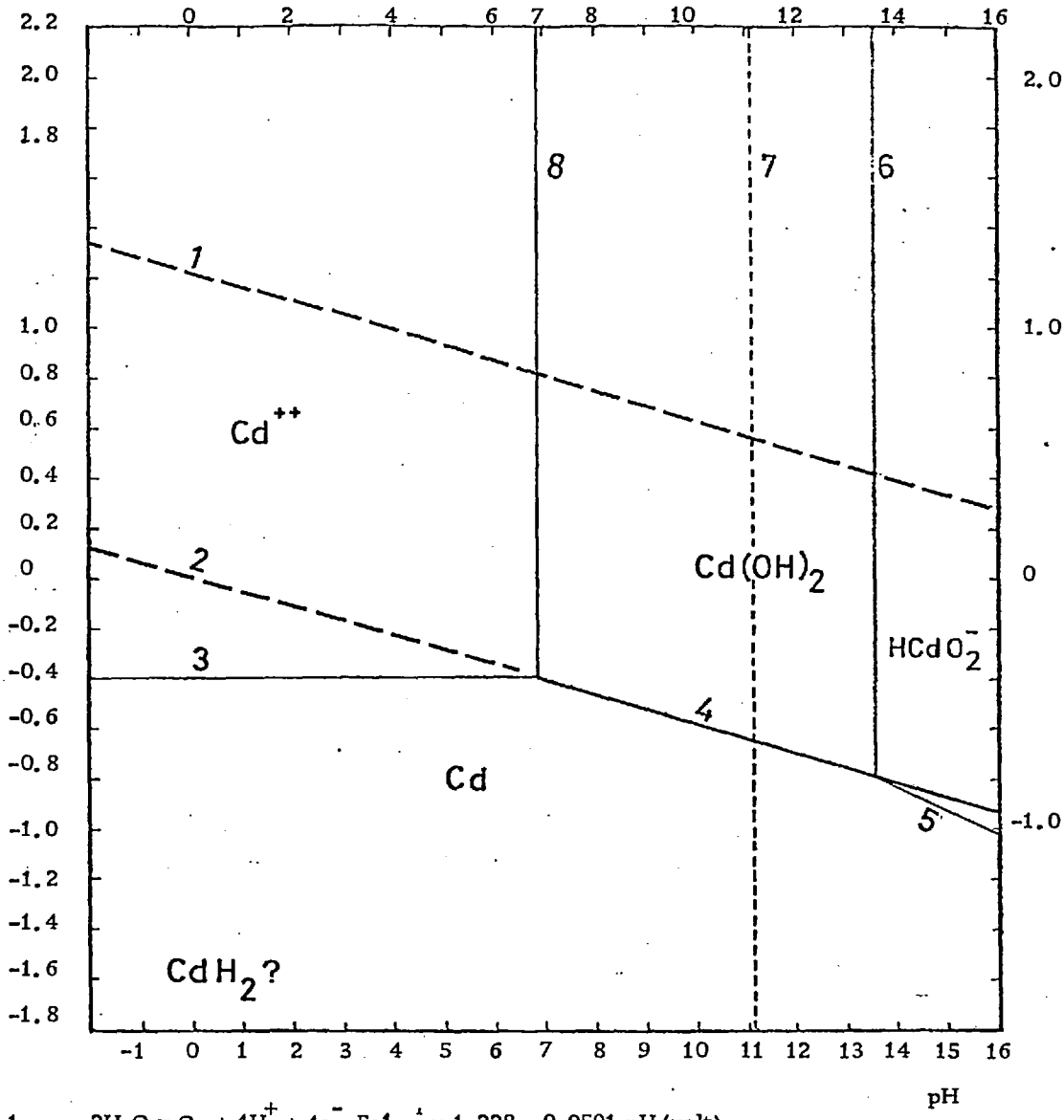
The range of oxidation potentials which exists in a natural aqueous environment is theoretically limited to those which cause the thermal decomposition of water and the evolution of oxygen or hydrogen i.e.

1. $2H_2O = O_2 + 4H^+ + 4e \qquad Eo = 1.23V$
2. $2H^+ + 2e = H_2 \qquad Eo = 0.00V$

In addition large changes in oxidation potential take place when reactions occur which involve the presence of hydrogen or hydroide ions. In pure water at 20^oC the hydrogen ion concentration is 10^{-7} moles/litre, the negative logarithm of which is 7 and is known as the pH. As a rule the pH of natural water lies between 4 and 9, the great majority being near the pH of pure water (pH of 7). For a pH of 7 the oxidation potential necessary for the decomposition of water to liberate oxygen is +0.82V and the oxidation potential necessary for the liberation of hydrogen is -0.41V, although values as low as -0.5V have been recorded in organic-rich marine deposits (Mason 1958). In a natural environment with a

pH of 7 and oxidation potential ranging from -0.41 to +0.82V, cadmium exists as the bivalent cation (see Figure 1.1). In more reducing environments and where the pH is greater than 7, cadmium is present as the hydroxide.

During weathering zinc goes readily into solution below a pH of 6.8 and cadmium below a pH of 8.0; consequently in acid weathering conditions the zinc:cadmium ratio in solutions would be expected to increase. The soluble forms of cadmium during weathering would be chloride and sulphate although Boyle (1972) further suggested that cadmium may also migrate as nitrate, carbonate, hydroxide or ammonia complexes or even as a variety of organo-metallic compounds. Humic substances formed from the maturation of plant and animal debris usually accounts for most of the organo-metallic complexation. In reducing environments the presence of hydrogen sulphide, formed by the action of bacteria in anaerobic conditions may cause the cadmium to precipitate as a very insoluble sulphide and become enriched in, for example, the zone of reduction surrounding an ore body. Where hydrogen sulphide is evolved under reducing conditions in soils, cadmium will precipitate as sulphide. Under more normal conditions it is suggested by the author that the metal ion would adsorb onto materials with high cation exchange capacities such as clay minerals and organic matter. The presence of oxidate sediments will adsorb significant quantities of zinc and cadmium (Rankama and Sahama, 1950) and furthermore, the catalysing actions of iron-loving bacteria species, such as Leptothrix ochracae in the precipitation of iron and manganese oxides may increase this capacity (Butt, 1971).



1. $2H_2O = O_2 + 4H^+ + 4e^-$. Eo1 = 1.228 - 0.0591 pH (volt)
2. $H_2 = 2H^+ + 2e^-$. Eo2 = 0.000 - 0.0591 pH (volt)
3. $Cd = Cd^{++} + 2e^-$
4. $Cd + H_2O = CdO + 2H^+ + 2e^-$
5. $Cd + 2H_2O = HCdO_2^- + 3H^+ + 2e^-$
6. $CdO + H_2O = HCdO_2^- + H^+$
7. $Cd^{++}/HCdO_2^-$, pH = 11.1.
8. $Cd^{++} + H_2O = CdO + 2H^+$

FIG. 1.1 POTENTIAL/PH EQUILIBRIUM DIAGRAM FOR THE SYSTEM CADMIUM - WATER, AT 25°C (ADAPTED FROM POURBAIX, 1966)

CHAPTER 2

2 AN INTRODUCTION TO CADMIUM IN THE ENVIRONMENT

2.1 INTRODUCTION

The uncontrolled use of cadmium by man can lead to serious health problems amongst people occupationally exposed to the element and in addition to people living in areas of cadmium fall-out from cadmium using industrial installations. Under extreme circumstances cadmium poisoning in humans may result in maiming and even death such as has been reported after World War II by the much documented Itai-Itai disease in Japan. Although such instances should not be overlooked, it does appear that Japanese-type toxication is not necessarily the natural progression of events such as have been professed in the scientific literature since the discovery of cadmium's inclusion in the human food-chain. For example, in a 'market-basket' study of 82 items obtained in retail food stores in the USA, all food-classes examined contained cadmium, although the resultant average daily intake computed (0.026 milligrams) was much lower than had been predicted by previous studies (Duggan and Lipscomb, 1969). Such levels of cadmium in food are not regarded as being especially hazardous, although some indication of the toxicity of the element can be gauged from the considerable number of epidemics of acute nausea which were reported following the attempts to use cadmium plated articles as food containers (Fairhall, 1957). Experimentation upon animals indicated that soluble inorganic forms of cadmium fed in drinking water accumulate in the liver and kidney (Decker et al, 1958). In contrast to mercury, which is grouped alongside cadmium and zinc in the periodic table, cadmium is not known to form highly toxic organic compounds. The intervention of the Lanthanide series between cadmium and mercury in the Periodic Table is the fundamental cause of the greatly different electronic structures of the two elements. Mercury has fourteen

electrons in the fourth orbital which may account for its marked covalency and its tendency to form stable mercury-carbon compounds (Sidgwick, 1950).

2.2 UPTAKE AND ELIMINATION OF CADMIUM

Absorption by inhalation is the most common route for entry of cadmium into the body. Some metal may be transported into the blood but most would be distributed to the gastrointestinal tract where it would eventually be excreted. Concentration of cadmium in 'normal' blood is very low: 0.5 microgram was detected per 100 millilitres of blood in a study by Kubota et al (1968). However, knowledge of the effects of cadmium fume inhalation in humans is provided only by medical case histories of occupationally exposed industrial workers and the effects are therefore difficult to assess. Friberg (1950) described the occurrence of an unusual protein in the urine of persons chronically exposed to cadmium in the air and reported that the amount of metal absorbed by the body amounted to 10-15% (and may be as high as 40%) of the total inhaled. The efficiency of the kidney and liver to concentrate the metal can be gauged by comparing the 'normal levels' of cadmium in human tissue with the elevated levels in the tissues of people exposed to cadmium contamination (see Table 2.1).

A second and less efficient route of entry for cadmium into the body is through ingestion. Despite the efficiency of cadmium retention in the kidney, something like 98% of the dietry cadmium intake by humans is excreted, normally within 48 hours. Friberg (1950) indicated that the average amount of dietry cadmium taken up by the body seldom exceeds 20% of a single dose or 1% of a continual dose. The normal value for urinary cadmium excretion in occupationally exposed humans is less than 5.0 micrograms (μgm) a day although most adults

TABLE 2.1 NORMAL AND "ELEVATED" LEVELS OF CADMIUM IN MAN

MAN "Normal levels"

Tissue	Cadmium 'range of means'	Location
Hair	0.4 - 0.9 (ppm wet wt.)	Sweden, Yugoslavia
Blood	<0.2 - 0.85 (ug/100 ml)	Sweden, USA, W. Germany
Urine	1.0 - 3.1 (ug/1)	Japan, USA, W. Germany
Kidney	10 - 23 (ppm wet wt.)	UK, Sweden, W. Germany
Liver	1.4 - 2.3 (ppm wet wt.)	UK, Sweden, W. Germany
Muscle	0.06-0.13 (ppm wet wt.)	UK, Sweden, W. Germany

"Elevated levels" (for people exposed cadmium contamination

Tissue	Cadmium	Location
Hair	3.5	US
Blood	2.7 - 4.1	Sweden, W. Germany
Urine	3 - 487	England; Japan
Kidney	13 - 395	England, Japan
Liver	23 - 330	various locations
Lung	2.5 - 500	various locations

Tables 2.1 to 2.6 are all reproduced, with minor modifications, from the Science Research Council Report on Cadmium in the Environment, 1973.

register a loss of 1.0-2.0 µgm of cadmium on average per day. Decker et al (1958) fed cadmium to rats in their drinking water at concentrations between 0.1-50.0 ppm over a period of twelve months and realised that the subsequent presence of cadmium in liver and kidney tissue was more or less in proportion to the initial dose. He concluded that 0.3 to 0.5% of the total cadmium ingested over the year was retained by the organs.

Medical knowledge regarding the storage of cadmium in the body as a result of occupational exposure has been accumulated over the past half century. In all post-mortems of smelting workers the analysis of liver and kidney tissue revealed relatively high concentrations of cadmium in comparison with that found in tissue of unexposed subjects. The explanation for this followed the discovery by Morgoshes and Vallee in 1957 of an unusual cadmium protein from equine kidney cortex which they named metallothionen and which, on analysis, was found to contain 4.2% cadmium and 2.6% zinc.

1.3 TOXICOLOGY

Cadmium has been known to exert toxic effects since 1858. Knowledge has been gained from studies on industrial workers as well as from records of accidental poisoning and attempts to use cadmium therapeutically. In 1862, B. Wood in 'Chemical Notes' bravely described the effect of inhaling cadmium vapour as follows: "orange-yellow coloured fumes which, when inhaled too freely, leave a disagreeable, sweetish, styptic sensation upon the lips and an intolerable brassy taste in the mouth with constriction in the throat, heaviness in the head and nausea". The prescribed acute effects upon humans of oral ingestion are immediate nausea and vomiting which can occur from an intake of as little as 15 milligrams of total cadmium (Fairhall, 1957).

As a consequence of occupational exposure, such as the inhalation of cadmium oxide fume or dust following cutting or welding objects containing cadmium the acute effects are delayed coughing, pain in the chest and then pneumonitis (distress in breathing). Fatalities have occurred from exposure to fume levels ranging from 3 to 100 milligrams of cadmium per cubic metre. Although present-day acute poisoning from inhalation of cadmium is rare, the death rate as a result of such an action is estimated to be as high as 15% of those exposed. Today, more than thirty years after the first serious warnings about the danger of the metal to health by industrial hygienists and some eighteen years after the registration of the chronic Itai-Itai-Byo disease prevalent in wartime Japan, strict monitoring of the presence of the metal has almost removed the risk of possible chronic exposure. Although there is no firm evidence that uptake of cadmium in the kidney could result in total renal failure, doctors are worried by a possible link between kidney damage and the onset of high blood pressure or hypertension, particularly in older people. Gradually increasing kidney damage could contribute to the development of high blood pressure.

Chronic accumulation of cadmium may give rise to total inhibition of bone repair mechanisms, so that the load-bearing bones of the skeleton progressively deform and collapse, to bone softening and fragility and, in some cases, to actual liver and kidney damage. Cirrhosis of the liver and severe damage to the lungs has been reported (Mills, 1970). Animal experiments have recorded cancer-inducing properties, malformation of the central nervous system and irreversible destruction of the testicular function (the last clinical effect being demonstrated on a rhesus monkey). Most of these effects are, perhaps significantly, encountered only after administration of cadmium levels far in excess of those taken by man. Potts (1965) noted death by

carcinogenesis of 8 out of 74 industrial workers who had greater than ten years occupational exposure to cadmium. Industrial physicians, however, suggested that there is no obvious incidence of cancer in workers despite chronic effects to the liver and kidneys. Malignant tissues tend, in any case, to have very erratic distributions of metal. Roe (1973) concluded that there was no unequivocal evidence that exposure to cadmium by any natural route constituted a carcinogenic hazard.

Where kidney and liver damage has been shown to exist, the consequential harmful effects on the enzymic processes of the organs inhibits the body's natural detoxification defences. Tucker (1973) recorded that cadmium has the characteristic of producing highly toxic compounds with commonly used chelating agents, which means that any attempt to remove cadmium artificially results in the production of even more toxic substances. Chronic industrial exposure effects are therefore more or less irreversible.

Margoshes and Vallee (1957) have shown that it is possible to induce the production of metallothionen by the administration of cadmium and zinc. The manufacture of this protein has been viewed in two ways (Webb, 1973): firstly, that the normal biological function of the protein is in the regulation of essential zinc ions in nutritional metabolism; and, secondly, that the synthesis of the protein in the liver upon exposure to low levels of the metal cadmium or high levels of zinc provides an important defense mechanism against these and other toxic cations. Subsequent transport of cadmium metallothionen to the kidney has been suggested by Piscator (1962). He postulated that cadmium is then accumulated in the kidney until it is saturated causing renal damage, when cadmium metallothionen and protein-uria

are excreted. It has been noted by Piscator (1962) that low concentrations of cadmium will reach the bloodstream as cadmium is accumulated in the kidney, although Friberg (1971) asserted that blood values may give some information as regards recent exposure and do not necessarily reflect kidney accumulation. Slow excretion of cadmium accumulated over a long life-span in humans complemented by the long 30 years biological half-life of the metal results in a linear increase in cadmium concentration in the kidney with age.

2.4 CHRONIC CADMIUM POISONING

2.4.1 KNOWN INSTANCES OF CADMIUM POISONING

Itai-Itai-Byo disease was officially recognised, after many deaths were attributed to it, at the seventeenth meeting of the Japanese Association of Orthopaedic Surgeons in 1955 where it retained its onomatopoeic name, which can be translated to mean ouch-ouch! Cases of the disease were first observed about 1912 in an area potentially contaminated by metals from a lead mine. These cases increased in frequency following the additional mining of zinc and cadmium. Over a period of fifteen years (which included those of wartime malnutrition) some 200 people along the banks of the River Jintsu suffered (Kobayashi 1970). About one half eventually died as a result of the disease. Women who had borne many children and who were aged between 50-60 years were especially at risk. Since new cases have not been identified in the region since 1955 it is hard to correlate the disease with dietry intake although contaminated food was probably involved. Cadmium levels of white rice in the area were five times the national average at 0.5 micrograms per gram and the levels in brown rice were between six to eight times the levels in control crops (Tucker, 1973). Although cadmium contamination of crops by mine and smelter waters was undoubtedly the major factor in the

appearance of the disease, the area was inhabited by people who, as a result of the war, suffered from malnutrition with low calcium and vitamin-D intakes. The influence of other factors, such as lead and flourine intake was also cited by Kobayashi. In early 1971, two years after a much publicised suicide of an Itai-Itai diseased smelter-worker, legislation in Japan reassessed industrial controls on the use of toxic metals and introduced a basic health scrutiny in the approximately 1,000 industrial plants producing or using cadmium in Japan.

2.4.2 LONG-TERM, LOW-LEVEL EXPOSURE

The known symptoms of low-level exposure to cadmium are complex. Perry et al (1965) recorded that the injection of low levels of cadmium into the bloodstream of small mammals produces an immediate rise in blood-pressure with various other symptoms such as shortening of life span. A statistical analysis in 1965-66 of 28 US cities by Carroll revealed a strong correlation between measured presence of airborne cadmium and the incidence of heart disease. Perry has since (1968) drawn attention to the presence of either more cadmium or similar cadmium levels but altered cadmium : zinc ratios in the kidneys of humans suffering from hypertension. However, strong arguments can be levelled against such an association. Morgan (1969) performed post-mortem examinations on 80 people with cardiovascular disease (including a hypertensive group) and found no significant difference in renal cadmium levels from control post-mortems. Likewise no correlation was discovered by Szadkowski et al (1969) between arterial pressure and cadmium excretion in the urine of 169 persons. The only fact of note which emerged was the increase of cadmium in urine, with age. Hunt (1970), in an epidemiological study of 77 Midwestern cities in the USA found no apparent correlation between cadmium content of dustfall and cardiovascular death rates in urban areas. Also no

association was found between cadmium concentration in milk and cardiovascular disease. Finally, industrial physicians claimed that there was little or no evidence of hypertensive desease in occupational workers. Nevertheless Schroeder(1971), assessing work of his own on atmospheric cadmium levels in Swedish cities, categorically stated, "..... there is little doubt ..... that cadmium pollution is a major factor in human high blood-pressure."

2.4.3 CADMIUM IN MAMMALS

Hill and Matrone (1970) commenting on the effect of acute cadmium toxication in mammals confirmed that cadmium is a metabolic antagonist of zinc and further suggested that the amounts of commonly encountered environmental cadmium were sufficient to induce a metabolic zinc deficiency. On the basis of similarities in outer electronic structures this same concept has been advanced concerning cuprous copper and cadmium. Some symptoms of copper deficiency can be induced by acute cadmium toxication and this led Mills (1973) to suggest that the copper-status of an animal may be an important determinant of its tolerance to cadmium. The presence of zinc, manganese and cadmium in plants would appear to interact in some way and thus inhibit cadmium uptake.

2.5 CADMIUM UPTAKE BY PLANTS AND ANIMALS

Hodgson (1969) noted that the ratio of cadmium in plants to that in soils was of the order of 10 which, when compared to the ratios of copper, lead and zinc (which ranged from 0.45 - 0.6) indicated the ease with which cadmium was taken up by plants. Jones (1973) however, reported that only a small proportion of the total cadmium in soil is available for plant uptake. Contamination of exposed parts of plants

as a result of fall-out does not, in general, give rise to concentrations which are usually high in the plants and which would constitute a hazard to grazing animals. He continued by stating that 40-70% of the cadmium present in plants around the Avonmouth zinc smelter, near Bristol could be removed by washing. Kobayashi (1972) also studied contamination from a zinc refinery and reported that the principle cause of high trace element content in plant tissues was absorption through and accumulation in, the roots of plants from metal polluted soil, rather than by direct deposition of metal onto the plant surface from metal-rich air. From a knowledge firstly of normal concentrations of cadmium in soil and secondly of the low, though efficient, uptake of cadmium by plants, one would expect levels of 0.1 ppm cadmium in cereals. Although natural levels were just above this value, a survey by Schroeder (1957) showed that processed cereals contained very much higher concentrations (0.3 to 0.5 ppm). Seafood and meat analyses revealed enormous variability in cadmium presence which was attributable to variations in general world pollution levels. The use of cadmium-rich fertilizers and plant additives could explain high cereal cadmium but the higher levels of the metal discovered in tinned food appears to question the safety and reliability of food production processes. For example cadmium used in tree fruit spraying like the metal mercury translocates from the foliage to the maturing fruit and hence is made available to the human food-chain.

In the absence of aerial contamination cadmium is present in greater concentrations in the roots of plants rather than in the exposed plant surfaces and this enhancement was found to be especially apparent in the fibrous roots of some vegetables, such as the raddish (Wakeley, 1973). The fact that cadmium tended to accumulate in the fibrous roots of plants (a part which is not normally eaten) meant that effective cadmium participation in the human food-chain was restricted. Wakeley (1973) discovered a greater propensity for cadmium

accumulation in some species of plants compared with others but this was commonly related to experimental soil conditions, for example, a plant growing in low phosphate, acidic soils showed increased absorption. A summary of the presence of cadmium in plants is presented in Table 2.2.

Many laboratory experiments on animals have been carried out with a view to extrapolating the results obtained, in order to determine the real environmental and biological hazards due to cadmium. The results led to the publication of long lists of symptoms which frequently show discrepancies in their statements of cadmium tolerance. It can be reasonably argued, for example, that a heavy enough dose of any trace element in the diet of an experimental animal could produce carcinogenic effects and, as mentioned in section 2.3, claims to date of cadmium-induced cancer growths in animals have been unsubstantiated in man.

Postmortem examinations by Goodman and Roberts (1971) on livers and kidneys from horses which had lived and died in the Lower Swansea Valley region of South Wales, indicated grossly enhanced levels of cadmium. The only clinical manifestation revealed by feeding a maximum dietry concentration of 12.3 ppm cadmium to ewes was a deterioration in wool quality (Mills and Dalgarno, 1972). Although no significant effects of cadmium administration on the kidney were noted, cadmium, zinc, and iron concentrations were detected and the administration had a significant effect on the copper built-up in the liver. Cunningham (1946) noted a high incidence of bone fragility and cases of ataxia in lambs with less than 34 ppm liver copper. In the Mills-Dalgarno study the livers of only 2 out of 15 lambs contained less than this level and the lack of cadmium, which was predicted, in brain tissue was probably due to the late stage of the initiation of the project with respect to pregnancy. Swayback, which results from a depletion of copper in the brain tissue early in foetal development, was therefore not detected.

TABLE 2.2 NATURAL AND CONTAMINATION LEVELS OF CADMIUM IN PLANTS

Natural levels	Cadmium ppm (dry weight)	Location
Mosses	0.7 - 2	Scandinavia, S. Wales
Higher Plants	0.1 - 1	S. Wales
Contaminated Levels		
Mosses	10 - 150	Around smelter complexes Swansea, Bristol
	5 - 25	Around a Cadmium emitting factory, Sweden
Higher Plants	10 - 50	Grasses around zinc smelters Bristol, Swansea

2.6 CADMIUM: ECONOMIC IMPORTANCE AND USE

Cadmium is an economically valuable metal: the price paid per pound on the free market for the year 1973 ranged from £1.553 - 1.602 (Metal Bulletin Handbook, 1974). Wedepohl (1969) recorded that the world reserve of cadmium in ore in 1963 was valued at 900 million pounds.

In the United Kingdom about 1,300 metric tons are produced annually out of a world-wide production of 150,000 tons (Zinc Development Association, 1973). The USA, USSR, Japan and Belgium in ranked order accounted for 81% of total world production in 1963. The bulk of United Kingdom production, which takes place at the Rio Tinto Zinc plant at Avonmouth, Bristol, was 0.17% of the total world production in 1971. The ore and concentrate of zinc, from which cadmium is retrieved solely as a by-product is imported mainly from Australia but also from Holland, Canada and the USA.

Cadmium is used predominately in the plating of anodes and for production of colour pigments. It is employed also as a component of some of the lowest melting-point alloys, for example, bearing alloys with low coefficients of friction and great resistance to fatigue. To a lesser extent cadmium is used in many types of solder, for standard EMF cells, in batteries for use in aircraft, missiles, portable tools, etc. in semi-conductors and as rods to control nuclear fission rates. In addition, cadmium compounds are employed in black and white television phosphors and in blue and green phosphors for colour television tubes. In the first half of 1973, 77% of cadmium used in the UK was for the making of colours, for plating anodes and for plating salts.

World production of cadmium had fallen from about 170,000 metric tons in the late 1960s to just over 150,000 metric tons in the 1970s. This decline in the use of cadmium is due primarily to three

facts which outweight the better qualities of cadmium use: the relative cheapness of zinc as a substitute, recent improvements in electroplating techniques and awareness of the dangers of cadmium use with regard to its toxic properties.

The quantity of cadmium produced from recycling of scrap and waste in the UK has been quoted in the SRC report on Cadmium in the Environment (1973) as representing no more than 5% of total UK production. The existence of over 200 cadmium platers in England and Wales is known, situated predominantly in London, the Home Counties and South East England. Cadmium pigment production is located essentially in the Potteries around Stoke but paints are also manufactured at Bletchley. The main cadmium-containing battery manufacturer is sited at Reddich, Worcestershire. Cadmium-copper alloys and wire are produced at Enfield and Wembly, Salford and Manchester, Willington (Derbyshire) and Llanelli (Carmarthenshire). A map showing the location of the main cadmium producing and using industries in England and Wales has been produced for Chapter 3 (Figure 3.3, p.43).

2.7 SURVEY OF CADMIUM PRESENCE IN THE ENVIRONMENT

2.7.1 CADMIUM IN SOILS

The average content of cadmium in soils probably lies between 0.1 to 0.5 ppm (Green 1959) although in exceptional circumstances, such as with industrial contamination, contents can increase to 26 ppm (Lower Swansea Valley, Goodman and Roberts, 1971), 33 ppm (Montana, USA, Gordon, 1972) or even 95 ppm (Canada, John et al 1971, see Table 2.3). Goodman and Roberts analysed soils from an area of heavy metal pollution around Swansea and found the cadmium levels in topsoils dropping from 26.0 to 0.5 ppm in a distance of 8 km. from Swansea to Gower. They concluded that the effect of aerial contamination, originating in Swansea, could have a radius of greater than 32 km.

TABLE 2.3 NATURAL AND ELEVATED LEVELS OF CADMIUM IN SOILS

Soil	Cadmium (ppm dry weight)	Analysis	Location
'Uncontaminated'	0 - 0.5	'Available'*	Gower, South Wales, Unmineralized areas of S. W. England
	0.5 - 1.5	'Total'**	
Naturally elevated	2 - 4	'Total'	Ystwyth valley Wales, Lead mining areas (Alluvial soils)
Industrially contaminated	10 - 33	'Total'	Around zinc smelters

* Extractable with dilute acetic acid

** Extractable with concentrated nitric acid

Vinogradov (1959) wrote that the character of the parent rock was the main factor in determining cadmium content in soil, although in addition to this the influence of the secondary environment in enhancing trace element content and presence of mineralisation contamination were also important (Horsnail, 1968, Fletcher, 1968). High content of organic matter in soils according to Vinagradov was accompanied by high cadmium and also high zinc content. This was especially true of the chernozem horizons in the USSR where cadmium content ranged up to 6.0 ppm. Zinc and cadmium are both immobile at high pH values such as exist in alkaline soils rich in calcium carbonate; conversely both are very mobile in acid, peaty soils with a pH of 5.0 of lower.

2.7.2 CADMIUM IN NATURAL WATERS

Most natural waters are low in cadmium content, containing generally less than the World Health Organisation standard maximum of 10 ppb for drinking water. This level may rise within the regions of sewage works, smelters, old mine disposal sites or abandoned mine-shafts and mines, as a result of the breakdown of organic matter, ore minerals, etc. The formation of acid waters may lead to the leaching of cadmium out of parent rocks.

Cadmium is retained in the sea for 500×10^3 years, after which time 0.05% or 0.00011 ppm of the original remains. This retention figure is very much higher than that for lead (0.000002% of which is retained after 2×10^3 years) and higher than those for zinc, copper and mercury chloride (Bowen 1966). In the Irish Sea and the English Channel, Mullin and Riley (1956) reported on average cadmium concentration in 37 samples of 0.11 ppb with a range of 0.024 to 0.25 ppb depending on factors such as the locality of sampling to estuarine outflows and the sampling season. Three samples from Japan contained 0.08 - 0.17 ppb (Ishibashi et al, 1962).

Comparison of concentrations in vatious water bodies showed that cadmium values were higher in coastal waters and estuaries than in oceanic waters. The input has been calculated in the Severn Estuary at 1 kilogram of cadmium a day (Preston, 1973), the source arising from zinc smelters and industrial waste. In the Bristol Channel concentrations of zinc and cadmium were abnormally high in the East of the region and on the Southern shores this was consistent with the supposition that the major source of contamination was to the South East of the estuary. Along the South coast to the West, a gradual reduction in the levels of metals had been found (Butterworth et al, 1972) and along the Northern coast a reduction had been found with locally high cadmium and zinc concentrations in parts of Carmarthen Bay coinciding with areas of higher population.

Cadmium content in spring water from California has been spectrographically determined by Silvey in 1957 to have an average of 8 ppb (with a high of 20 ppb). No cadmium was detected in samples of 65 streams in the same State and in only 5 out of 82 well and oilfield brine samples was the element detected. Cadmium ranged from 5 to 70 ppb. Udodov and Parilov (1961) reported average cadmium levels of 3 ppb (range 0.1 to 207 ppb) from 3,490 samples of natural waters in Siberia. Gardiner (1973) concluded that a substantial proportion of the total cadmium in rivers and lakes will normally be present as free cadmium ion and the lower that both the pH value of the water and the proportion of sewage effluent present in the water are, the higher this proportion will be. Levels of cadmium in contaminated and uncontaminated water are listed in Table 2.4

2.7.3 CADMIUM PRESENCE IN MARINE SEDIMENTS AND MARINE ORGANISMS

Mullin and Riley (1956) have detected in diatomaceous, globegerina and radiolarian oozes levels of cadmium of 0.39, 0.42 and 0.45 migrograms

TABLE 2.4 CADMIUM PRESENCE IN WATERS

	Range of mean values	Location
Uncontaminated Levels		
Surface waters	trace - 1.0 µg/1	USA, W. Germany
Drinking water	trace - 2.0 µg/1	USA
Seawater - oceanic	< 0.01 - 0.2 µg/1	Finland, Atlantic
coastal	0.1 - 0.4 µg/1	N. Sea, Irish Sea
Contaminated Levels		
Surface waters	10 - 4000 µg/1	Japan, Vermont, USA, Nassau Co. USA.
Drinking water	10 - 130 µg/1	Various, USA, Japan
Sea Water	5 - 10 µg/1	Coastal, Bristol Channel Coastal, Gulf of Finland

per gram (μgm/gm) respectively. These levels were close to the average cadmium level of 0.5μgm/gm in the Upper Lithosphere calculated by Goldschmidt (1958). In analyses of oceanic sediments Aston et al (1972) found that samples from the mid-Atlantic ridge and ridge-flank systems contained almost twice as much cadmium as did those samples collected away from the ridge systems. The average, carbonate-free cadmium content of the ridge samples was 650 ppb and that of other sediments, 335 ppb. On their work on marine organisms, Mullin and Riley (1965) noted that cadmium presence in algae and asteroidea was higher than cadmium presence in crustacea, although lower than that in mollusca. Cadmium presence in calcareous shells and mussels of molluscs was usually less than 0.2μgm/gm and 1.5μgm/gm respectively.

High concentrations of up to 500 micrograms/gm were present in the digestive tracts and renal organs of the same organisms. The authors suggested that cadmium substitution was more or less excluded from the process of biochemical calcium carbonate production in contrast with the behaviour of cadmium in the process of chemical calcium carbonate precipitation. The work of Nickless et al (1972) on concentrations of heavy metals in organisms from the littoral zone of the Severn estuary, indicated that concentrations of metals in the digestive tracts of certain animals was related firstly to the size of the animal and secondly to its position on the shore. Fuge (unpublished results) working on the presence of cadmium in the species Fucus Vesiculosus from the same area quoted concentrations of 25.6 ppm in specimens from Portishead near Bristol, and consistently less in all specimens collected progressively westward to Freshwater East, where the cadmium presence was quoted as 6.07 ppm. Natural and elevated levels of cadmium in aquatic animals are listed in Table 2.5.

TABLE 2.5 NATURAL AND ELEVATED LEVELS OF CADMIUM IN AQUATIC ANIMALS

	Cadmium ppm (dry weight)	Location
Natural Levels		
Marine Molluscs	1 - 5	Irish Sea, English Channel
Marine Crustacea	0.1 - 0.5	Irish Sea, English Channel
Fish	$<$0.1 - 0.26	Gulf of Finland, Bristol Channel
Contaminated Levels		
Marine Molluscs	7.8 - 120	Bristol Channel Coast
Marine Crustacea	3.5 - 33	North Somerset Coast
Fish	0.1 - 9.0	Bristol Channel, Hudson River, America

2.7.4 CADMIUM PRESENCE IN AIR

The normal background content of cadmium in air is probably around 0.001 microgram per meter ^{3} ($\mu gm/m^3$). A survey of 36 North American cities sponsored by the US National Air Sampling Network recorded a range of 0.002 to 0.37$\mu gm/m^3$. For 17 rural localities the range was 0.0004 to 0.026$\mu gm/m^3$. (see Table 2.6). In the air of cities which contained no zinc (15 out of 36), no cadmium was found either and where cadmium was detected, the particle size was mostly between 1-2 microns and the metal was probably present as the oxide. Ruhling analysed control masses from Sweden and found them to contain between 0.7 to 1.2 ppm cadmium (dry weight). In comparison up to 7.5 ppm cadmium was found to be present in genetically similar mosses from the polluted Central Stockholm urban area and up to 817 ppm cadmium was found to be present in mosses collected from the vicinity of storage battery works in Southern Sweden. In an attempt to demonstrate the existence of cadmium in air Shacklette (1970) analysed topsoils downwind from a smelter stack in a valley in Montana, USA and found them to contain up to 26 ppm cadmium, whilst 13 km downwind the soils contained only 2 ppm cadmium.

TABLE 2.6 NATURAL AND ELEVATED LEVELS OF CADMIUM IN AIR

Air	Cadmium Air Concentration (range of mean values)	Location
Rural	0.0009 - 0.026 $\mu g/m^3$	Rural Stockholm Wraymires, England Shetland Isles
Urban	0.005 - 0.080 $\mu g/m^3$	Manhattan, NY. Stockholm urban Chicago
Industrial	0.055 - 0.60 $\mu g/m^3$	Around zinc smelters, Bristol, Japan, Sweden

CHAPTER 3

3 STUDY OBJECTIVES BASED ON THE STREAM SEDIMENT MAPS OF ENGLAND AND WALES

3.1 INTRODUCTION

Man is sustained by other species in the environment - by crop plants, domestic animals and fish as well as by the lesser organisms at the base of the food chain which renew oxygen supply and break down dead matter. Intake of cadmium by man through this food chain, in air breathed, or in water consumed increases the proportion of metal which is retained by the body. Cadmium has a biological half-life of 30 years, is notably persistent, and in addition has such a long residence time in sea water that the dumping of metal in oceans is strictly banned by international law as are other particularly toxic and residual substances for example, mercury and DDT.

However, at the present time the use of cadmium in industry is well controlled and well monitored and although there are certain environments not contaminated by cadmium of industrial origin where local levels are raised, levels of cadmium in the environment are generally low. Present-day monitoring of levels of pollution in the environment is carried out in order to gain further information about levels of harmful or potentially harmful pollutants in discharges to the environment or in living organisms which survive in the environment and which may be affected adversely by these pollutants. A continual environmental assessment of metal presence also provides an 'early warning' system which may give some indication as to when the concentration of pollutants in the environment is rising to a level where hazard or even damage is expected. Although much of the information on the toxicology of cadmium given in paragraphs 2.5 to 2.11 detailed adverse reactions to very much higher levels of cadmium than may be expected in England and Wales the metal appears notably to be harmful in much smaller amounts.

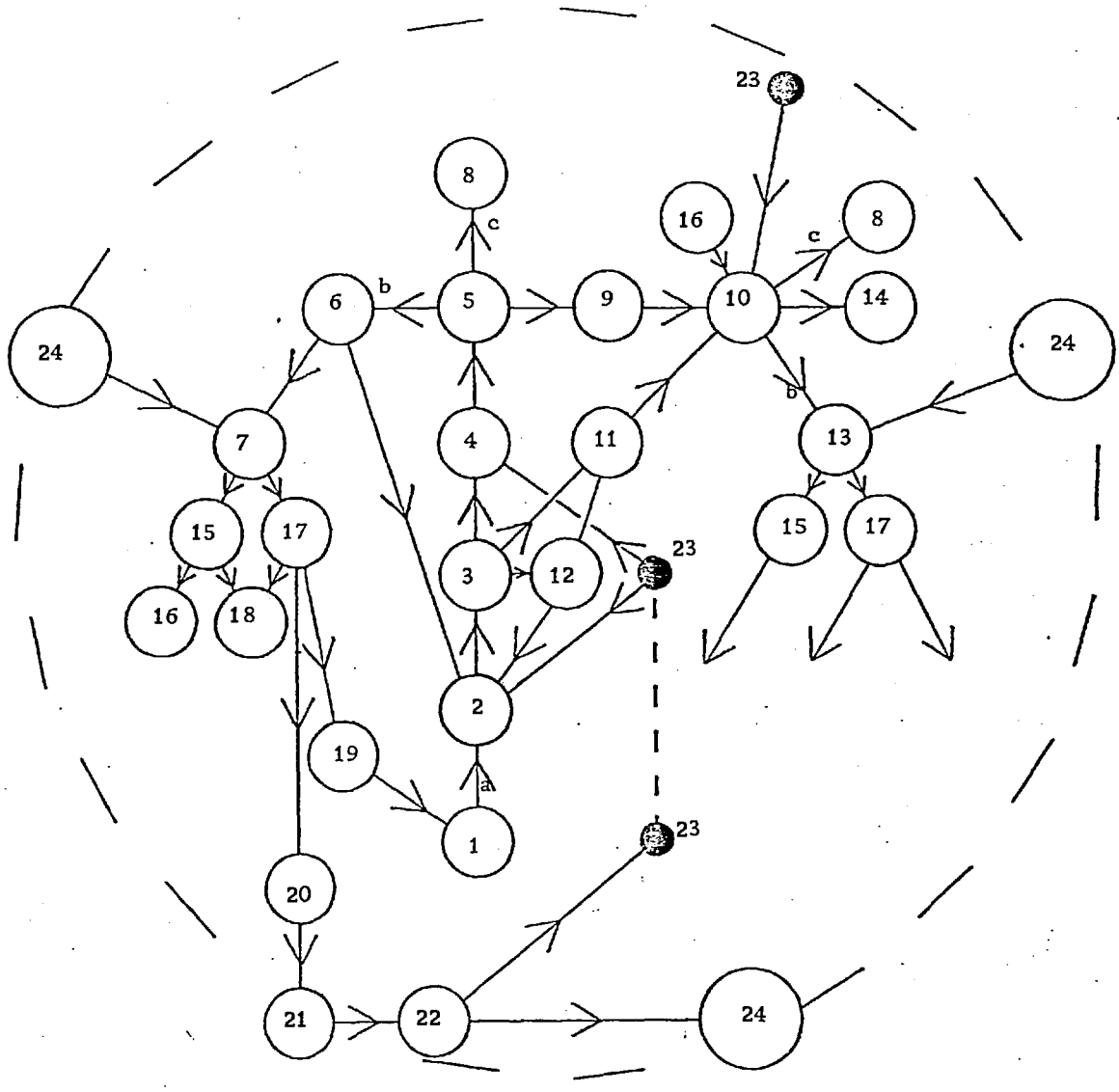
The movement of cadmium from one environment to another can be ideally visualised in a closed cycle, as shown in Figure 3.1. The main source of cadmium into the animal and human food-chains is from man's exploitation of hydrothermal ore deposits.

The natural weathering of cadmium-enriched rocks provides an additional source. The major source of cadmium intake for people in England and Wales is through the ingestion of cadmium containing plants, fish and animals. However, a far greater health hazard is experienced by those people living in the immediate vicinity and some distance downwind of a cadmium-using industry who would have occasion to inhale low levels of airborne cadmium over a long period of time - a situation which may lead to hypertension epidemics. Fortunately in the world of industrial economics such a loss of this very valuable metal would not be tolerated, although with the incriminating evidence of anomalous cadmium concentrations in stream sediments sampled from around industrial complexes in this country and presented in this chapter, it appears that total preventative measures cannot be exercised.

Fortunately hypotheses on the possible genetic transfer of cadmium from one generation to the next have not been verified and consequently if a population has been contaminated with the metal no part of this contamination will be transferred to the off-spring. Likewise cadmium is arrested in the food-chain cycle as a result of its apparent willingness to become concentrated within the roots of plants which are generally not eaten by humans or animals (with the notable exception of such vegetables as the raddish).

In the natural environment cadmium is a highly mobile element which can be transported with relative ease from contaminated and naturally-

FIGURE 3.1 A PROPOSED FLOW-DIAGRAM OF CADMIUM IN THE ENVIRONMENT



KEY:

1 Cadmium enriched rocks
2 Weathered/taken into soils
3 Cadmium uptake in plants/especially root plants
4 Animals graze on plants/eat soil/ breathe fume
5 Build up in kidney/liver
6 Cadmium returned to soil on decay
7 Cadmium dispersed in drainage system to estuaries sea
8 Next generation cadmium free
9 Organ meats eaten by humans
10 Build up in kidney/liver of humans
11 Some root plants eaten
12 Most roots not eaten
13 Cadmium dispersed in drainage/sewage system to sea/ests.
14 Evertual clinical symptons, possible death
15 Build up in shellfish/fish in sea/estuaries
16 Fish/Shellfish eaten by humans
17 Precipitation in sediments
18 Sediments form cadmium-containing rocks
19 Enters a reducing environment, precipitation as sulphide, enriched
20 Mobilised by hydrothermal activity
21 Emplaced as ore
22 Economic activity; collection/smelting of ores; industry
23 Fume emissions
24 Industrial toxic waste

(a) weathering
(b) excretion/death
(c) reproduction

enriched soils, enriched rocks and ores to the sea where, particularly in the restricted or seasonal water circulation of estuaries it can readily be distributed amongst the flora and fauna of the coasts. The human ingestion of cadmium-enhanced shellfish may therefore constitute the biggest threat to the perpetuance of the low dietry cadmium intake of the average person in this country.

There is at present a distinct lack of scientific knowledge of the epidemiological effect of long-term, low-level cadmium exposure in relation to the nutritional state of a population, but it is becoming increasingly apparent that more and more people are exposed. More epidemiological work on man and cadmium is therefore of fundamental importance: after strict environmental monitoring, sensible correlations of the relationships between low and high cadmium exposure, tissue concentration and medical history must be made.

3.2 THE STREAM SEDIMENT MAP OF ENGLAND AND WALES FOR CADMIUM

The map for cadmium illustrated in Figure 3.2 is one of the stream sediment maps which are being produced by the Applied Geochemistry Research Group as part of a project to produce geochemical maps of England and Wales. The method of stream sediment sampling techniques employed in the construction of this map, as described in chapter 13 of Hawkes and Webb (1962), is based upon the principle that a stream sediment is an agglomeration of material which has been derived through the actions of a river upon the geological strata over which it and its headwaters have flowed and deposited at the point of sampling. The modification of the original detritus by combinations of secondary environmental processes within the zone of weathering should not, under most circumstances, destroy or greatly change the variations in composition of the sediment caused fundamentally by the composition of the underlying rocks and soils.

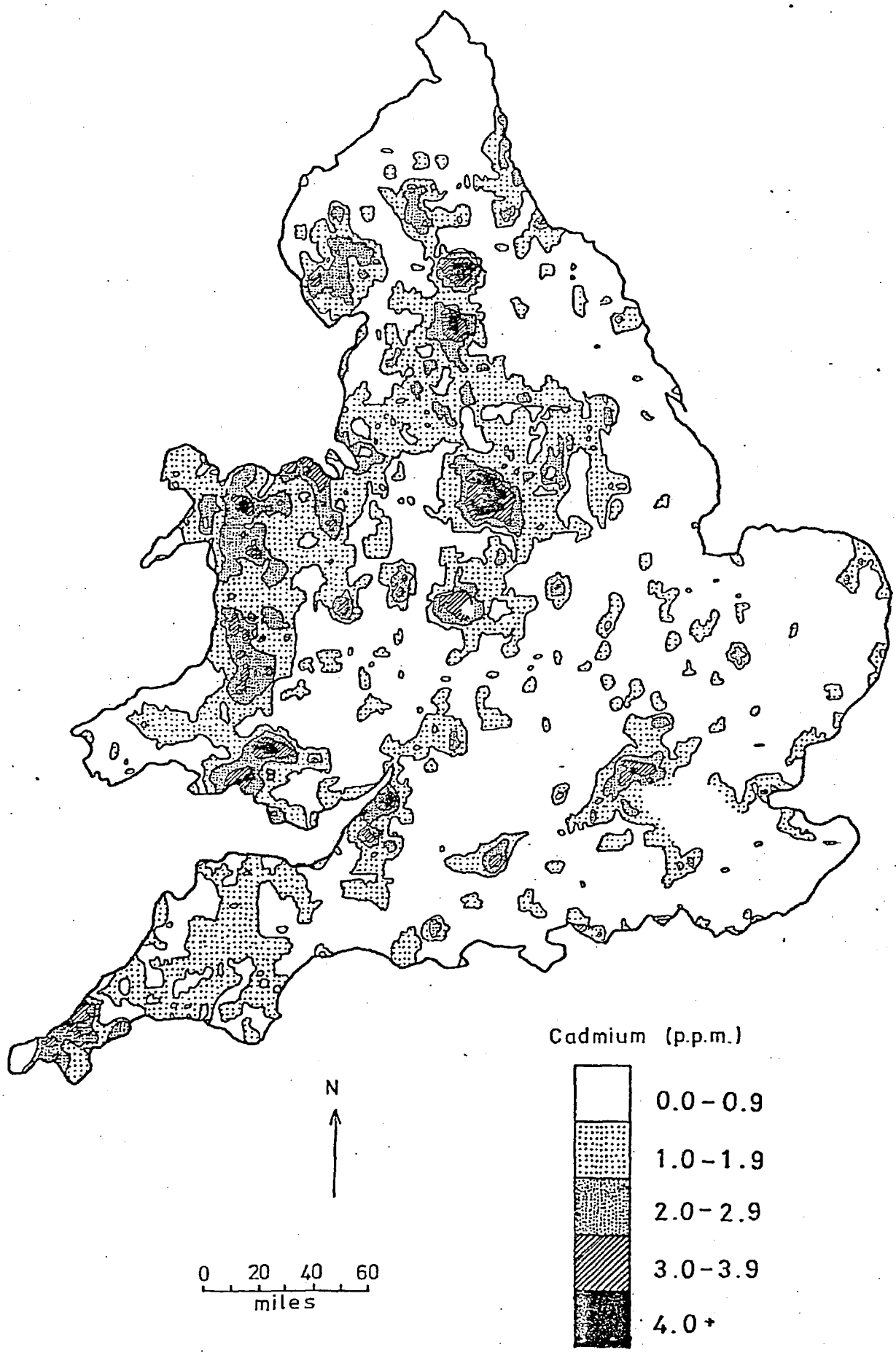


Figure 3.2 Cadmium in stream sediments in England and Wales.

The England and Wales survey samples were collected from tributaries which had catchment areas generally less than 10 square miles in area and at a density of approximately one per square mile. The composite samples, in some cases duplicated, were oven dried overnight, sieved to minus-80 mesh (about 200 microns) and analysed firstly using a 40-channel automatic emission spectrometer and secondly in the case of cadmium by atomic absorption spectrophotometry. Following certain analytical correction procedures described by Howarth (1973) a computer plotting programme was used to construct a series of maps on the computer line printer in which symbols of varying intensities of grey indicate the presences of an element in geographically co-ordinated samples. Applications of a one-cell radius, low pass filter, together with limited gap filling in a process known collectively as 'smoothing' were then made to the data and this had the effect of enhancing the broad-scale patterns of variation which previously could have been extracted by eye from the original, unsmoothed map.

The original 1:1 million scale smoothed map of cadmium in the sediments of England and Wales is presented in a reduced form in Figure 3.2. The anomalous stream sediment patterns present can be broadly divided into three classes according to the total cadmium detected in the samples which constitute them. The more distinct (and more analytically reliable) concentrations of 3.0 ppm and over delineate two major classes representing firstly, areas of known lead and zinc mining activity or the presence of incipient lead-zinc mineralisation and secondly, areas and halos of pollution and contamination surrounding small industrial towns and large urban sprawls. The patterns produced by cadmium concentrations between 2.0 and 2.9 ppm making up the third and more minor class, cannot be so easily resolved.

The first major class represented in the anomaly pattern can be directly related to areas of known mining activity. This is particularly evident where sediments have been collected in and near the lead-zinc mining areas of the North Pennines, the Derbyshire Dome, Flintshire, the Conway Valley, West Cornwall etc. Names and geographical localities of the largest lead and zinc mines in England and Wales are illustrated in map Figure 3.3.

The extent of the second major class can be correlated with the presence of cadmium using industries and large urban areas. The map (Figure 3.3) shows, in addition to mine localities, the location of all non-ferrous metal rollers and smelters in England and Wales and also the geographical locations of the major manufacturers of paint. In the first half of 1973, 77% of cadmium used in the UK was in the non-ferrous metal and paint industries. The major employers in the non-ferrous metal industry are located in Leeds, Stoke-on-Trent, Wolverhampton, West Bromwich, Birmingham, Nuneaton, Clydach, Avonmouth and London. The major paint makers are located in Hebburn (Newcastle-upon-Tyne), Hull, Birmingham, Stoke-on-Trent, Bletchley, Bristol, Stow-Upland and London. The anomaly extension from the Liverpool-Preston coast of West Lancashire across to the Leeds-Wakefield area of Southwest Yorkshire can be adequately explained by the concentrated presence of cadmium producing and using industry (Figure 3.3). In conclusion any mineralised area and any locality of the non-ferrous metal and paint industries is reflected in a definite stream sediment cadmium anomaly.

Apart from any 'buffer' areas which surround the major centres of cadmium enhancement, numerous small and usually isolated areas exist which form the bulk of Class Three. A study of these areas may indicate whether or not the underlying geology of England and Wales is playing a significant role in their production. The outcrop of black shales in England and Wales is illustrated in Figure 3.4. The effect of

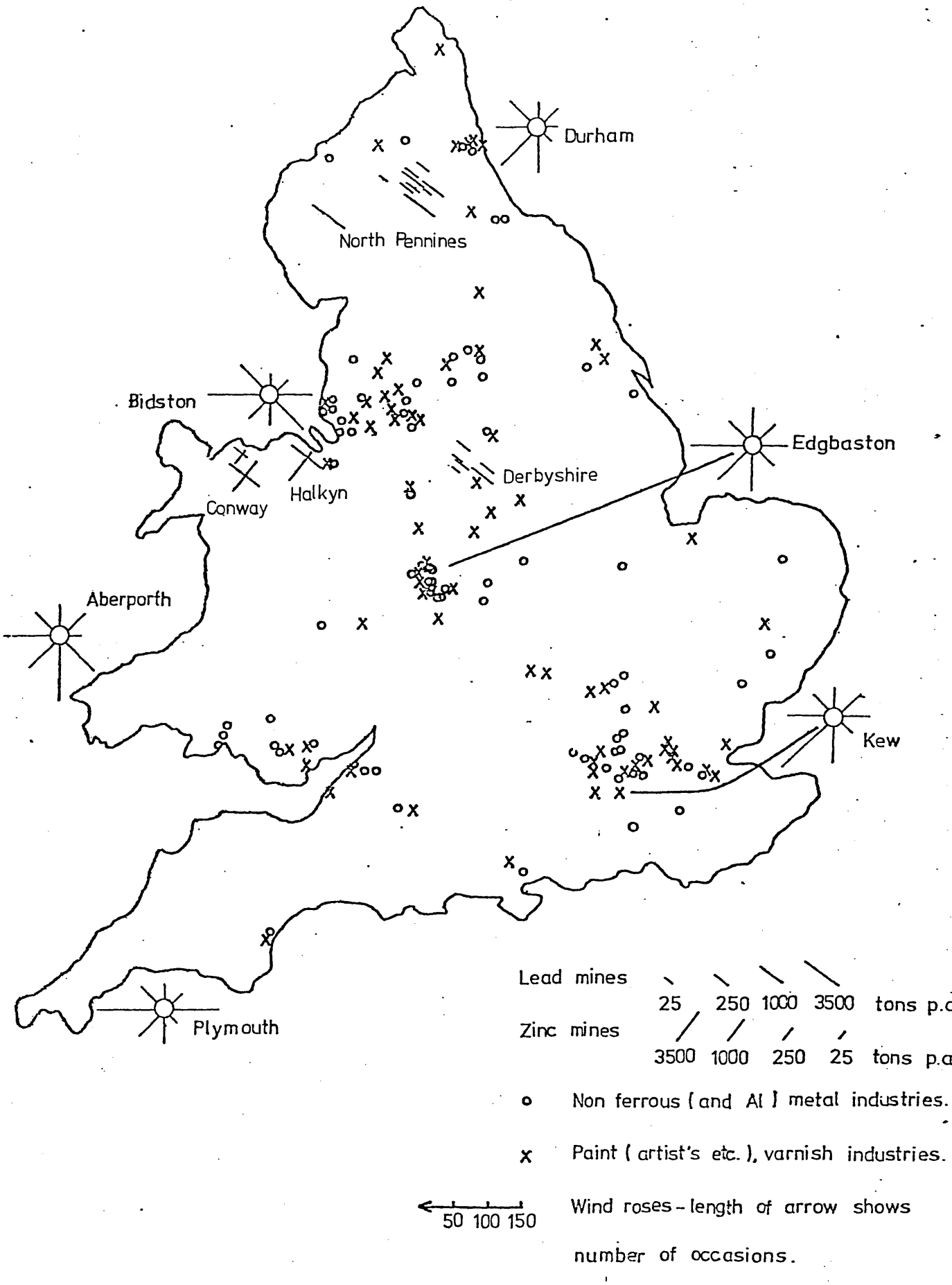


Figure 3.3 Geographical location of potential cadmium polluting industries and prevailing winds in England and Wales.

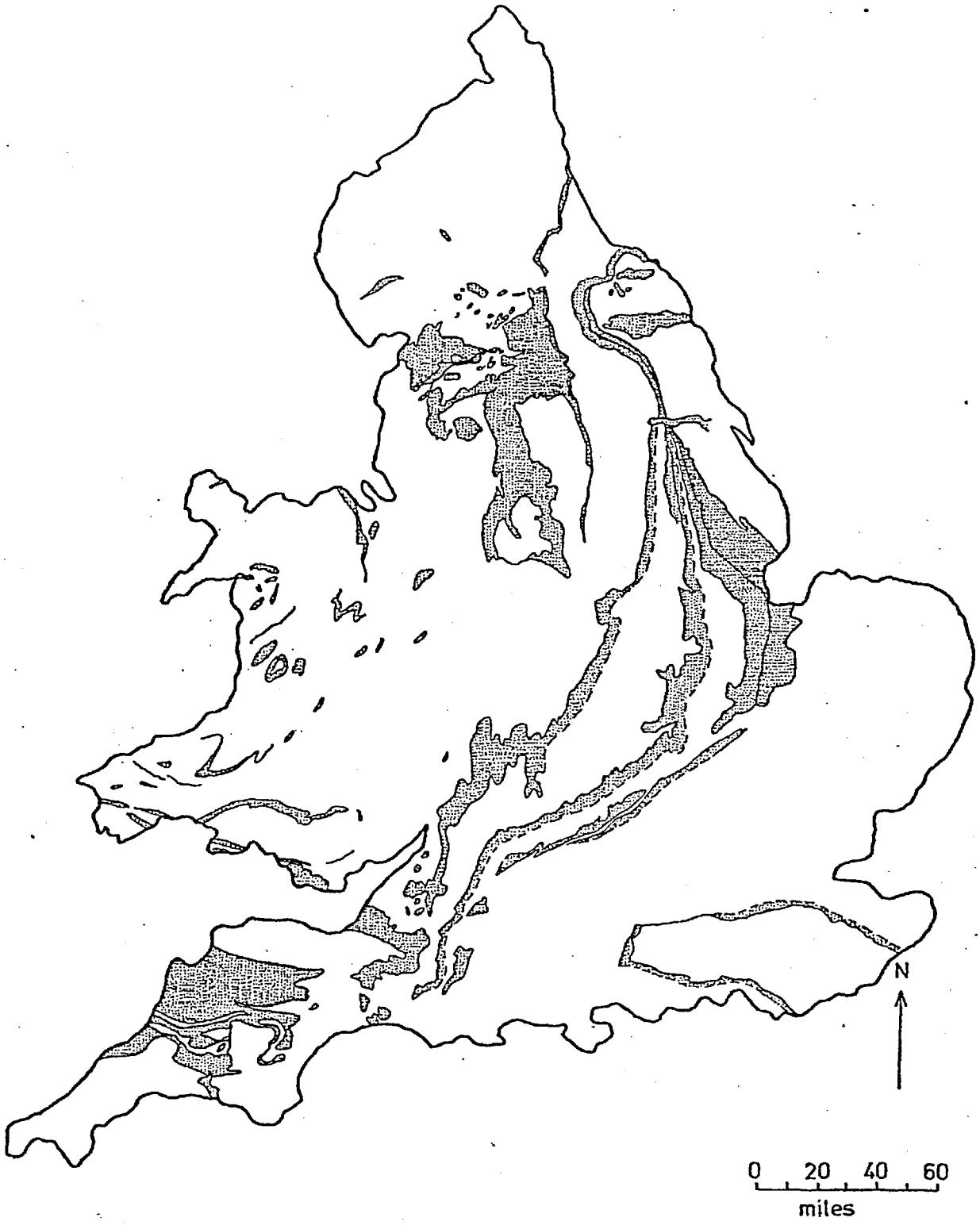


Figure 3.4 Outcrop of black shales in England and Wales

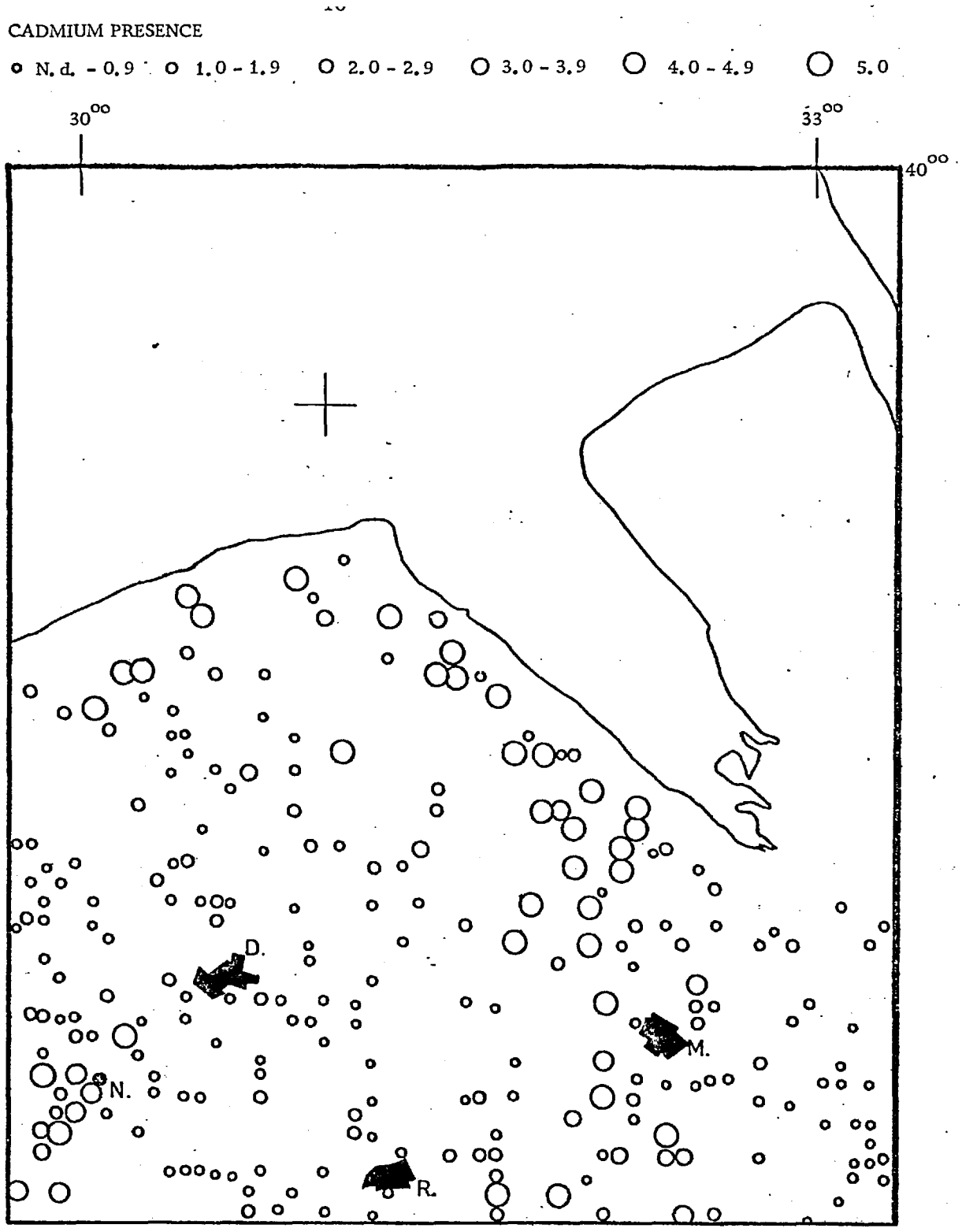
these cadmium-enriched rocks on the anomaly patterns is heavily masked by the major cadmium contamination sources in the country. However, several areas of interest can be identified. There is, firstly, the outcrop of Visean rocks of the Carboniferous era in Central and Northern England, marked in Figure 3.4, the aerial extent of which coincides with a part of the Northern England stream sediment anomaly; secondly, the conspicuous cadmium anomaly around the Gloucester-Worcester-Stratford corridor which lies upon the narrow outcrop of the Lower Lias. In addition the outcrop of the Lower Lias from Scunthorpe southwards almost to Grantham similarly coincides with an easterly extension of the Central England stream sediment anomaly. Finally, the large Class Three anomaly in Devon and Cornwall may possibly reflect cadmium presence in the black shales of the underlying Culm Measures of the Carboniferous era.

3.3 UNSMOOTHED DATA

3.3.1 The effects of low-pass filtering and value interpolation for missing data have already been mentioned in paragraph 3.7. Detailed study of the original unsmoothed data for areas prior to 'follow-up' surveys on maps of scale 1:63,360 proved to be of greater value in the process of geographically locating local anomalies. Four unsmoothed reconnaissance maps will be examplified in this subsection.

3.3.2 FLINTSHIRE, NORTH WALES

The area represented in Figure 3.5 includes the lead-zinc mining region of the Clwydian Range centred on the mine of Halkyn, Northwest of Mold. The highly anomalous sediments were collected from streams draining off the Carboniferous Limestone outcrop northwest of Mold where surface drainage was intermittent. The other area of interest on the map is located southwest of Nantglyn. Underlain by the Ludlow Series of the Silurian the rocks are not known to be mineralised by the base metals or be rich in cadmium. The anomalous streams all emerge from the high,



D. Denbigh
M. Mold
R. Ruthin
N. Nantglyn

All values in parts per million
N. d. = not detected
Scale: 4 miles = 1 inch

FIG. 3.5 CADMIUM PRESENCE IN STREAM SEDIMENTS OF THE FLINTSHIRE/DENBIGHSHIRE DISTRICT OF NORTH WALES

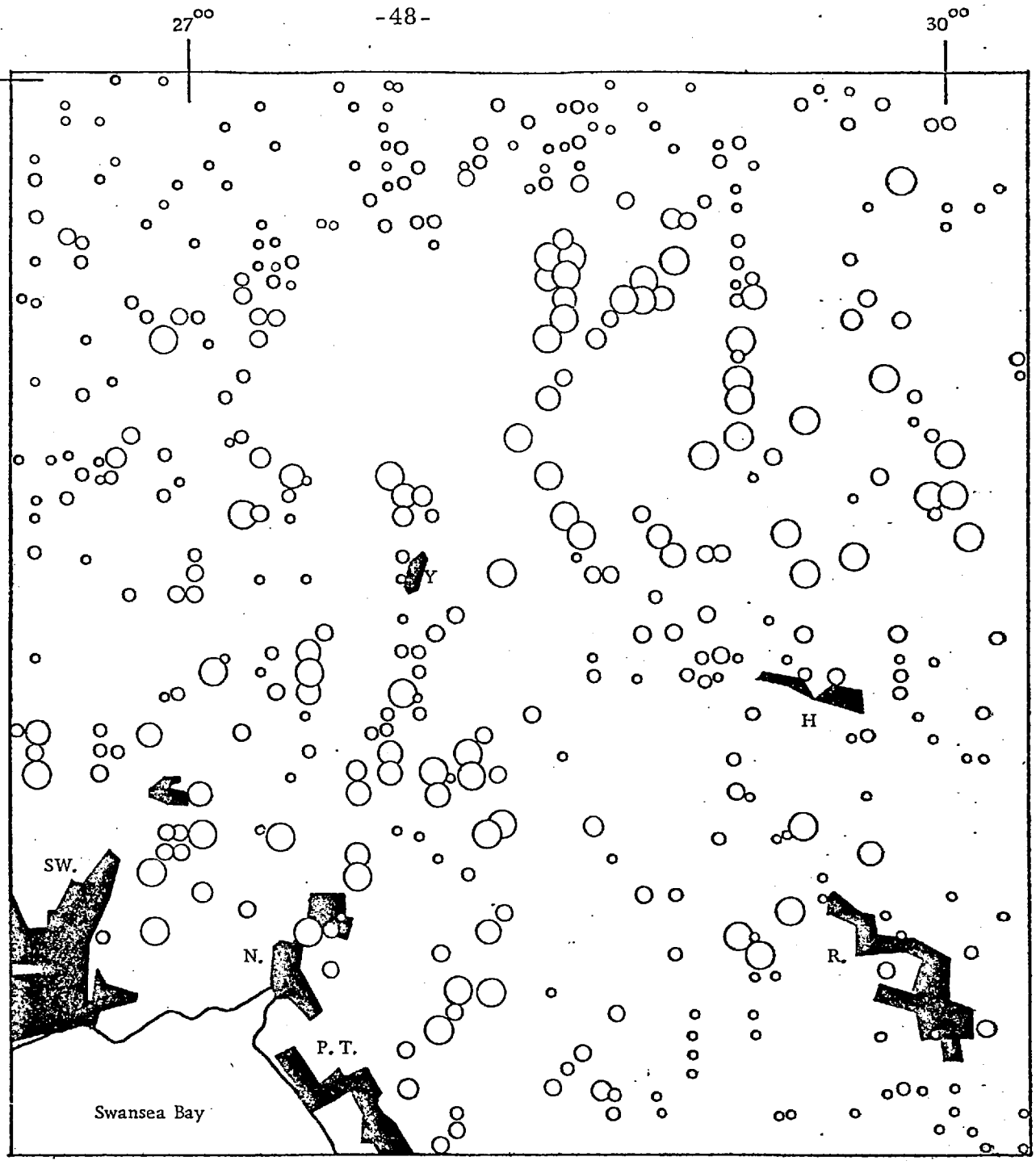
marshy Denbighshire Moors which have developed over the Ludlow Series of the Silurian. The rocks of the area are not known to be mineralized or enriched in cadmium. In order to explain this anomaly the area was subsequently designated as a follow-up area. The survey report is presented in Chapter 12.

3.3.3 SWANSEA AND NEATH VALLEYS, SOUTH WALES

The area illustrated in Figure 3.6 includes the valleys and catchments of the Tawe and Neath rivers in South Wales. Anomalous cadmium sediments completely surround the urban areas of Swansea-Clydach, Neath and Port Talbot with a semicircular area of radius 14 km centred on the coast half way between Swansea and Neath. Beyond a narrow band of sediments at Ystradgynlais which was made up of samples with background cadmium concentrations, highly anomalous sediments can be traced up the River Tawe and its tributaries to a cluster at their source. The pattern extends Eastward and Westward above Ystradgynlais contouring the southward-facing slopes of the Brecon Beacons and the Black Mountains. The likelihood of the Old Red Sandstone rocks of the headwaters area containing sufficient cadmium to account for the presence of such a continuous, anomalous area was, from the outset considered unlikely and consequently the area in this headwaters zone was designated as a follow-up area. The results of the survey are reported in Chapter 12.

3.3.4 BOWLAND FOREST, LANCASHIRE

The map Figure 3.7 represents the sediments collected in an area of about 70 square kilometers surrounding the town of Clitheroe in Lancashire. The area is underlain predominantly by Carboniferous Limestones, but large areas of outcropping black Visean shales are present.



Cadmium o N.d. - 0.9 O 1.0 - 1.9 O 2.0 - 2.9 O 3.0 - 3.9 O 4.0 - 4.9 O > 5.0

Sw.	Swansea	P. T.	Port Talbot
C.	Clydach	R.	Rhondda
N.	Neath	H.	Hirwaun
Y.	Ystradgynlais		

N. d. = Not detected

Scale 4 miles = 1 inch

FIG. 3.6 CADMIUM PRESENCE IN STREAM SEDIMENTS OF THE TAWE AND NEATH VALLEYS, SOUTH WALES

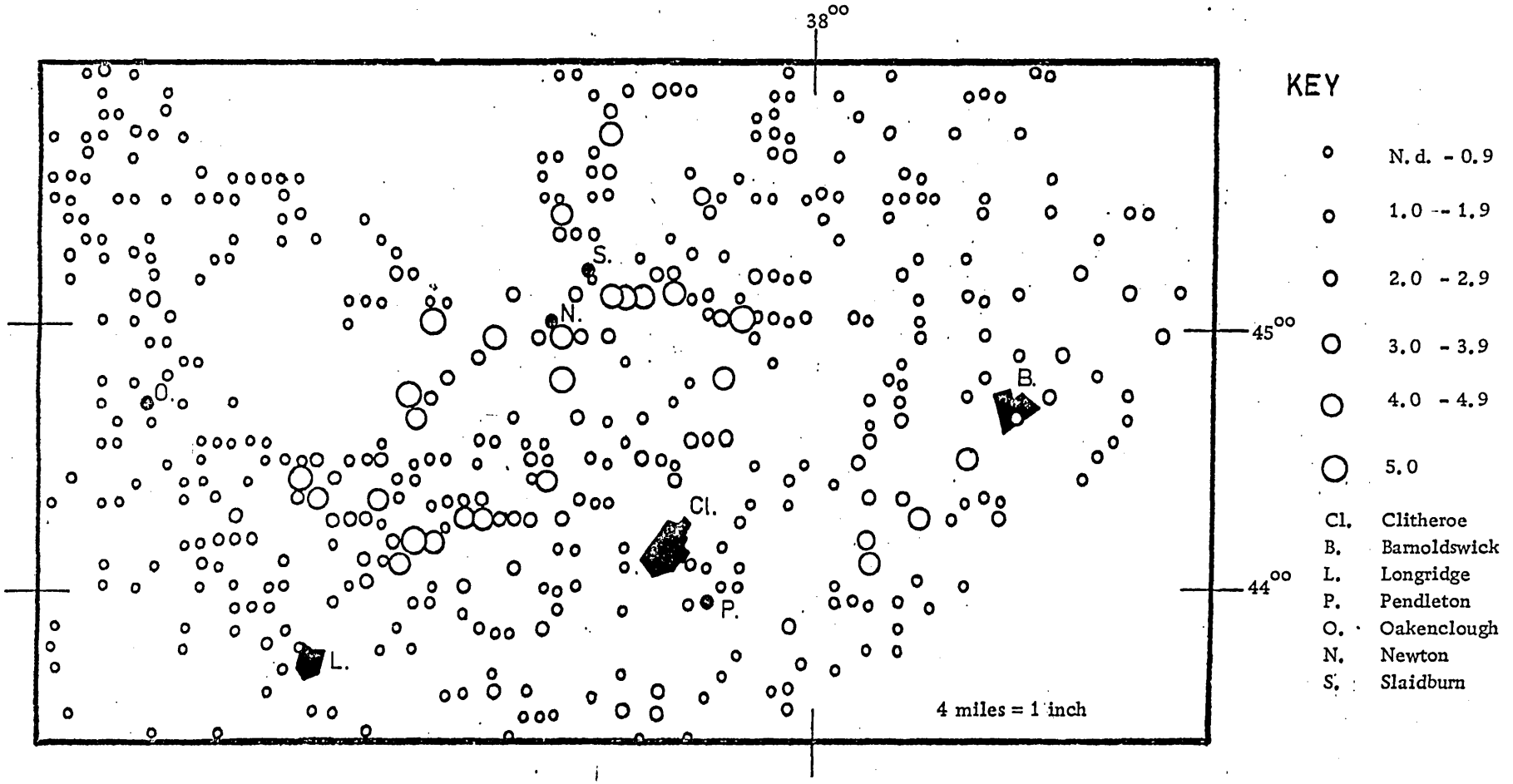


FIG. 3.7 CADMIUM PRESENCE IN STREAM SEDIMENTS OF THE BOWLAND FOREST DISTRICT OF YORKSHIRE

Although the anomalous sediment pattern is represented in the minor class in the smoothed map Figure 3.2 the unsmoothed map displays a noteworthy preponderance of highly anomalous sediments with cadmium values over 5.0 ppm especially off Longridge Fell, Newton Fells and Pendle Hill. Filtering obscures the full effect of these high cadmium concentrations in the smoothed maps since they are statistically swamped by areas of drift-covered limestone which yield sediments with persistent background cadmium concentrations. In the absence of possible industrial contamination the anomalous sediments appeared to indicate either the presence of cadmium-enriched bedrock or the presence of more extensive lead-zinc mineralisation than was recorded in local geological literature. The results presented in Chapters 6 to 10 and summarized in Chapter 13 are the outcome of the ensuing geochemical investigation.

3.3.5 BUXTON-ASHBOURNE REGION, WEST AND SOUTHWEST DERBYSHIRE

The Bakewell-Matlock area is underlain primarily by the mineralized Carboniferous Limestone of the Derbyshire Dome which represents a large area where stream sediment sampling was rendered impossible by the lack of surface drainage. The central limestone is surrounded by younger shale-rich rocks of Visean age which yield conspicuously anomalous sediments to the northwest and east of Ashbourne (see map Figure 3.8). By contrast, in the Edale - Chapel-en-le-Frith area of the Carboniferous Limestone even the close proximity of the Eyam mine lead lode at the limestone-shale contact, is not reflected in anomalous stream sediments. Consequently both these areas were considered worthy of further study, the first near Buxton to explain the presence of the strong cadmium anomaly and the second in the limestone shale contact North of Bakewell to explain the absence of any anomaly. The results of investigations from both areas are considered in Chapters 4 to 10 and summarized in Chapter 13.

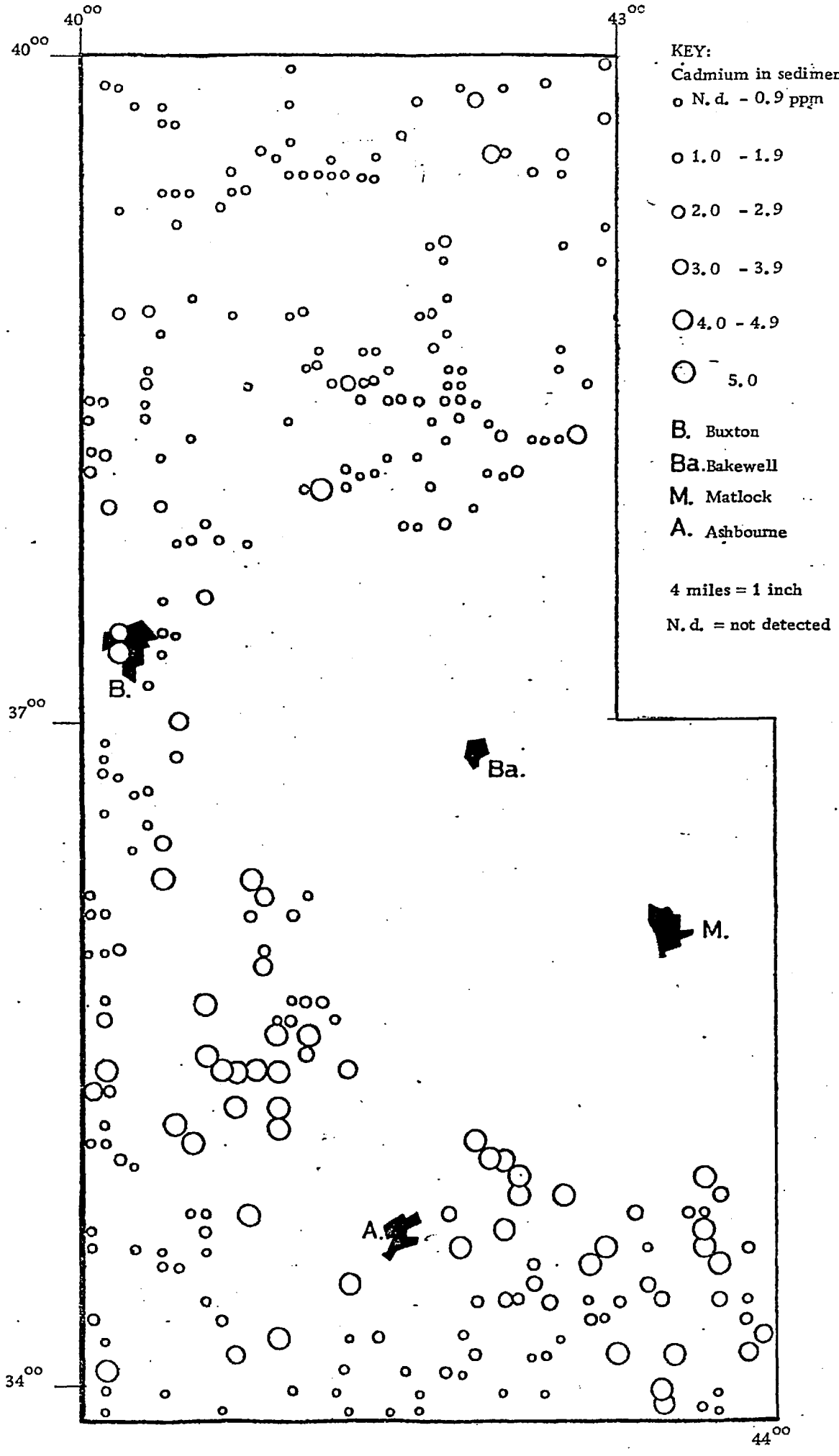


FIG. 3.8 CADMIUM PRESENCE IN STREAM SEDIMENTS OF THE BUXTON/ ASHBOURNE DISTRICT OF DERBYSHIRE

3.4 STUDY OBJECTIVES

The Science Council Report on 'Cadmium in the Environment' (1973) outlined recommendations for further research concerning the protection of the environment from pollution which must be urgently implemented, in addition to the provision of a more detailed knowledge of background levels of cadmium in soils and vegetation. Several of these recommendations will be considered in the course of the thesis, namely:-

1) 'Contributions to the environment from air, sewage, artificial fertilizer etcetera.'

2) 'The availability and mobility of cadmium in different environments.'

3) Interrelationships of cadmium with other elements including zinc:cadmium relationships in soils and plants.'

4) 'The chemical forms of the element in soils, water and air.'

The approach to the study is very much guided by the presence of anomalous stream sediments in England and Wales. The influence, for example, of human industrial activity in the build up of cadmium in the environment is studied with respect to the South Wales area follow-up surveys. In addition the influence of mineralization on the presence of cadmium in surface sediments and soils is considered to be of relevance in the studies based in the area of the Derbyshire Dome. The less obvious sources of cadmium to the environment provided by local geology are much more difficult to identify confidently. Areas of outstanding interest identified for study in depth are demarcated following a series of nationwide rock-sampling surveys. Within these areas the expected presence of cadmium in the geology is gauged and the metal's

potential availability to sediments and soils judged following the identification of cadmium's chemical form in the rocks and soils by the two methods of aqueous chemical extraction and evolved gas analysis. In each area computer-based statistical analyses of a suite of elements are used to identify the palaeogeochemical environments conducive to enrichment and this enables conclusions to be made concerning secondary environmental effects on the mobilisation and retention of cadmium in the drainage systems subsequent to its release therein, upon weathering. Finally, areas of England and Wales in which the potential input of cadmium to the food-chain cycle is of sufficient magnitude to cause concern are outlined.

CHAPTER 4

4 AN INTRODUCTION TO THE GEOCHEMISTRY OF BLACK SHALES

4.1 INTRODUCTION

Following the development of the emission spectrograph technique for the study of minor element presence in geological materials in the 1920s, Goldschmidt, upon analysing some Palaeozoic shales of Europe gave the first indication of the amounts of each element which could be expected in a fine-grained rock. Shales generally contain greater quantities of minor elements than do sandstones and limestones (Turekian and Wedepohl, 1961). However Krauskopf (1955) drew attention to the fact that carbonaceous rocks and black muds in present day seas contained even higher amounts of trace metals than the average fine-grained rock. Black Shales have subsequently been studied as possible low grade sources of metals by many authors (e. g. Tourtelot et al, 1969). Numerous authors (e. g. Cissarz 1930) have formed opinions on the origin and type of trace metal enrichment which is known in the black shales of the Mansfield Kupferschiefer deposits of Germany (deposits which have been mined for copper for centuries). Concentrations of copper have often been observed in black shales, although usually not in as great amounts as in the Kupferschiefer (up to 2. 9%). In Ordovician black shales in Norway and Sweden copper contents of 1, 000 ppm were common. The black sulphide bearing Dictyograptus shale (Lower Ordivician) contained 0. 05 to 0. 1 ppm gold, 0. 1 to 1. 7 ppm silver and 1000 - 3000 ppm vanadium. Investigations also showed that the average lead content in marine shales is about 20 ppm (all figures from Goldschmidt, 1954). Furthermore, black shales are known to be the parent materials of soils associated with various animal disorders, such as molybdenum induced copper defficiency in Derbyshire livestock (Thompson 1970) and chronic selenium poisoning of livestock pastured on certain Irish soils (Fleming

1957). Concentrations of minor elements in black shales can therefore be seen to have many economic implications.

4.2 A DEFINITION OF BLACK SHALE

The term black shale describes a series of dark-coloured, fine-textured sedimentary rocks with a carbon content of more than 2 per cent. The term is at present regarded as being synonomous with the concept of low-grade metal enrichment since the assertion of Krauskopf (1955) that carbonaceous sediments show an enrichment in the trace elements silver, arsenic, molybdenum and nickel. In a bibliography of minor element content in marine black shales Tourtelot (1970) laid the foundations upon which the following questions with regard to black shales can be asked: how common are metal-rich black shales? Are they limited to metallogenic provinces, to certain time periods or to specific environments of deposition? What is the origin of metal in black shales? Are they concentrated by means of biological activity, by sorption from sea-water, by decaying organisms, by sulphide precipitation in a reducing environment or by epigenetic mineralisation and can analogues be identified in modern sediments? The overview of black shale geochemistry which follows is meant as a guide to some of the background knowledge and published data on the subject and will serve as a suitable introduction to the following six chapters.

4.3 GENERAL GEOCHEMICAL ENVIRONMENT OF DEPOSITION

During the deposition of sedimentary rocks, detritus is carried into the depositional area in suspension and in solution. After sedimentation the detritus is in a state of disequilibrium with its physiochemical environment and changes will be expected to take place.

The buffer system CO_2-HCO_3^--$CaCO_3$ generally restricts the pH of most surface environments from 4 to 9 whilst the natural Eh potentials rarely exceed the range needed to release oxygen and hydrogen an Eh range of -0.5V to 1.0V. Cadmium, for example, exists as a reduced metal at an Eh well below that found in nature. At a higher Eh it exists as Cd^{++} in acidic environments and in natural basic environments, at a pH of about 10, the formation of cadmium hydroxide takes place. The behaviour of ions in water is most important. Goldschmidt (1933) was the first worker to point out that such behaviour is governed by ionic potentials, which are the ratios of ionic charge to ionic radius. Those elements with a high ionic potential form complex anions, those with intermediate potential form hydroxides, whilst those with lowest ionic potentials are insoluble.

Atkins (1930) wrote that the pH of terrestrial water is generally less than 7.0 whilst that of the sea is greater than 7.0. Therefore iron, which is soluble in acid waters will precipitate on contact with sea-water, to form hydrated iron oxides. The higher the pH in a system generally the lower is its oxidation potential and oxidation proceeds more rapidly. Thus, for example, as the oxidation potential of iron is lower than that of manganese, then iron forms a hydrated iron oxide and enters the sea as a solid whereas manganese enters in solution. Thus the manganese: iron ratio would be expected to increase in offshore sediments (Spears 1963). The presence of growing organisms will affect the Eh by liberating oxygen and causing it to rise and, conversely, the decay of organic matter will cause Eh to fall by liberating hydrogen, methane and hydrogen sulphide.

The presence of non-detrital minerals in a succession was viewed by Spears (1963) as providing a good indication of the physicochemistry of

the environment in which they were formed. Dunham (1960) noted a change in physicochemical conditions in a dominant d5 age Coal Measures cyclothem, sufficient to cause a change in the dominant non-detrital mineral form from iron sulphide to iron carbonate. A similar change up succession from sulphide to carbonate formation was reported by Nicholls and Loring (1962) in a Coal Measures cyclothem from North Wales. This was attributed to one or a combination of the following possibilities:-

1) A change in oxidation potential to less reducing conditions or

2) A change in pH towards higher values.

The pH range is restricted by the solubility of the carbonate which, in this instance, was determined by the concentration of ions in the range 6.0 to 8.5. Co-existence of iron sulphide and iron carbonate in natural aqueous environments is possible in the Eh region of -0.2 to -0.3V, according to the diagramatic scheme of Krumbein and Garrels (1952, see Figure 4.1). Thus the determination of possible Eh - pH conditions of sedimentation by a study of the presence of carbonate and sulphide in a sequence is a useful guide to physicochemical palaeodepositional conditions. However, Von Straaten (1954) showed that iron sulphide formed below the water-sediment interface and commented on the fact that siderite is thought to be diagenetic rather than syngenetic in behaviour. Eh often decreases with depth of burial (Zobell, 1946).

4.4 . BLACK SHALE ENVIRONMENT OF DEPOSITION

In the black mud environment the presence of sulphate reducing bacteria leads to the formation of high concentrations of hydrogen sulphide which reduces the localised pH. Postgate (1959) discovered that all the bacterial sulphate-reducing species are variants of the freshwater species desulphovibrio desulphuricans which lives on the energy derived by the

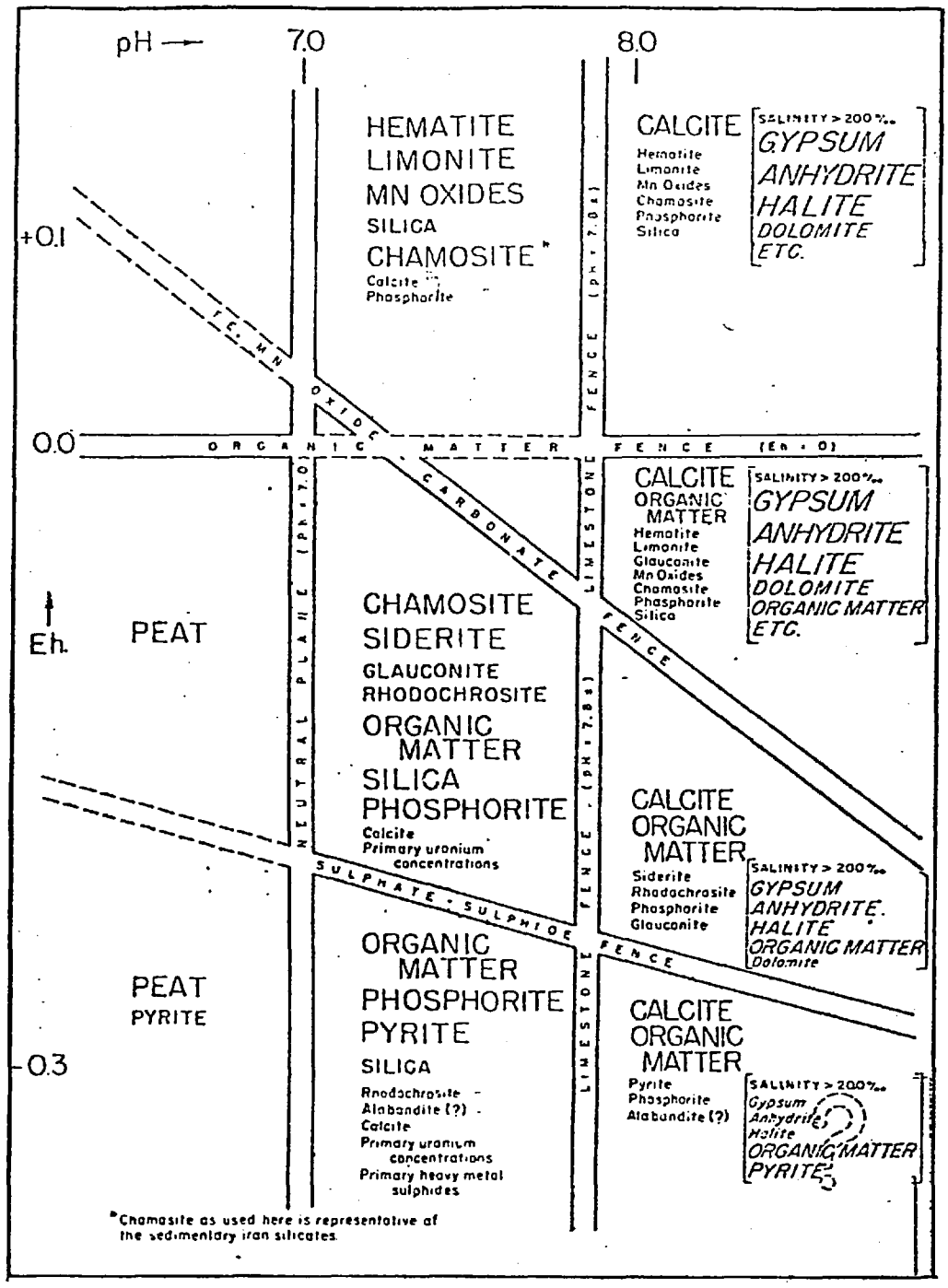


FIG. 4.1 SEDIMENTARY END-MEMBER ASSOCIATIONS IN THEIR RELATIONS TO ENVIRONMENTAL LIMITATIONS IMPOSED BY SELECTED Eh and pH VALUES. ASSOCIATIONS IN BRACKETS REFER TO HYPERSALINE SOLUTIONS (AFTER GARRELS, 1952).

reduction reaction and in physical conditions which credit them with a higher tolerance for life than any other living form apart from viruses. Carroll (1958) showed that the addition of 40 mls of hydrogen sulphide per litre of sea-water reduced the pH from 7.95 to 7.0 and caused an Eh change from +380mV to -25mV. This stressed the importance of bacterial generation of hydrogen sulphide to the physical conditions of the marine environment. Although sulphates are not always present in great amounts, the anionic group is, on average, the third most abundant in natural waters. The reducing reaction of sulphate is:

$$SO_4^{=} + 3H_2 \longrightarrow H_2S + 4OH^- + \text{energy}$$

The reduction of divalent metal sulphides in a two-stage reaction catalysed by sulphate-reducing bacteria has been shown by Caspers (1957):

1. $R^{++}SO_4 + 2C \longrightarrow R^{++}S + 2CO_2$
2. $H_2O + R^{++}S + CO_2 \longrightarrow R^{++}CO_3 + H_2S$

the evolved carbon dioxide will lower the pH locally whilst the metal carbonate if sufficiently insoluble, will remain in the sediment.

In summarizing his views on the formation of black shales Dunham (1961) wrote that stagnation under euxinic or similar conditions or rapid deposition in organically productive waters leads to the preservation of carbon mostly as stable kerogen. He also noted that the role of anaerobic bacteria in the precipitation of sulphide was important. Thus a presence of organic matter, quiet undisturbed sedimentation and a low oxidation potential caused by restricted water circulation are seen as essential requirements in the formation of black shales. Five different types of black shale environment can thus be broadly outlined (after Dunham, 1961):

1) Terrestrial swamps such as peat bogs, where highly acidic conditions predominate causing most cations to go into solution. As the sulphur content is generally too low, sulphides do not form.

2) Eutrophic lakes where excessive plant and animal life rob the waters of oxygen and permit the presence of sulphate reducing bacteria in the muds. Provided that any metal cations are in supply the sulphide form may precipitate.

3) Littoral and epineric environments such as estuaries and mudflats where water circulation is restricted and burrowing organisms abound.

4) Partially restricted marine basins such as the Black Sea or fjords of glaciated high-lands. Stagnation is emphasized by slow sedimentation and an abundant supply of organic material from the nektonic fauna.

5) Sea-bottom basins where water circulation has been limited. Such basins may have formed in the Central Province of England and Wales in Visean times.

An investigation of the relationship between depositional environment and elemental distribution in sediments from the Baltic Sea by Manheim (1961b) showed that maximum heavy metal contents existed not in the central most stagnant and organic-rich parts, but in the peripheral transition zones characterised by aerated bottom-water and moderately reduc ing sediment environments. Elemental concentrations as high as 250 ppm copper, 250 ppm zinc, 80 ppm molybdenum and 32 ppm uranium were found in the peripheral areas. In another paper Manheim (1961a) reported a prominent salinity stratification in the Baltic Sea which gives rise to changes in bottom sediment character from oxygen-rich to stagnant as greater depths are reached. The depletion present in the most stagnant parts of the basin was therefore perpetuated. Trace element enrichment

is a function of supply, removal and dilution. In the transition zones copper, lead, zinc and silver appeared to be enriched in the sediment by precipitation from the water as sulphides. In a study on the Black Sea Glagoleva (1961) discovered that copper, cobalt, organic carbon, phosphorus, calcium and strontium attained a maximum content in the finer sediments further from shore whilst maximum concentrations of vanadium, chromium, iron, nickel and manganese occurred in coastal silt and clay. Copper and the last-named elements increased in content from sand to clay and decreased in lime mud. Analysis for minor elements in modern sediments from the Gulf of Paria, West of Trinidad by Hirst (1962) indicated that gallium, chromium, vanadium, copper, lead, barium, titanium, lithium and to a lesser extent cobalt, nickel and boron were probably deposited with degraded clay minerals structurally combined in their lattices. Non-detrital gallium, chromium, cobalt, nickel, copper, lead, tin and possibly beryllium and molybdenum were concentrated in near-shore areas. This concentration was possibly related to adsorption onto clay minerals which were flocculating due to changes in salinity in the Gulf and also to association with organic carbon and limonitic concretions and calcareous detritus on the platforms. Control by organic carbon may have been significant for non-detrital gallium, chromium, vanadium, nickel, copper and molybdenum. In a final example of environments of deposition, a survey of trace element levels in the estuarine sediments in Corpus Christi Bay (Texas) by Holmes et al (1974) has shown the presence of anomalous levels of zinc and cadmium. Maps of element abundance within the bay indicated large concentration gradients, the highest values being near the harbour entrance. Seasonal determinations of metal levels in the harbour and bay waters revealed significant variations with time. During summer, stagnation of the harbour water increased the concentration of metals so that precipitation in the reducing environment of the bottom waters took place. In Winter the exchange of metal between the bay and harbour increased and metals were redissolved from harbour deposits, washed into the bay and adsorbed by particles settling to the bottom.

4.5 PROCESS AND SITE OF ENRICHMENT

4.5.1 ADSORPTION

Enrichment in a fine-grained sediment may take place by processes of trace element adsorption. In simple adsorption, elements are held at the phase boundary by purely physical forces whilst in chemical sorption processes such as base exchange, sorption may take place when one ion substitutes for another in a clay mineral. Krauskopf (1956) suggested that adsorption increases as grain-size decreases. Thus colloids of organic matter and clay minerals are important for adsorption.

4.5.2 CLAYS

Weaver (1958) contended that most clay minerals strongly reflected the character of the source material and the environment of weathering and are only slightly modified in the depositional environment. Correns (1949) concluded that the solubility of silicon and aluminium was a function of pH. At pH 4.0, aluminium is much more soluble than silicon whereas in more basic environments (pH 5.0 to 9.0) silicon increases in solubility whilst the solubility of aluminium remains the same. Thus, aluminium-rich montmorillonite would be expected to form in a low to high pH environment, whilst kaolinite would be expected to form in a very low pH environment.

According to Katchenkov (1961) the distribution of many elements in clay-minerals depends on the physicochemical properties of the element, the environment of formation of the mineral, composition of parent rocks and intensity of chemical weathering or climate. In clay minerals of marine deposits, minor element content was found by Katchenkov to be 170 ppm vanadium, 100 ppm nickel, 20 ppm copper, 13,300 ppm organic carbon and 300 ppm bitumen. Tourtelot (1964) has shown that the

differences in minor element content of samples of shales of late Cretaceous age reflected the effects of clay minerals and organic matter. In general, arsenic, chromium, copper, molybdenum, selenium, vanadium and zinc are concentrated in those offshore marine samples having the most organic carbon with sorption as a most important enrichment process. The chemical characteristics of the environment of accumulation and the diagenesis of clay minerals and organic matter were the most important factors controlling this process. Part of the organic material and the original colloidal hydrates will not survive in their original form on diagenesis and included trace elements will be redistributed from them.

4.5.3 ORGANIC MATTER

Cadmium content of 84 samples of the Pierre shale (USA) had an average of 1.4 ppm and a range of less than 0.3 to 11.0 ppm. The median content of 0.8 ppm represented the content of the average shale according to Tourtelot (1964). Some samples with high cadmium were found to contain relatively large amounts of organic matter which may have served as a collector for cadmium. Deul (1956) made semi-quantitative spectrographic analyses on the ash of organic and mineral separates from sedimentary rocks and concluded that the most dominantly lithophile elements, vanadium, iron, cobalt, nickel, copper, zinc, molybdenum, silver, lead and tin characteristically formed complex compounds which might have been fixed by organic material. In addition uranium, lanthanum and cesium were concentrated in the organic fraction. Blumer (1952) wrote that trace elements can be collected by living substances or by organic compounds released after death. Boron, germanium, arsenic and bismuth were taken up from ground water by plants and concentrated in the processes which led to the formation of coal.

In a hypothesis to explain the origin of carboniferous seat earths in England, Evans (1964) wrote that the relatively insoluble sulphides of manganese, cobalt, nickel, iron and copper were profoundly influenced by organic solutes whilst oxides and hydroxides of iron and aluminium were practically insoluble. Barghoorn et al (1965) reported the direct association of copper minerals with finely disseminated carbonaceous matter and partly or wholely devolatized alsphatic organic residues, in the Precambrian Nonesuch Shale (USA) and suggested that the presence of organic materials facilitated in the precipitation of the minerals. The presence of the organic material collagen in apatite-bearing-skeletal debris on the ocean floor had convinced Arrhenius (1959) that heavy metal ions such as zinc, copper, lead and tin could be transferred to the organic debris from sea-water.

4.5.4 SULPHIDES

Trace metals in carbonaceous and black shales commonly form macrocrystals of sulphides and in some instances the presence of this mineral form has been postulated even when direct evidence was lacking. Wedepohl (1964) for example, showed that 33 to 50% of total zinc present in a German black shale was in the sulphide form and the remainder was associated with the clay minerals. Krai skopf (1955) concluded that concentrations of the elements, zinc, copper, lead, mercury, silver, chromium and probably bismuth and cadmium in sea-water could in part be controlled by the precipitation of sulphides in a reducing environment. However, for sulphides to exercise a significant control over trace element concentration in the ocean there must have been a circulation to replenish trace metal supply which would, in addition, have retarded the reducing conditions. Degens and Keith (1959) noted similar abundances of trace elements in pyrite and in organic matter and this was attributed to trace elements collecting initially in the organic material and then released during decay and finally incorporated into the diagenetically forming pyrite. Differences in the trace element content of pyrite was in part limited by the supply of trace elements available in their growth environment.

4.5.5 CARBONATE

During analysis of copper, lead and zinc sulphide ores from Mount Isa in Australia Stanton (1963) recorded a close association between the presence of sulphide ore types and carbonate forms which indicated important biological influence on sulphide deposition, probably in a reducing environment. He concluded that copper sulphides were probably deposited with reef debris and lead-zinc sulphides with off-reef shales. In a further paper Stanton et al (1962) investigated present-day shoreline geothermal activity in the Solomon Islands as a possible guide to ore-forming processes in the past. Acid, volcanic waters were found to contain heavy metal ions such as iron, copper and zinc in solution and when these solutions entered the sea-water, pH rose and Eh fell. This caused precipitation of the metals as oxides, hydroxides, carbonates and basic carbonates. If the precipitates sank into organic-rich stagnant muds, sulphate-reducing bacteria could reduce the oxides and carbonate forms to sulphides. Such deposits, they concluded, may be expected near the shores of volcanic islands where Eh and pH conditions were suitable for primary oxidation.

Following a series of laboratory experiments Temple (1964) reported that not only soluble metal salts, but also many insoluble oxides, carbonates and silicates would be converted into sulphide in the presence of a sulphate-reducing culture at atmospheric pressure and room temperature, in a short time.

4.6 ORIGIN OF METALS

The type of black shales dealt with up to the present have been those which contained unusual concentrations of trace elements but which are also of syngenetic origin, i.e. enrichment has taken place before and during the period which the sediment was being deposited. However, mention has briefly been made in the introduction of the Kupferschiefer

deposits of the Mansf eld basin in Germany. In the Kupferschiefer, conspicuous sulphide mineralization is present and its presence has been described as authigenic (i. e. developed in place, during or after diagenesis) in nature (Love, 1962). The Kupferschiefer is a thin bedded, bituminous marine shale about 30 cms thick, of early Permian age, exposed as far afield as Northeastern England and Poland and containing local metal accumulations of economic grade which appear to be palaeogeographically controlled (Wedepohl, 1964). The metals were found in two principle groups, one with copper and the other with zinc. The elements found in association with copper were: Cobalt, nickel, vanadium, silver, gold, platinum, iridium, paladium and molybdenum. These found in association with zinc were: lead , cadmium, tin, manganese, tungsten, chromium and subordinate arsenic, antimony and bismuth. The zinc values were highest when beds were bitumen poor (Cissarz, 1930). According to Love (1962) the Kupferschiefer was formed in a foul-bottomed sea whose upper, oxygenated waters abounded in a planktonic life which was the main source of the high organic contents of the shales (up to 20%). The rock was found to contain myriads of small pyrite spheres enclosing delicate microfossils which he regarded as being responsible for the authigenic precipitation of primary pyrite. The demonstration of the early formation of pyrite allows consideration of early diagenetic replacement by other sulphides. Ekiert (1958) envisaged, during lower Zechstein sedimentation hydrothermal solutions carrying heavy metals reaching the surface through fissures to the sea and rivers, to be precipitated as sulphide simultaneously with the deposition of the Mansfeld shales in the highly reducing environment of the Zechstein lagoon. This popular hypothesis is used to explain the presence of metal deeps in the Red Sea described by Holmes\Tooms,1973. In Atlantis II deep, at depths of 2,000 m and a temperature of 56°C, weakly acidic (pH 5.3) highly saline, exhalative brines with a

sodium chloride level of 300 gm/l., precipitated amorphous iron oxides, goethite, silica, sphalerite, siderite and rh-o-dochrosite at the contact with the slightly alkaline bottom sea-water. Iron, manganese, copper, barium and lead were present in the brines in concentrations up to 50,000 times that of sea-water concentrations.

4.7 CONCLUSIONS

Probably the most significant factor in determining the enrichment of trace elements in black shales is the contact of metals in solution with organic matter. For some deposits the most significant period of enrichment appears to be during the stages of circulation and expulsion of interstitial waters from sediment pores as a result of compaction of deposits. During these stages muds themselves may loose up to 95 - 99% of their included water content which may be as high as 50 - 95% of the mud volume. Pering et al (1974) studied the presence of solid hydrocarbons and associated metals below exposures of Edale Shales in Derbyshire and concluded that distillation of asphalts took place from the shales during diagenesis. The maturation of organic material by the elimination of volatiles, oxygen, hydrogen and nitrogen during diagenesis may have important chemical repercussions.

The remaining prime chemical changes which take place upon diagenesis of shales include the inversion of less stable iron sulphides (such as marcasite) to pyrite and the stabilization and homogenisation of a variety of fine-grained minerals to a more coarsely crystalline form. Such processes can occur, according to Rickard (1968), at relatively shallow depths and at temperatures less than 200^{o}C. According to Vine and Tourtelot (1970) there is a possibility that epigenetic trace element enrichment in black shales could result from the use of thin beds

of interstratified black shales as a sink for mobile elements transported by pore waters expelled during sediment compaction.

As this survey is intended only as an introductory guide to the study of black shales and is not by any means comprehensive the reader interested in the enrichment behaviour of a specific trace metal is referred to the annotated bibliography of minor element content of marine black shales and related sedimentary rocks 1930-1965 compiled by E. Tourtelot (1970). For the sake of completeness a thorough introduction to the distribution of uranium, which is not considered in this thesis, has been compiled in the form of an annotated bibliography by Fix (1958) and should, in addition, be referred to if necessary.

CHAPTER 5

THE GEOLOGY AND STRATIGRAPHY OF AREAS CHOSEN FOR FURTHER SURVEY

5.1 INTRODUCTION

On commencement of this study the unpublished geochemical maps for England and Wales were available (see Chapter 3) and it was from this nationwide primary reconnaissance that areas with anomalous cadmium in sediments were chosen for study.

Of the rock types analysed for trace elements in the literature and summarized in Chapter 1, the argillaceous and carbonaceous rocks alone appeared to concentrate trace elements. Consequently those areas underlain by carbonaceous (black) shale were located. This detailed location of black shales resulted in the isolation of three areas for study in the so-called Central Province of Britain of the Carboniferous era which extended north from the residual Devonian land mass known as St. George's land. The northern shoreline of the Central Province basin marked the coast of a great land-mass which covered Scotland and which lay in a line from the North of Ireland across Southern Scotland.

5.2 THE SAMPLING OF BLACK SHALES

Field exposures of black shale are commonly monotonous and repetitive in character, and difficult to sample because of the impracticability of separating a whole, homogeneous substratum into multiple, smaller scale rock bodies. In addition, the exposures of such rocks are severely limited, their presence more often being revealed by the existence of flat-lying waterlogged tracts even in steep scarp slopes such as Pendle Hill in Lancashire. Resultantly the greatest area of the 'target' population,

in this case, the total aerial extent of black shale exposure, is removed from the attentions of the sampler who is restricted to the outcropping of rocks along river sections and in quarries. At a locality the collection of an unclustered number of samples, randomly distributed throughout the body of rock will indicate the extent of local geochemical variation caused by subtle, ever changing local lithologies. An optimum and predetermined number of samples is collected in order to minimise variable bias in the sampling due to these inherent local lithological variations. During the course of sampling it was discovered that the definitive black shale was such a subjective concept that one was forced into the practical sampling of those rocks approaching the 'ideal'. In order to give some indication of the fluctuation of palaeogeochemical conditions, sampling included calcareous and other chemically precipitated rock bodies and also diagenetic material such as pyrite.

5.3 INTRODUCTION TO THE GEOLOGY OF THE CARBONIFEROUS ERA

The Carboniferous era, so-called because it contains the principle coal-bearing strata of the British Isles, can be divided into three periods: Carboniferous limestone, Millstone Grit and Coal Measures.

After Devonian times the Carboniferous sea invaded the mature, low-lying land-mass of Britain and separated into a number of water-bodies divided by barriers and stumps of the Devonian landscape. In the first period little detritus entered into the clear, shallow waters as great thicknesses of Carboniferous Limestone were laid down. Several thin coaly deposits formed on coastal swampy areas and occasional sea-water incursions, resulting in the formation of marine limestones, briefly upset the continuum. This was followed by a period of quiet, deeper water sedimentation of organic-rich argillaceous rocks which was eventually overwhelmed by widely dispersed deltaic deposits of the second Millstone Grit Period spread by a great river sweeping down from the Northeast. Different parts of Britain were covered by arenaceous

deposits at varying times during this stage, paving the way for the huge areas of swampy forest which developed upon the deltaic flats in the succeeding final Period Coal Measure times. A long period of stable deposition followed, characterized by cyclical sedimentation and occasional insursions of sea-borne and river-borne detritus. Gradual dessication brough this era to a close.

The depositional time-period which is of most interest in this study extends from the top of the Carboniferous limestone, when black shale sedimentation succeeded limestone deposition, to the lower stages of the Millstone Grit before the total incursion of the Grits. The silting up of the clear, shallow waters of the Carboniferous limestone in the late Visean, early Namurian times resulted in the deposition of thicknesses of carbonaceous argillites. As the deltaic front advanced Southward the silty swamps of early Namurian times were overwhelmed by arenites reaching the Bowland Forest area of Lancashire before the end of E1 times, the Edale area of Derbyshire a little later, after the start of R1 times and the Onecote-Dove area of Southwest Derbyshire later again, in R1 times (see Table 5.1 for explanation of zonal symbols). The onset of the Millstone Grit in these three areas is represented by the Pendle Grits, the Mam Tor sandstone and the Longnor sandstone respectively.

Each of the formations has been divided up into stages either by the use of corals and brachiopods, or by lamellibranchs and goniatites. Throughout the discussion which follows, the zonal names and symbols are based on the latter classification, as illustrated in Table 5.1. The Visean Period is divided up into four stages from B1 to P2 and the succeeding Namurian Period is divided into six stages from E1 to G1. The stratigraphy described in the remainder of this chapter is confined to these periods. Four areas will be considered in detail, three from Hudson and Cotton's (1945) Central Province illustrated in relation to the

TABLE 5.1 THE NOMENCLATURE AND FOSSIL ZONING OF THE CARBONIFEROUS ERA IN ENGLAND AND WALES

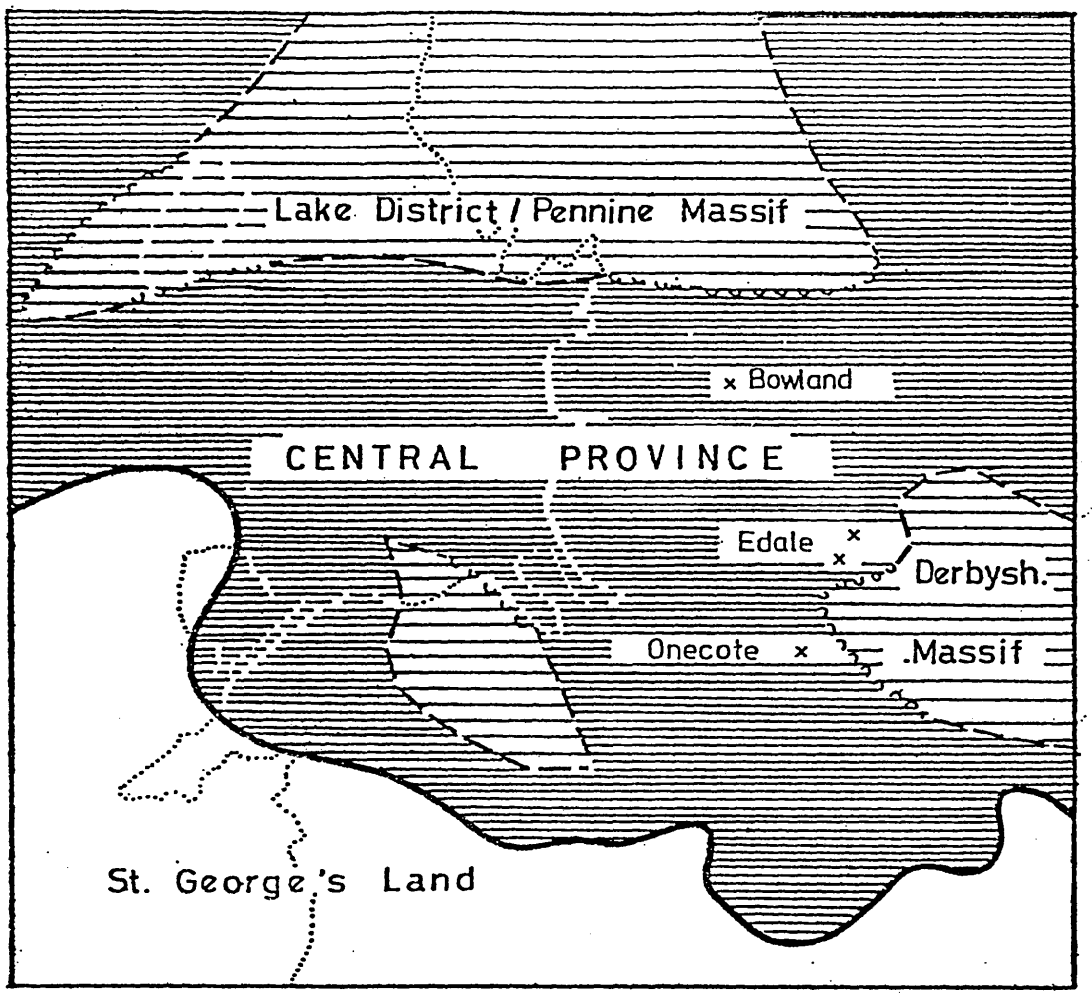
ERA	PERIOD	FORMATION (common name)	STAGE	
UPPER CARBONIFEROUS (SILESIAN)	STEPHANIAN	COAL MEASURES		
	WESTPHALIAN			
	NAMURIAN	MILLSTONE GRIT	Lower Gastrioceras	G2
			Upper Reticuloceras	R2
			Lower Reticuloceras	R1
			Homoceras	H
			Upper Eumorphoceras	E2
			Lower Eumorphoceras	E1
LOWER CARBONIFEROUS (DINANTIAN/AVONIAN)	VISEAN	CARBONIFEROUS LIMESTONE	Posidonia Zone	P2
				P1
			Beyrichoceras Zone	B2
				B1
	TOURNASIAN	LIMESTONE SHALES	Pericyclus Zone	Pe
			Protocanites Zone	Pr

present-day shoreline of North West England in Figure 5.1 and the fourth located South of St. George's land in present-day Cornwall and Devon. In Middle Visean times reef facies developed in Central Derbyshire and over the Lake District, restricting water circulation to a great extent. The areas studied, marked on Figure 5.1 are located close to the limestone massifs: Bowland in Lancashire, Edale in North Derbyshire and Onecote in Southwest Derbyshire. In order to facilitate cross-referencing between all four areas (including Southwest England, which was isolated by the barrier of St. George's land from the Deltaic incursions which typified Central Province evolution) Figure 5.2 has been constructed, after modifications, from Hudson and Cotton (1945). The staggered onset of the Millstone Grit delta can now be fully appreciated.

5.4 MINERALOGY

Only nine samples and a duplicate were mineralogically analysed by x-ray diffraction. The conclusions drawn from elemental associations, correlations and presence (Chapter 6) justified the decision made not to impliment a full and more detailed mineralogical study of the shales. The traces were made from homogenised rock powders and the duplicate sample from the Bowland Shales was analysed in a second batch. The resultant precision for the ten identified mineral groups is shown in Figure 5.3 and indicates that although the precision for the clay minerals was greater than $\pm 10\%$ at the 95% confidence level, reproducibility was moderately good. In order to enable a better classification of the shales to be made analyses of sandstone (Clarke, 1924) and limestone (Leith and Mead, 1915) are included in Table 8.3.

Mineralogically, the sample representing the Culm Measure of Cornwall is very different from the rocks of the Carboniferous era of the rest of England. The effects of low grade thermal metamorphism



× Boreholes in study areas (after Hudson and Cotton 1945).

Shallow water facies

Deep water facies

Mainland

Reef edge

Figure 5.1 Palaeogeographic map of Northwest England during mid-Visean (Carboniferous) times.

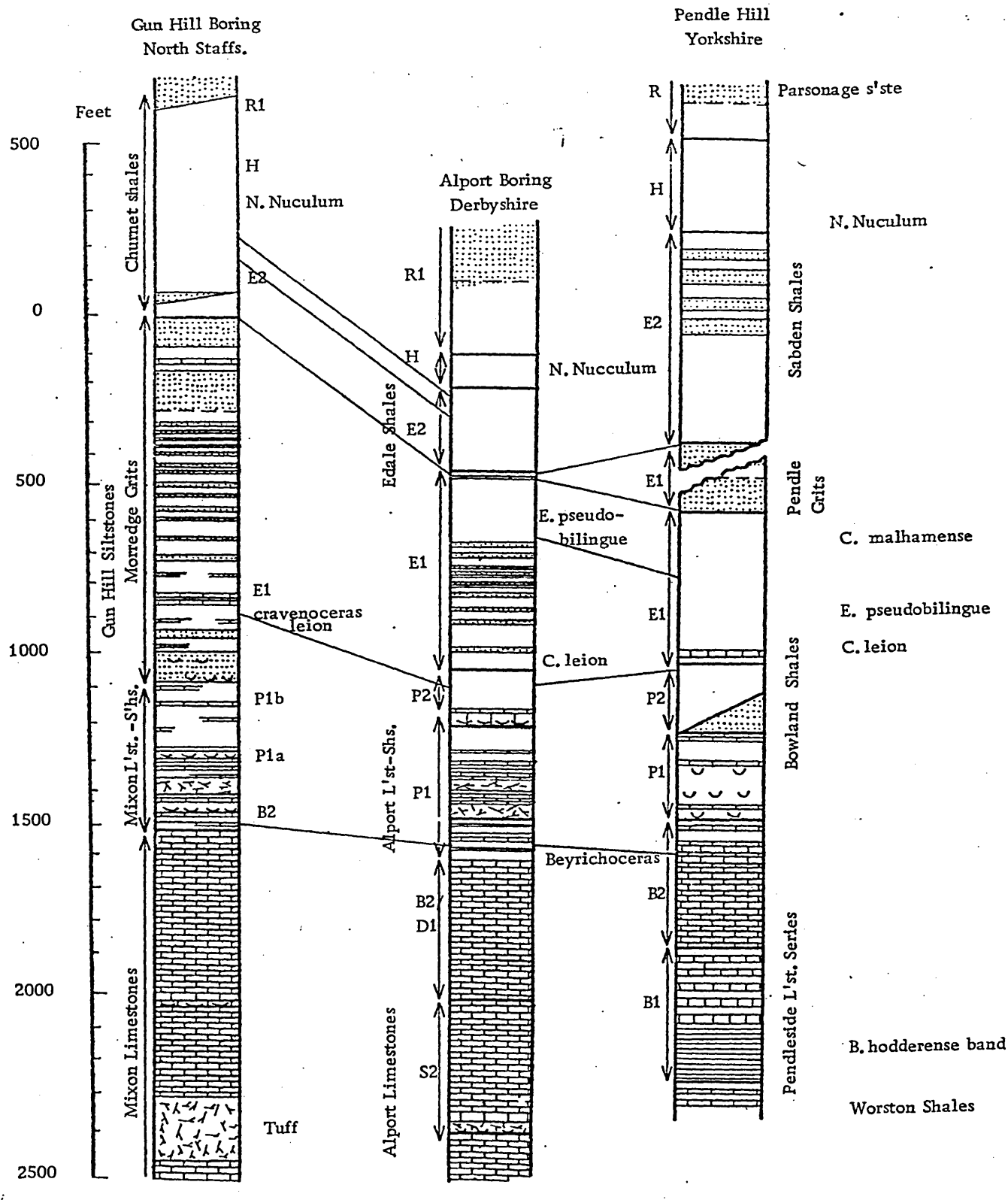
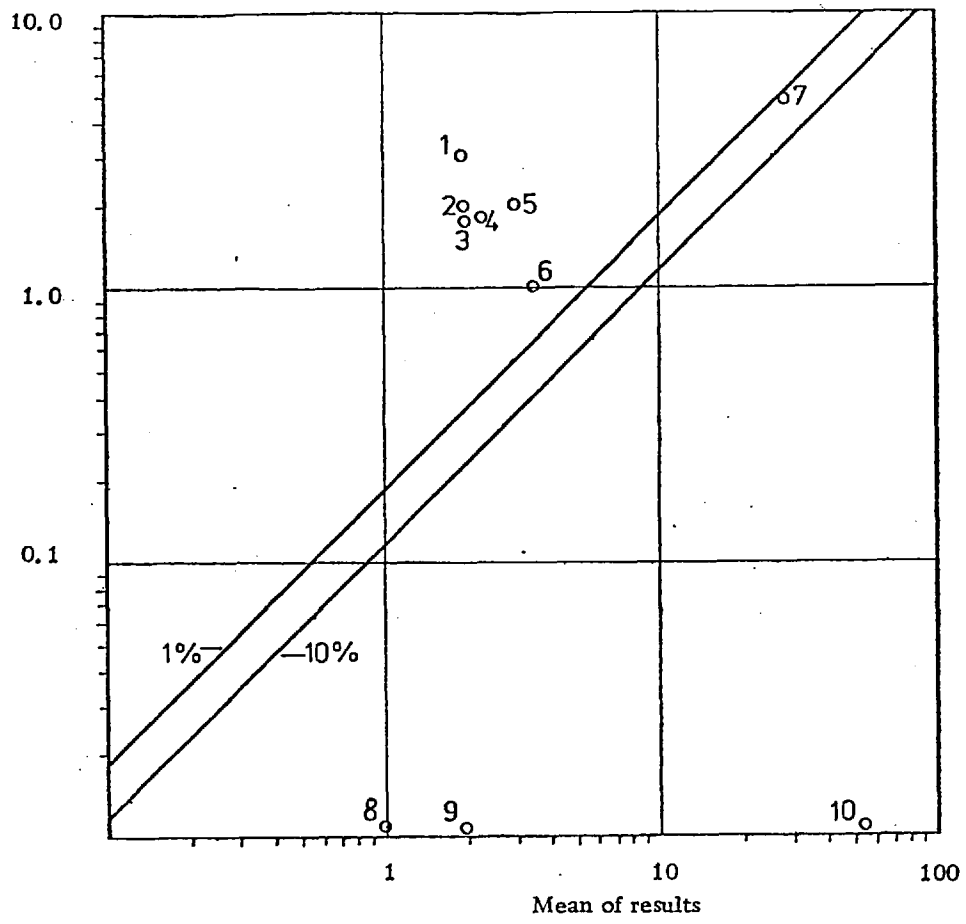


FIG. 5.2 COMPARATIVE VERTICAL SECTIONS OF THE UPPER VISEAN AND LOWER NAMURIAN BASIN FACIES IN THE CENTRAL PROVINCE (AFTER HUDSON AND COTTON, 1945)



1. Graphite
2. Montmorillarite
3. Mica
4. Feldspar
5. Illite
6. Dolomite
7. Calcite
8. Kaolinite
9. Haematite
10. Quartz

In a set of duplicate measurements, the precision of measurement is 10 percent at the 95 percent confidence limit when the indicated proportion of points falls above the diagonals.

FIG. 5.3 XRD IDENTIFIED MINERALS IN BLACK SHALES. PRECISION CONTROL CHART FOR DUPLICATE RESULTS

TABLE 5.2 THE MINERALOGY OF SELECTED BLACK SHALE SPECIMENS AS DETERMINED BY X-RAY DIFFRACTION

MINERAL SPECIES	SAMPLE LOCATION				
	Onecote	Edale	Bowland	Culm Measures	Lake District
Quartz	51 - 80 (62)	36 - 50 (43)	54 - 55 (54)	48	51 - 59 (55)
Montmorillonite	1 - 4 (2)	1	1 - 3 (2)	N. d.	N. d.
Kaolinite	4 - 27 (17)	4 - 13 (7)	1	3	2
Illite	2 - 5 (3)	3 - 9 (5)	2 - 4 (3)	3	1 - 2 (1)
Mica	1 - 4 (2)	3 - 6 (5)	1 - 3 (2)	29	12 - 14 (13)
Chlorite	1	5 - 7(6)	N. d.	14	17 - 20 (18)
Feldspar	N. d.	2 - 4 (3)	1 - 3 (2)	3	4 - 6 (5)
Haematite	2	7	2	N. d.	N. d.
Goethite	2	N. d.	N. d.	N. d.	N. d.
Calcite	7 - 12 (9)	24	26 - 31 (28)	N. d.	N. d.
Dolomite	N. d.	3 - 19 (10)	3 - 4 (3)	N. d.	N. d.
Siderite	2 - 4 (3)	5	N. d.	N. d.	2
Chalcopyrite	5 - 9 (7)	4 (2)	N. d.	N. d.	3
Pyrite	N. d.	3 - 5 (4)	N. d.	N. d.	N. d.
Sphalerite	N. d.	1	N. d.	N. d.	N. d.
Epidote	N. d.	N. d.	N. d.	N. d.	2 - 4 (3)
Graphite	N. d.	3 - 5 (4)	1 - 4 (2)	N. d.	N. d.
Number of specimens	5	3	5	1	3

All figures are percentaged, ratioed, major peak heights given as ranges with the mean in parenthesis

N. d. = not detected in any samples

All values are semi quantitative: comparisons should be made cross-table NOT down-table.

have caused the reconstitution of the rocks and initiated the formation of micas and chlorites which now constitute 43% of the total identified minerals in the rock. Comparison can be made between this analysis and the average analyses of the Silurian age black shales from the Lake District. The only significant difference between the rocks was the recognition of the presence of the low-grade metamorphic mineral epidote in the Silurian rocks. The rocks of the Upper Visean of the Central Province are carbonate and quartz rich and clay poor. On average between 31-39% of the total identified minerals in Bowland and Edale were carbonates. In comparison the rocks of the Onecote sequence are carbonate poor and 8-19% more quartz rich. Graphite was recognised in the Bowland and Edale sequences and sulphides were positively identified in Edale and Onecote rocks (see Table 5.2).

5.5 PETROGRAPHIC AND MINERALOGICAL CONSIDERATIONS

The Onecote, Bowland and Edale shale successions were laid down from Middle Visean to early Namurian times and they represent argillaceous sediments in which highly reducing conditions have prevailed as a direct consequence of the deposition and accumulation of organic matter. Evidence of synchronous high masses in shallow water near the deposition areas of the carbonaceous matter is afforded by the coral reefs of the Derbyshire Massif and the Lake District Pennine Massif (see Figure 5.1). None of the areas is more than 16 kms. away from a massif and the depressions around these high areas allowed for the deposition of organic matter away from the influence of bottom currents. Within these stagnant depressions the action of anaerobic bacteria caused decay of the soluble organic matter which resulted in increase of pH, the reduction of sulphates to sulphides and such alterations of primary minerals as, for example, the solubilization of tetrahedral silicon and aluminium within montmorillonites producing highly adsorptive mixed-layer minerals and illites.

The rocks at Onecote, deposited nearest to St. George's Land, from which the majority of the detritus originates, are least influenced by the synchronous Derbyshire Massif and are mineralogically a series of clay-rich, high quartz rocks with low carbonate content. At a distance of 12 kms. Northwest of Onecote and only 6 kms. from the reef edge, the Edale rocks are by comparison more carbonate-rich and less siliceous, indicating that bottom water disturbance near to the reef was more apparent and that this basin was not so much of a residual trap as was the Onecote basin. Although deposited 55 kms. to the Northwest of St. George's Land the rocks of the Bowland area form a succession which, in lithology and faunal content, is similar to that of the Midland Embayment Gulf area to the South. Deposited 16 kms away from the Pennine Massif the Bowland Shales consequently show the comparitive lack of reef influence, the rocks are intermediate in quartz content, have a high carbonate content, are clay-poor and contain less total carbon than the other sets of samples.

In the final analysis all black shales of the Central Province are strongly trace element enriched by virtue of the reducing conditions of their formation which were initiated and enhanced by the presence and ease of accumulation of excess organic matter.

5.6 THE ROCKS OF THE CENTRAL PROVINCE

5.6.1 THE BOWLAND SHALE GROUP

The Bowland Shale Group is composed of two major types of shales outcropping in the Upper Visean and Lower Namurian Periods: the Lower Bowland Shale Group, including the Pendleside sandstones; and the Upper Bowland Shales.

The Visean Group is composed of dark grey to black mudstones anf flaggy shales interbedded with bullions and limestones whilst the Upper Group comprises predominantly well-bedded, papery, grey to black shales with pyritous bands, limestones and a fauna which is more lamellibranch than goniatite rich. Lenticular, medium-grey, flaggy sandstones outcrop predominantly in the Lower shales and thin sandstones outcrop in part of the Upper shales. The development of these three lithological types within the predominantly black shale Group is evidence for the great fluctuations in conditions which were taking place about the time of the Variscan earth movements.

Below the Bowland Shale Group, the limestone and shale sequence of the Worston Shale Group succeeds the dominant limestone precipitation of the Chatburn Limestone Group (the source of the Formation nomenclature was the Clitheroe memoir of Earp et al, 1961). The Worston Shale Group comprises grey, calcareous shales and mudstones interbedded with light-grey limestones and cherty limestones. Black shales and grey shales outcrop amongst dominant limestones at the top of the Worston Shales. The 400 feet (120 m) of Worston Shales outcropping on Pendle Hill are succeeded by 250 feet (75m) of impersistent massive grey, poorly-bedded limestones with thin grey, shaly partings known as the Pendleside Limestone. Where the Pendleside limestone is present, the gradation from grey shales of the topmost Worston Shale deposits, into dark-grey to black mudstones with subordinate limestones marks the beginning of Bowland Shale deposition. The type locality for the Bowland Shale sequence is exposed in the bed of Upper Mearley Clough on Pendle Hill. A detailed description of this will indicate the character of the rocks.

The lowermost strata of the Bowland Shale Group exposed immediately above the wood around Little Mearley Hall on Mearley Clough (see map, Figure 5.4) are a series of medium to dark grey mudstones

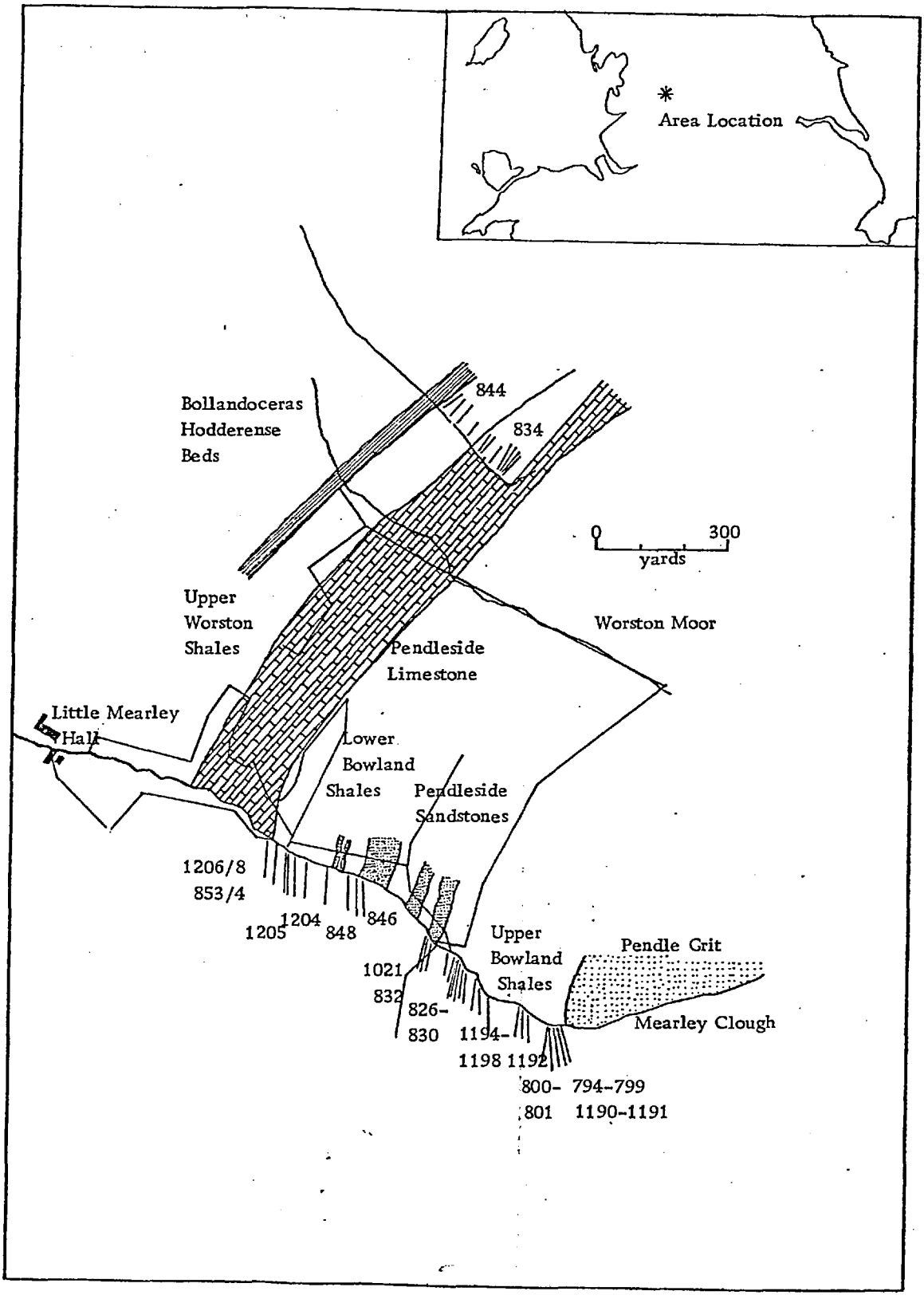


FIG. 5.4 LOCATION, ROCK SAMPLING LOCALITIES AND GEOLOGY OF LITTLE MEARLEY CLOUGH, BOWLAND

intermingled with small concretionary limestones of P1a age. These are succeeded by less well exposed dark shaly mudstones of P1b age which terminate in a small waterfall comprising the lowermost sandstone intercalation of the Pendleside Sandstone Series. Between the lower and upper leaves of the sandstone, hard siliceous and micaceous shales, dark grey shales and medium grey calcareous shales are exposed. Beyond the top of the Pendleside Sandstone a series of dark grey shales and mudstones pass up into 14 to 15 feet (4.2 to 4.5m) of soft, paper-bedded black shales which eventually grade into dark grey mudstones of the lower Upper Bowland Shales. Above the Cravenoceras Leion band (Moore, 1950) some 200 feet (60m) of paper-thin, dark grey to black poorly fossiliferous shales are exposed on both stream banks. Beyond the calcareous shales of the cataract section which follows and which have yielded Eumorphoceras pseudobilingue, a series of dark grey, fissile shales are overlain by 15 feet (4.5m) of blocky, medium-grey calcareous mudstones. The final 20 feet (6m) exposed to the Pendle Grit capped waterfall is a series of dark grey to black, paper bedded shales interleaved with thin, hard and medium-grained sandstones.

5.6.2 THE EDALE SHALES

The Lower Carboniferous limestone in the Edale Valley of Derbyshire is succeeded by an 800 feet (240m) succession of dark marine shales, the top of which is marked by the incursion of diachronous sandy grits of R1 age. The lowermost shales of E1a age above the Cravenoceras Leion band do not actually outcrop, but are known from boreholes. The Edale Shales were deposited predominantly in quiet, marine environments and they have been shown by Ramsbottom et al (1962) to have undergone cyclic sedimentation after the identification of repetitive faunal phases.

The chief lithological types within the shales, which are well exposed in stream sections are (after Stevenson et al, 1971):-

1 Soft-grey shales, which are interbedded with ironstone bands and nodules commonly displaying 'sulphurous' weathering resulting from alteration of pyrite. The sulphurous staining from the decay of pyrite was identified as the secondary mineral jarosite by Hartley (1957). Limestone bands or nodules are rare or absent.

2 Dark shales, which are usually calcareous and which contain an abundant fauna. Thin limestone bands are present and 3 feet (0.9m) diameter bullions occur at some horizons.

3 Silty-shales occur in part of E1.

4 White, pyritous clay bands, considered to be weathered volcanic ashes by Trewin (1968) are confined to the upper-middle and upper horizons of the Edale Shale sequence.

E2 age rocks outcrop with a thickness of about 60 feet (18m) West of Upper Booth and 50 feet (15m) south of the rectory footbridge in Grinds Brook (see map Figure 5.5). In the latter section the black, fissile shales are heavily weathered and iron-stained and their regularity is broken by the presence of hard sandy bands and nodular bands. North of Upper Booth farm the zone is represented by thinly laminated black and brown shales with iron and sulphurous weathering stains.

The succeeding H1 shales alternate with dark mudstone and carbonate bullions and attain a thickness, at Upper Booth, of about 30 feet (9m). The succeeding H2 beds repeat the sequence black mudstones and shales, although this 40 feet (12m) section is broken up by ironstone and bullion beds.

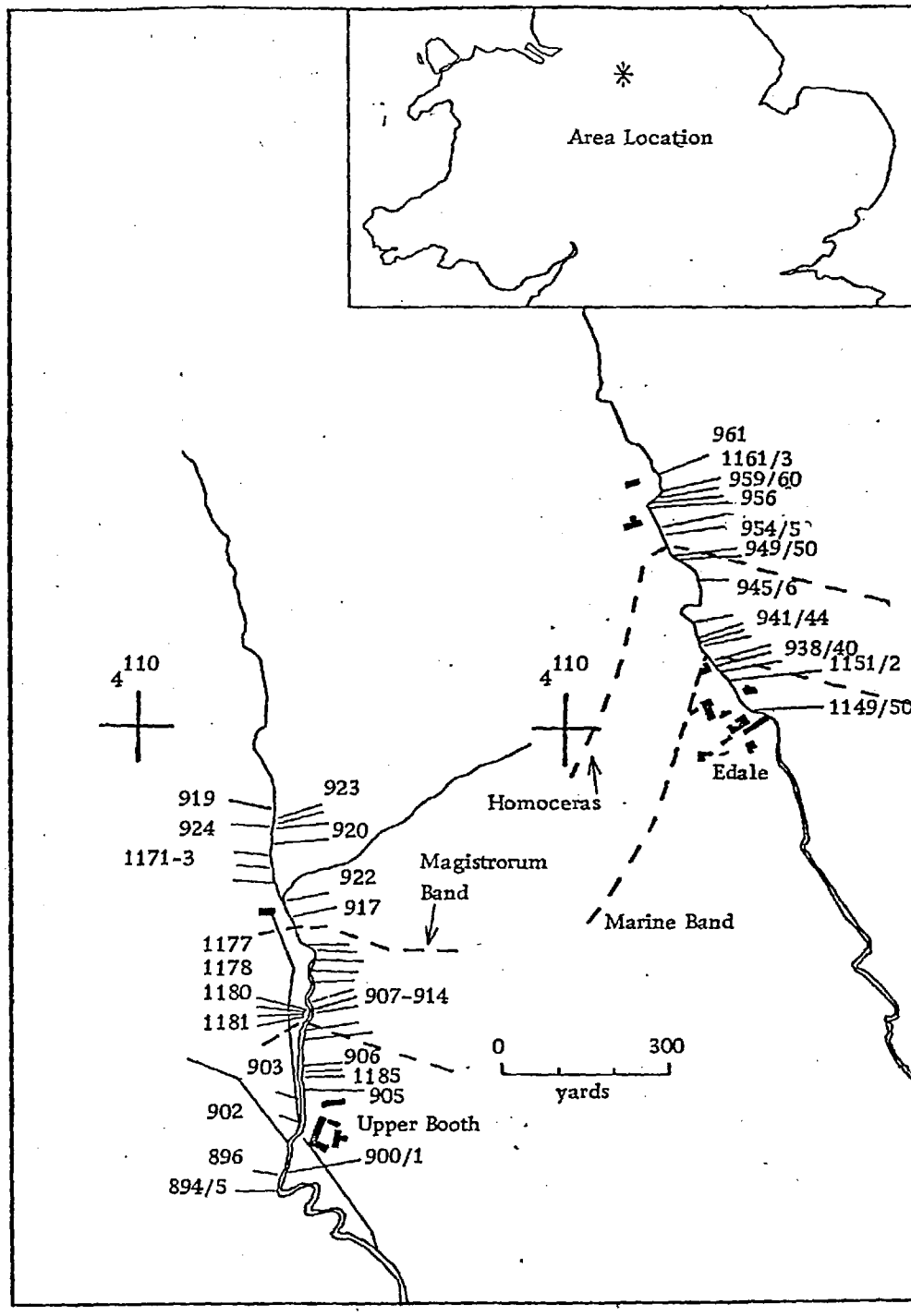


FIG. 5.5 LOCATION OF EDALE STUDY AREA ROCK SAMPLING SITES AND MARINE BANDS

In the Edale area the Reticuloceras circumplicatile, R1a, zone maintains a rather uniform thickness of 70 to 80 feet (ca 22m) and consists of shale with some silty bands and thin limestones. The following R1b, R. Nodasum zone is some 40 to 70 feet (12 to 21m) thick and is, except for being a little more silty, lithologically similar to R1a. At least 56 feet (17m) of this zone is exposed in the landslip below Mam Tor. The R. reticulatum, R1c zone, varies considerably in thickness as a result of the diachronous nature of the succeeding Kinderscout Grit Group. The grey to black, silty shales average 10 to 20 feet (3 to 6m) in thickness and contain increasing numbers of thin sandstones to the top where the transition to the Grit Group takes place.

5.6.3 THE ONECOTE/DOVE SHALES

In the Central Province the strata of P1a to P2, Upper Visean age, is afforded a general threefold division. The lower G. Orenistria zone is the most variable both lithologically and faunally. Considerable movements in the marginal areas between basin and massif resulted in a thinning of strata near to the massif and the formation of limestones, tuffs and breccias. The middle G. Sphaericostriatus zone consists foremost of shale and limestone with some chert which formed in a period of quiet sedimentation and transgression, followed by an upper zone of sandstone. This Onecote sandstone is equivalent to the Pendleside sandstone in Bowland and it heralds the arrival of the Millstone Grit. The development of a monosynclinal structure in late P times along earlier reef-building lines exposed the massif reefs to erosion and formed the B2 to E2 Namurian unconformity at the Upper Dove Valley (Holdsworth, 1963). The E1 stage was a marine depositional environment with widespread restricted circulation over Derbyshire and Staffordshire. A lack of autochthonous fauna in the reduced shales suggests highly toxic and acidic bottom waters interbedded only by coarser and sometimes

calcareous sediments which are possibly of turbidity current origin. The Dove Valley, 9 kms. to the North East has exposed intermittently in the banks of the river, black and dark grey shales of E2a to E2b age.

The P1 to P2 age Mixon limestone with shales Group was sampled to the North and South of the Mixon anticline inlier. The 300 to 400 feet (90 to 120 m) of sediment comprised mainly dark shale and mudstones with significant bands of limestones and sandstones (see map Figure 5.6). At the head of the River Hamps the group outcropped as a series of black, finely bedded shales alternating with sandstone and limestone. The Upper Onecote limestone-shale Group, exposed 500 m North of Onecote Grange, consisted of finely-bedded, black shales interbedded with limestones and thin sandstones.

5.6.4 THE CRACKINGTON FORMATION OF THE CULM MEASURES, SOUTHWEST ENGLAND

The predominantly Namurian age rocks of the Crackington Formation form part of the major Carboniferous synclinorium in Cornwall and Devon and are described in detail in the geological memoirs of the area by Edmonds et al (1968). The rocks of the Lower and Upper Carboniferous are commonly referred to as the Culm Measures after the local name for the sooty black coals which occur within the series. The Culm is divided into lower and upper sections, the lower being equivalent to the Lower Carboniferous and consisting of dark shales, slates, lavas, grits, tuffs and limestones (Dewey, 1948). The Upper Culm is known as the Crackington Measures and consists essentially of shaly turbidite facies with sandstones forming an important element. The Crackington Formation is succeeded via passage beds by the predominant grey-brown sandstones of the Bude Formation which contain subordinate

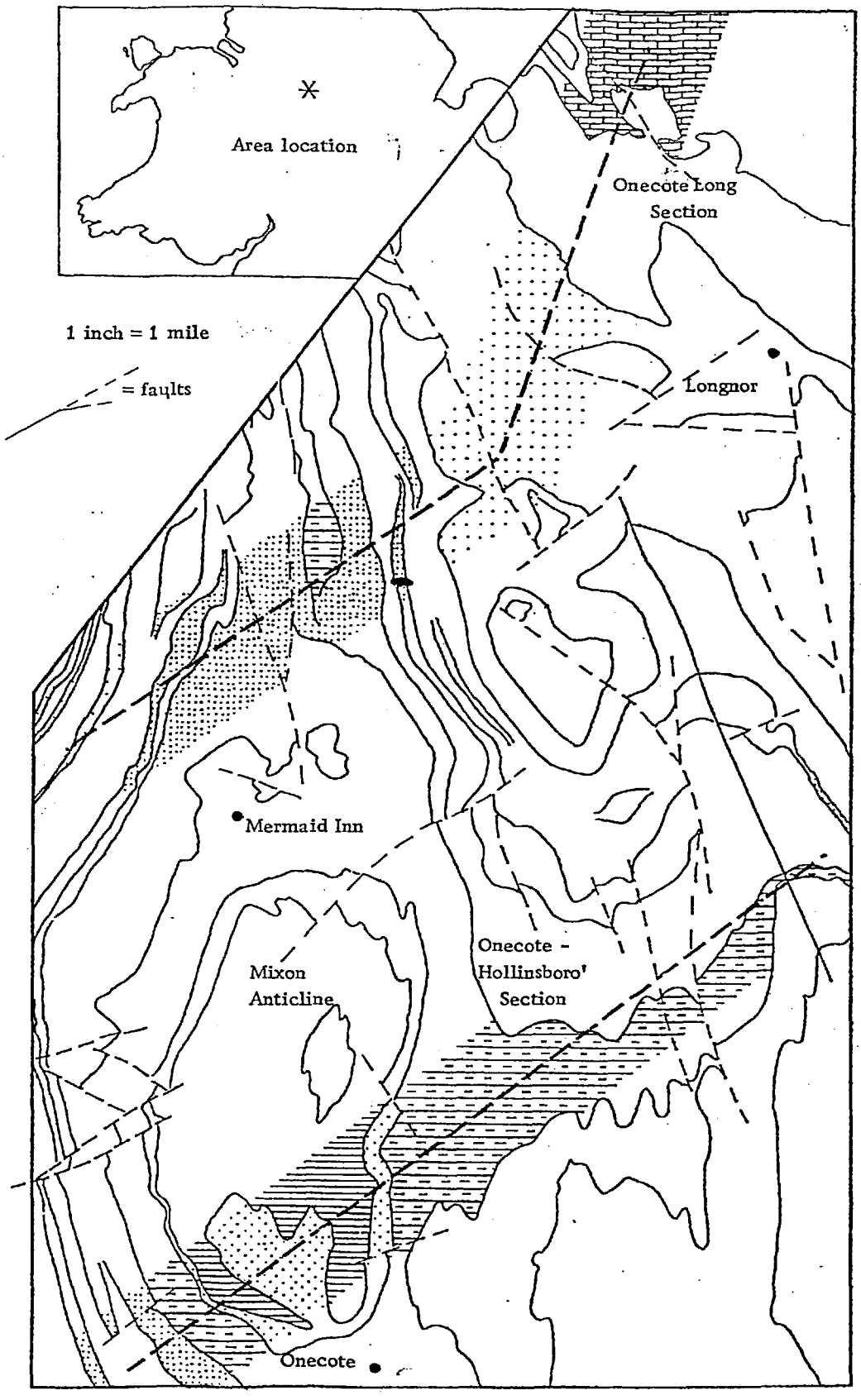


FIG. 5.6 LOCATION OF ONECOTE/DOVE STUDY AREA, GEOLOGY AND SOIL TRAVERSES

grey to black splintery shales. The upward stratigraphic limit of the 2,000 feet (600m) thick Bude Formation has not been adequately defined, nor has the age of the Bideford Formation which includes the Abbotsham and Northam Beds around Bideford. The Bideford Formation has been defined as G2, Westphalian age, representing the translocated lateral equivalent of the lowermost Bude Formation.

The Lower Crackington Measures is equivalent to E2 and H1 in age and is predominantly shaly; the Middle Group, corresponding to the H2 to R1 stages indicates the increase in the activity of turbidity currents with a large increase in sandstone presence; the Upper Group corresponds to those samples taken near Bude (see map figure 5.7) where black shales are subordinate to sandstones and grey shales. The rocks sampled from the Crackington Measures and the succeeding Bude-Bideford Formations (hereafter referred to collectively as the Culm Measures), ranged in lithology from medium-grey mudstone to black, pyritous shales.

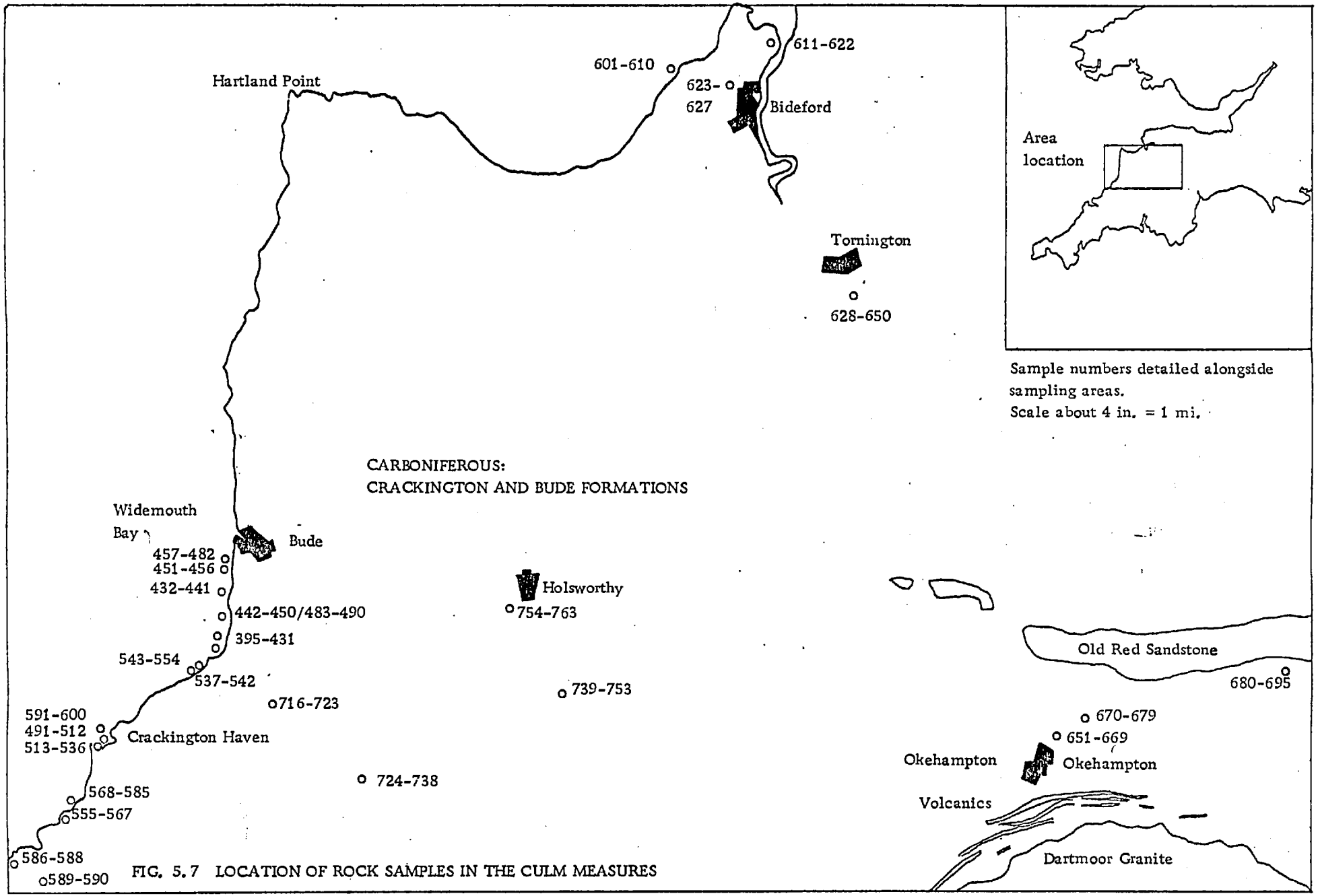


FIG. 5.7 LOCATION OF ROCK SAMPLES IN THE CULM MEASURES

CHAPTER 6

A STUDY OF THE GEOCHEMICAL ENVIRONMENT OF BLACK SHALE DEPOSITION

6.1 INTRODUCTION

The last chapter dealt with the facility of rocks with an organic-rich clay constitution to become enriched in minor elements. This ease of retention appeared to be related directly to the presence of organic matter and indirectly, through the formation of sulphides, as a result of the inauguration of an anaerobic type of depositional environment. However, a study of the presence of cadmium and other minor elements in the stream sediments from areas rich in black shale exposures indicates that enrichment sources are spasmodic in presence and in addition that the facility for enrichment is not a diagnostic feature of the rock type. The first consideration in the study of black shales therefore is to define some scheme whereby an individual shale or set of shales can be regarded as metal enriched or not. The association and dissociation of the metals involved within this scheme with the remaining elements for which the rocks have been analysed can then be interpreted to give an understanding of the geochemical environment of enhancement.

6.2 DEFINITION OF THE METAL ENRICHMENT VALUE

The analysis of black shales by the direct-reading spectrometer revealed in general, wide ranging values for each element within each set of samples, with large variations in median values of element concentrations between them. Direct comparisons of the Grand Medians or Grand Means of this data with the corresponding levels of trace elements in 'average' shales and 'average' black shales is made in Tables 6.1 and 8.3.

TABLE 6.1 TRACE ELEMENTS IN BLACK SHALES FROM FOUR SOURCES

ELEMENT	This Study (1974) Mean, μ	This Study (1974) Median, m	Vine and Tourtelot USA (1970) Median, m	Green (1959) Mean, μ	Turekain and Wedepohl Literature Survey (1961) Mean, μ
Titanium	3700	4105	2000	4400	4600
Manganese	690	600	150	6700	850
Silver	0.24	0.24	1.0	0.9	0.07
Barium	422	275	300	800	580
Beryllium	2.5	2.8	1.0	7.0	3.0
Cobalt	22	40	10	12	19
Chromium	182	200	100	160	90
Copper	69	58	70	38	45
Gallium	22	23	20	40	19
Molybdenum	12	3.6	10	0.74	2.6
Nickel	91	90	50	21	68
Lead	39	28	20	20	20
Scandium	6	8.4	10	10	13
Strontium	101	101	200	299	300
Vanadium	259	235	150	130	130
Zinc	111	95	<300	80	95
Cadmium	4.5	2.4	-	-	-
Carbon organic	-	-	3.2	0.65	-
Carbon mineral	-	-	0.33	1.62	-
Carbon total	5.72	5.7	3.53	2.27	-
Number of samples	530	530		*	*

All values in parts per million except carbon organic, carbon mineral and carbon total which are in percent

* Not quoted in original sources

The great contrast which exists between the data of Green (1959) and that of Turekian and Wedepohl (1961) emphasizes the subjective nature of sample selection. The initial parts of the present study also involved subjective sampling of rocks thought to be black shales and these were identified in the field purely in terms of blackness. In most cases, of course, blackness is indicative of the carbon content of the rock; the generally accepted definition of black shale accepts an average carbon content of more than 2%. However, it will have been seen in Chapter 4, that the 'average' black shale shows a wide range of mineralogy and consideration of the frequency distribution diagrams for the data presented in this chapter indicates just how meaningful the term 'black shale' is, when based on subjective observations (see Figures 6.1-6.2). In an attempt to view the wide-ranging data on more objective lines a method based on the identification of a metal enrichment value, which broadly follows the geochemical study of Vine and Tourtelot (1970) has been adopted.

A shale is defined here as metal rich for any single metal (or sets of metals) if it (or they) is seen to be present in greater amounts than the average of the cumulated 95th percentile values for that metal (or sets of metals) from each of the sets of samples processed. The Metal, or Minimum Enrichment Value is calculated as follows:

$$\lesssim_{i} \; P_{95}/n \qquad i = 1.....n \qquad ..... (1)$$

where P_{95} is the 95th percentile and n = number of samples per set.

$$\lesssim_{j} \lesssim_{i} \; P_{95}/_{ne} \qquad j = 1.....e \qquad ..... (2)$$

where e = number of sets of samples. The averaging of the 95th

All figures in p.p.m. unless stated otherwise.

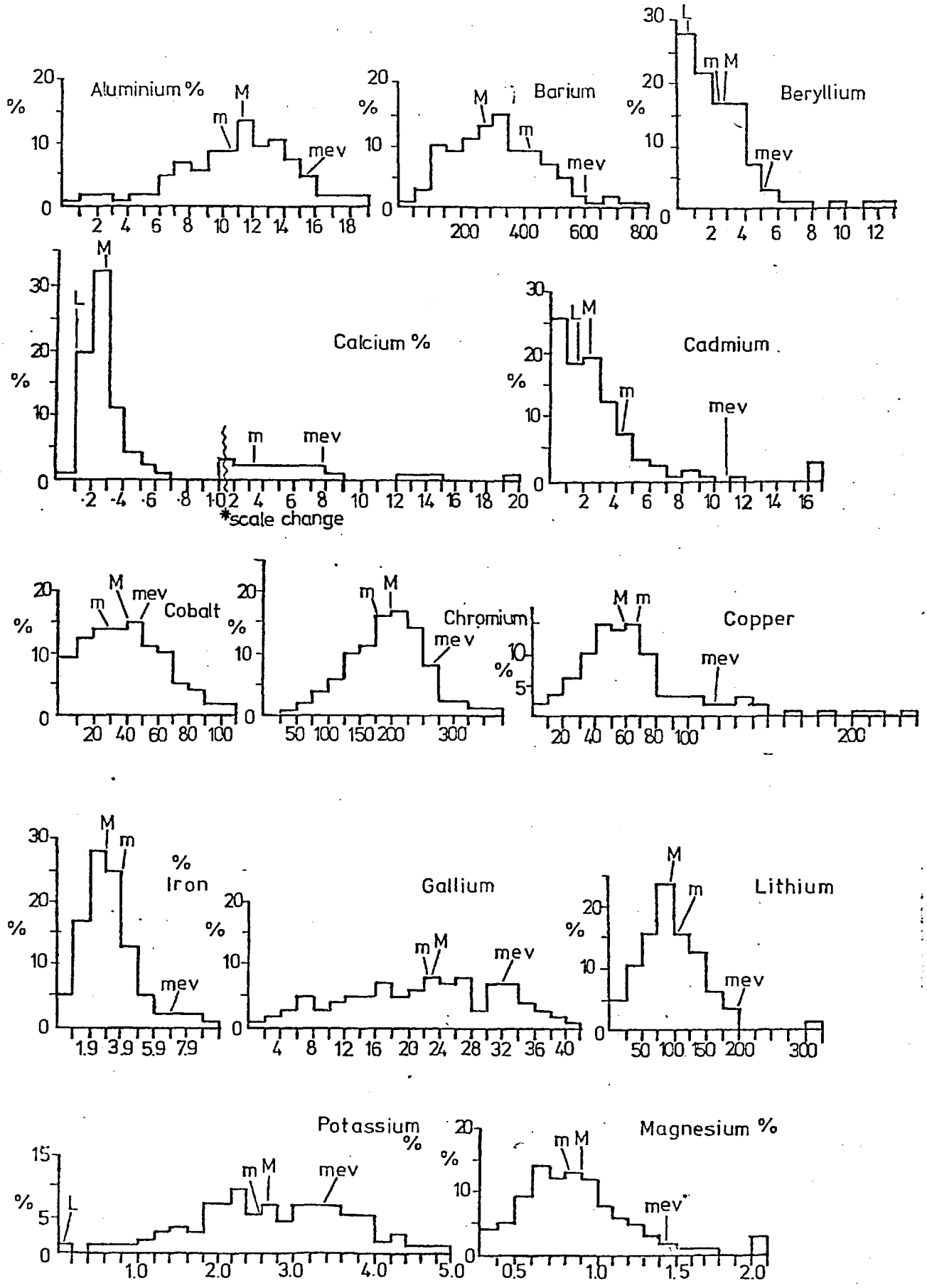


Figure 6.1 Frequency distribution graphs.

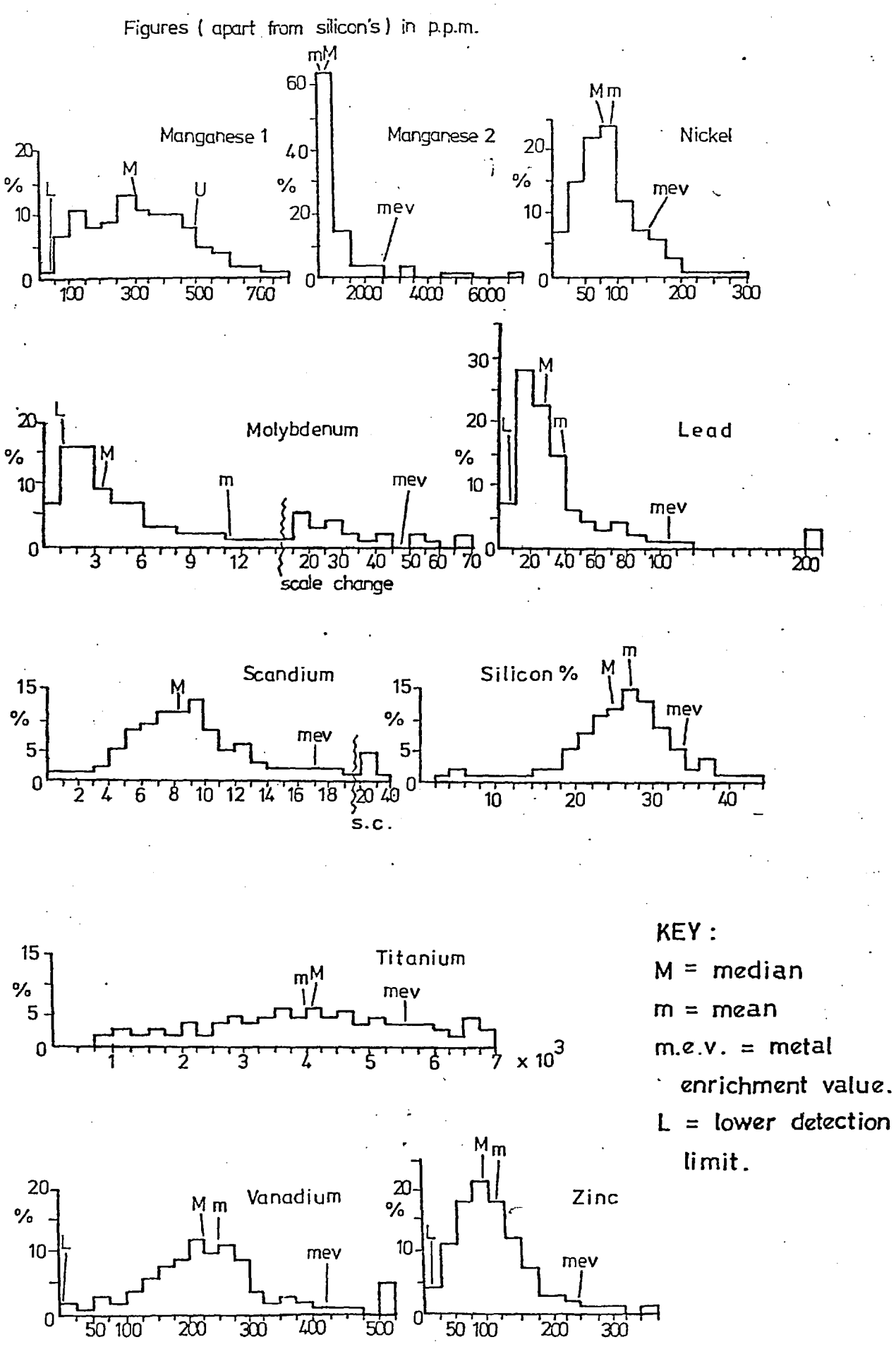


Figure 6.2 Frequency distribution graphs.

percentiles (calculated from equation (1)) in equation (2) minimises any possible bias towards a set of samples with a much larger population.

The number of samples in each set which exceeds the metal-enrichment value for an element is then expressed as a percentage of the total and named the Element Enrichment Index. Direct comparisons of these indic es can subsequently be made in order to discriminate between related sets of samples. The minimum enrichment values for the total data set are summarized in Table 6.2 alongside values obtained by Vine and Tourtelot(1970) using a similar method.

More detailed discussion follows below. The major advantages of the method are firstly, its efficiency in utilising pre-constructed, wide-range histograms and secondly its simplicity and ease of application.

6.3 THE IDENTIFICATION OF METAL-RICH SHALES

6.3.1 GENERAL

The use of the minor element enrichment index to identify metal-rich shales is based on the assumption that a rational (but arbitrarily chosen) index total of 115 or more for the group of 9 minor elements (i.e. copper, lead, zinc, cadmium, vanadium, molybdenum, cobalt; nickel and chromium) indicates an enriched black shale set.

This enables 7 of the 26 sets of samples to be isolated for further study. The enrichment indic es are given in the Figure 6.4 in which individual element percent enrichments are represented for each of the sets of samples. The remaining elements have been divided into two separate groups and are illustrated in Figure 6.3 :-

1 The NON-DETRITAL elements, comprising iron, magnesium, calcium and manganese and

TABLE 6.2 ELEMENT MEANS, 90th PERCENTILES AND MINIMUM ENRICHMENT VALUES FOR THE PRESENT STUDY AND FROM METAL RICH BLACK SHALES OF THE USA (AFTER VINE AND TOURTELOT, 1970)

ELEMENT		PRESENT STUDY			Minimum enrichment value (after Vine & Tourtelot 1970)
		Arithmetic Mean μ	90th Percentile	Minimum Enrichment Value	
Copper		69	94	118	200
Lead		39	92	109	100
Zinc	Minor	111	183	241	1500
Cadmium		4.5	8.7	11.0	N. d.
Vanadium	Element	259	340	429	1000
Molybdenum		12	22	49	200
Cobalt	Group	22	32	39	30
Nickel		91	132	157	300
Chromium		182	268	292	700
Iron %	Non-detrital	3.393	4.54	6.159	N. d.
Magnesium %	Element	0.93	1.258	1.459	N. d.
Calcium %	Group	3.33	3.367	7.759	N. d.
Manganese		698	1074	2584	1000
Barium		22	38	32	50
Titanium		3796	5136	5586	7000
Beryllium	Detrital	3	3	5	3
Strontium		101	169	253	1500
Barium	Element	422	598	600	1000
Potassium %		2.58	3.06	3.4	N. d.
Lithium	Group	105	159	209	N. d.
Aluminium %		10.6	13.7	15.4	N. d.
Scandium		6	14	17	30
Silicon %		26.4	32.1	34.5	N. d.

All values in parts per million except for those which are marked percent

N. d. = not determined

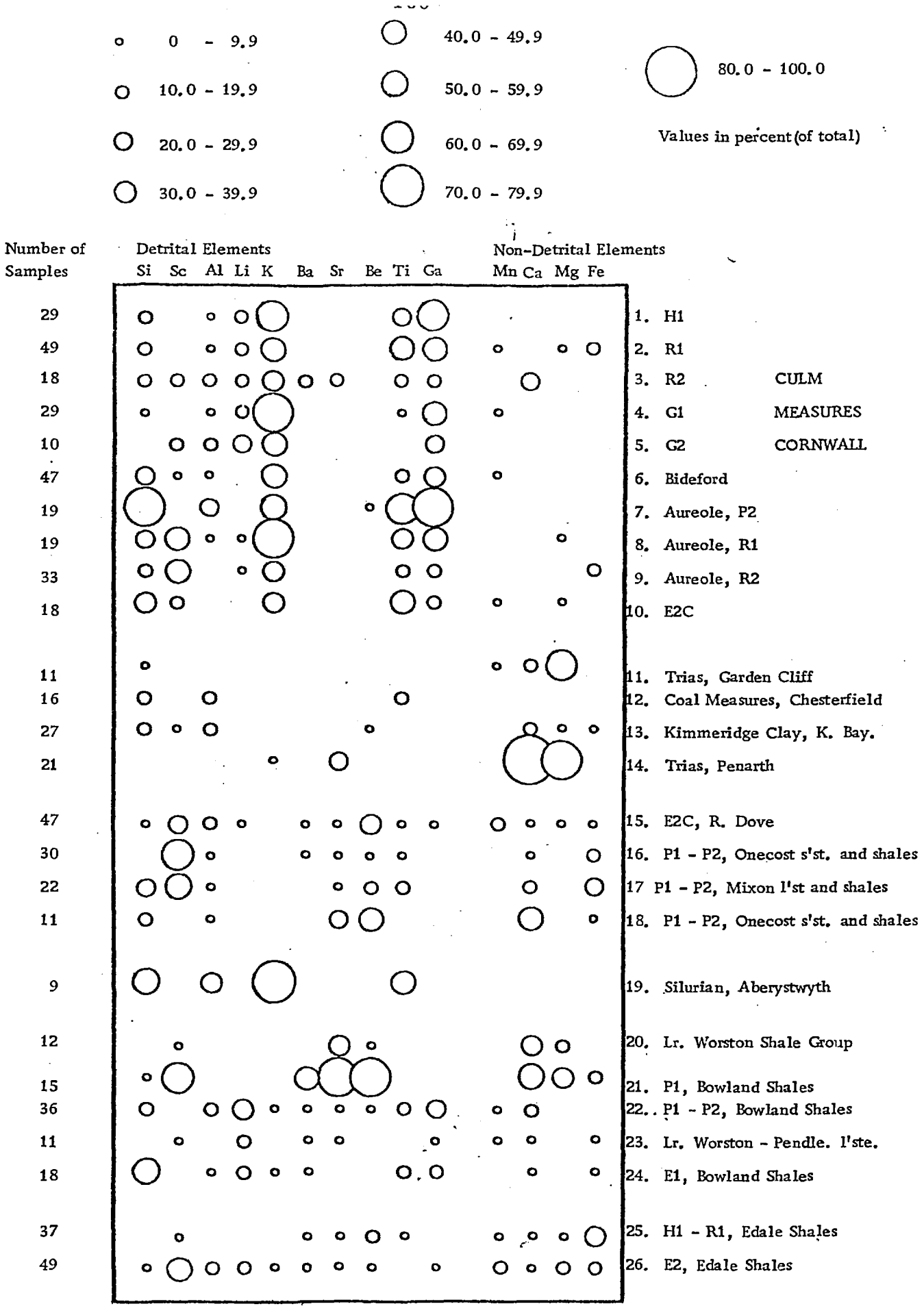


FIG. 6.3 PERCENT OF SAMPLES IN EACH SET OF SAMPLES GREATER THAN THE MINIMUM ENRICHMENT VALUE. DETRITAL AND NON-DETRITAL ELEMENTS.

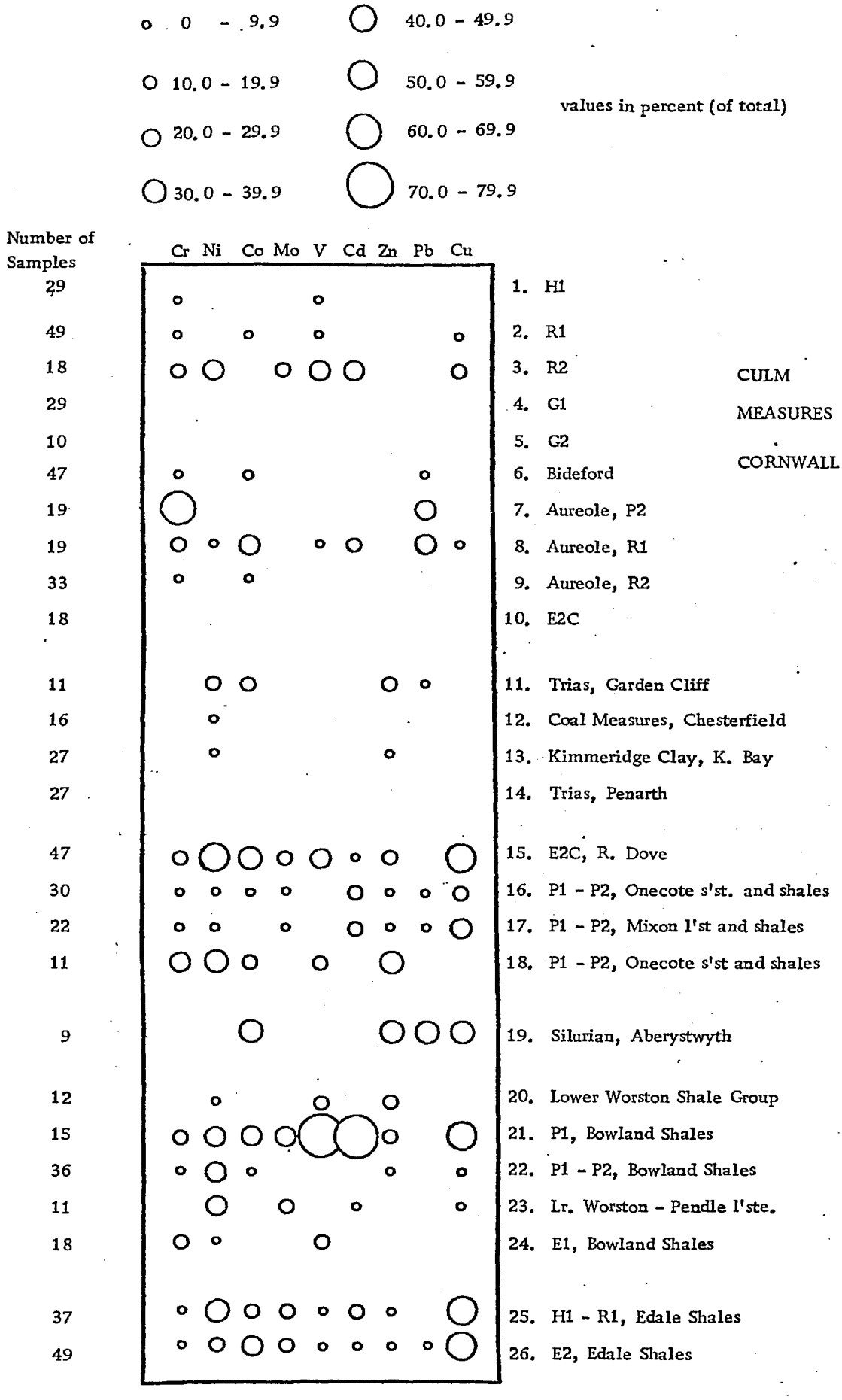


FIG. 6.4 PERCENT OF SAMPLES IN EACH SET OF SAMPLES GREATER THAN THE MINIMUM ENRICHMENT VALUE. MINOR ELEMENTS.

2 The DETRITAL elements, comprising gallium, titanium, potassium, aluminium and silicon and

3 The non-aligned elements beryllium, strontium, barium, lithium, and scandium included for the sake of completeness.

The two sets of samples which are enriched in the minor elements well in excess of the others are Carboniferous in age - the E2 rocks of the River Dove at Onecote, Derbyshire and the P1 rocks from Lower Mearley Clough in Bowland, Lancashire. Those which have no samples enriched in any of the minor elements are from the Bude Formation of G2 (Carboniferous) age from Cornwall and the Rhaetic at Penarth in South Wales.

The two remaining sets of samples representing the Onecote Shale series and both sets from the Edale shales are also enriched in the minor elements, especially copper and nickel. The Silurian black shales from the Rheidol Group of the Aberystwyth area are enriched primarily in titanium but also in copper, lead, zinc and cobalt, however, the smaller number of samples (9) may lead tc a relatively larger error in the enrichment figures owing to the poor analytical precision of some of the elements considered (see Appendix on Analytical Methods).

Three sets of samples from the Culm Measures of Cornwall are enriched, two of these having been collected within four miles of the present-day Culm-Granite contact at Okehampton, near Dartmoor. The rocks within this group are especially enriched in the strongly lithophile elements titanium and chromium, suggesting an unusual detrital provenance.

6.3.2 CADMIUM ENRICHMENT

Only 9 of the 26 sets of samples have specimens which exceed the cadmium enrichment value of 11.0 ppm. Of these, the most cadmium rich is of P1, Carboniferous age, from Bowland where 73% of the 15 specimens exceed this value. Cadmium is enriched in all of the already identified metal-enriched shale groups save for the early P1 - P2 age Onecote sandstone and shale set from the River Hamps area (group number 18), the Silurian shales (group number 19) and the P2 age Culm set from the Granite aureole (group number 7). In addition cadmium is enriched in the minor-element poor black shales from the Lower Worston-Pendleside limestone and shales group of West Mearley Clough, Lancashire (group number 23) and the P1 - P2 age Onecote sandstones and shales of Onecote Grange, Derbyshire (group number 16).

6.4 CLASSIFICATION OF SETS OF SAMPLES ACCORDING TO GEOCHEMICAL ASSOCIATIONS

A: THE USE OF ENRICHMENT INDIC ES FOR THREE GROUPS OF ROCK-FORMING COMPONENTS

6.4.1 INTRODUCTION

The criterion used in order to differentiate between the detrital, non-detrital and minor element associations in any of the sets of samples is the end result of the summation of the respective percentage enrichments of a series of elements which are taken to be representative of each of the three main rock-forming components: the detrital group, potassium, aluminium, titanium, silicon and gallium; the non-detrital group iron, calcium, magnesium and manganese; and the minor element group cadmium, zinc, molybdenum, vanadium, lead, cobalt, nickel and chromium. In order to normalise these enrichment indic es

the sums for each of the component groups are divided by the number of elements which constitute that group. Titanium and manganese have been omitted from the minor element group as they are included in the detrital and non-detrital groups, respectively. The 'significant' enrichment index level for the minor element group is therefore proportionately reduced from 115 to 86.

Each of the sample groups can now be categorised according to which of the three rock-forming components, or combination of components, dominates. Thus, for example, in Table 6.3 Group IV 'Areas predominantly enriched in non-detrital and minor elements' almost exclusively contains the metal-enhanced Central Province rocks. The categorisation is visually presented in the simplified triangular diagram Figure 6.5A which represents the repercentaged enrichment percentages of Table 6.3 plotted on a diagram with apexes 100% minor elements, 100% non detrital elements and 100% detrital elements. The regional location of the plots is schematically represented in Figure 6.5B. The original triangular diagram, with plotted group numbers, Figure 6.6 has been constructed using the enrichment percentage figures of Table 6.3 following an equal weighing technique whereby each group percentage is divided through by the maximum value in each component.

6.4.2 AREAS PREDOMINANTLY ENRICHED IN DETRITAL ELEMENTS

All the sets of samples enriched in the detrital elements are from the Upper Culm measures of Cornwall. Over half of the specimens in all of the Culm groups have potassium values exceeding the minimum enrichment value of 3.4%. The H1 and R1 groups also have small enrichments in vanadium and chromium (see Figure 6.4). In Figure 6.5.1 all the group 1 sets of samples plot together in the '100% detrital' corner of the diagram. The distinctive deficiency of minor elements in

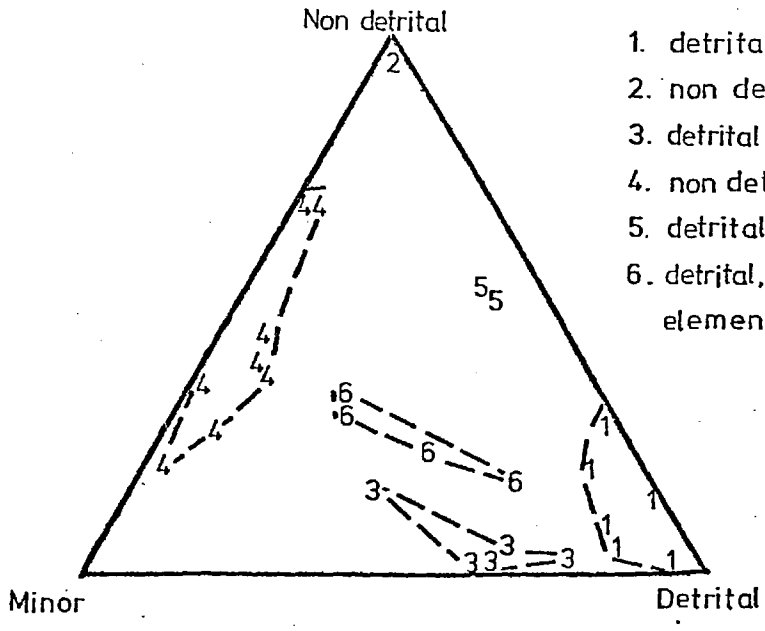
TABLE 6.3 THE GROUPING OF SETS OF SAMPLES INTO ASSOCIATION CATEGORIES USING THE ENRICHMENT INDEX

Association category	Geographical and Geological Location of sets of samples	Enrichment Index 1 Detrital	2 Non Detrital	3 Minor Elements	Number of species per group	Group identification number
I	Areas predominantly enriched in detrital elements					
	Cornwall E2C	127	12	0	10	10
	Cornwall H1	184	0	10	29	1
	Cornwall R1	143	20	18	49	2
	Cornwall G1	138	3	0	29	4
	Cornwall G2 Bude Formation	60	0	0	10	5
	Cornwall Bideford Formation	82	2	13	47	6
II	Areas Predominantly enriched in non detrital elements					
	Trias Penearth	5	171	0	21	14
III	Areas predominantly enriched in detrital and minor elements					
	Cornwall R2	95	22	116	18	3
	Cornwall Granite P2	300	0	84	19	7
	Cornwall Granite R1	200	5	94	19	8
	Coal Measures D5	32	0	19	16	12
	Silurian, Aberystwyth	222	0	132	9	19
IV	Areas predominantly enriched in non-detrital and minor elements					
	Bowland 4 Worston Shales	0	50	42	12	20
	Bowland 4 Worston - Pendleside, limestone	9	27	63	11	23
	Bowland P1	7	99	306	15	21
	Onecote E2C Dove	27	53	223	47	15
	Onecote P1 - P2 shales mermaid	27	54	135	11	18
	Edale E1 R. NOE	18	62	119	49	26
	Edale H1 - R1 village	5	45	155	37	25
	Trias Garden Cliff	9	91	63	11	11
V	Areas predominantly enriched in detrital and non detrital elements					
	Cornwall, Granite R2	81	57	18	33	9
	Kimmeridge Clay, Jurasic	34	25	8	27	13
VI	Areas enriched in detrital and non detrital and minor elements					
	Onecote Grange P1 - P2	45	27	74	30	16
	Onecote Hamps P 1 - P2 Mixon	50	37	87	22	17
	Bowland E1 Harrop	86	12	35	18	24
	Bowland P1 - P2 Mearley	69	19	51	36	22

1, DETRITAL GROUP comprises the elements potassium, aluminium, titanium, silicon, gallium

2, NON DETRITAL GROUP comprises the elements calcium, iron, magnesium, manganese

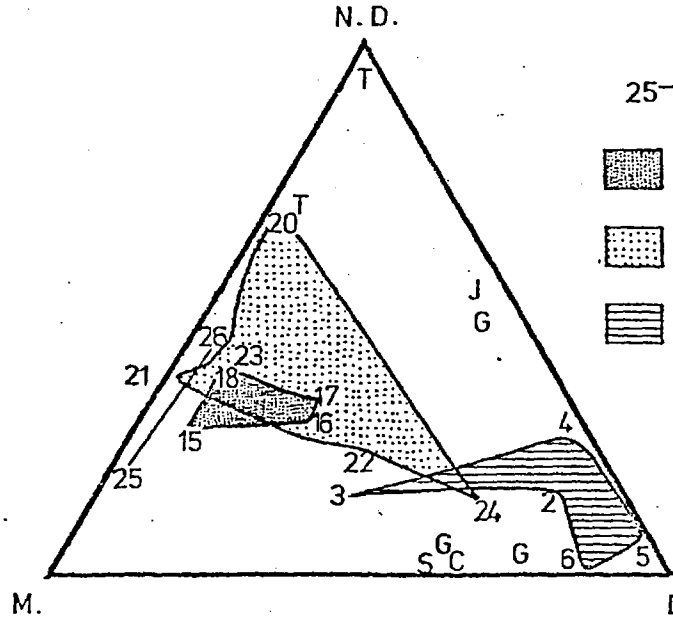
3, MINOR ELEMENT GROUP comprises the elements cadmium, zinc, molybdenum, vanadium, copper, lead, cobalt, nickel, chromium.



KEY: Areas enriched in :

1. detrital elements.
2. non detrital elements.
3. detrital and minor elements.
4. non detrital / minor els.
5. detrital / non detrital els.
6. detrital, non detrital and minor elements.

Figure 6.5.1 Clustering of sets according to enrichment type.



25——26 Eddle Shales

Visean : Onecote Shales

Bowland Shales

Culm Measures

T Trias

J Jurassic

G Aureole Culm

C Coal Measures

S Silurian

Figure 6.5.2 Clustering of sets according to geological origin.

the Culm rocks of Cornwall may have been caused by the late-Carboniferous age thermal metamorphism. Evidence will be presented in the following Chapter 8, which argues for the stoichiometric weakening of carbon-metal bonds and the possible mobilisation of minor elements following the reconstitution of the clays within the rocks to micas. A strong residual correlation however, between vanadium and carbon implies that some of the early-history associations, possibly biogenic in origin, may have remained intact.

6.4.3 AREAS PREDOMINANTLY ENRICHED IN NON-DETRITAL ELEMENTS

Only the Rhaetic beds of the Trias from South Wales (group number 14) are categorised under this sub-heading. In direct contrast to the other groups, the Rhaetic set of samples is enriched in calcium (100% of specimens), magnesium (71% of specimens) and strontium (29% of specimens). The rocks have no minor element enriched and the remaining enhancement concerns one from the compliment of twenty-one specimens which is enriched in potassium. Resultantly the group plots in isolation very close to the 100% non-detrital elements apex in the triangular diagram (Figures 6.5 to 6.6).

6.4.4 AREAS WITH COMPONENT COMBINATION ENRICHMENTS

None of these sets of samples are enriched solely in the minor elements, although all show some measure of enrichment.

The most common association is a combination of minor element and non-detrital element enrichment. These plots are represented as group 4 in Figure 6.5.1 scattered as a 'low detrital' component cluster around the 50-50% minor-non detrital component axis.

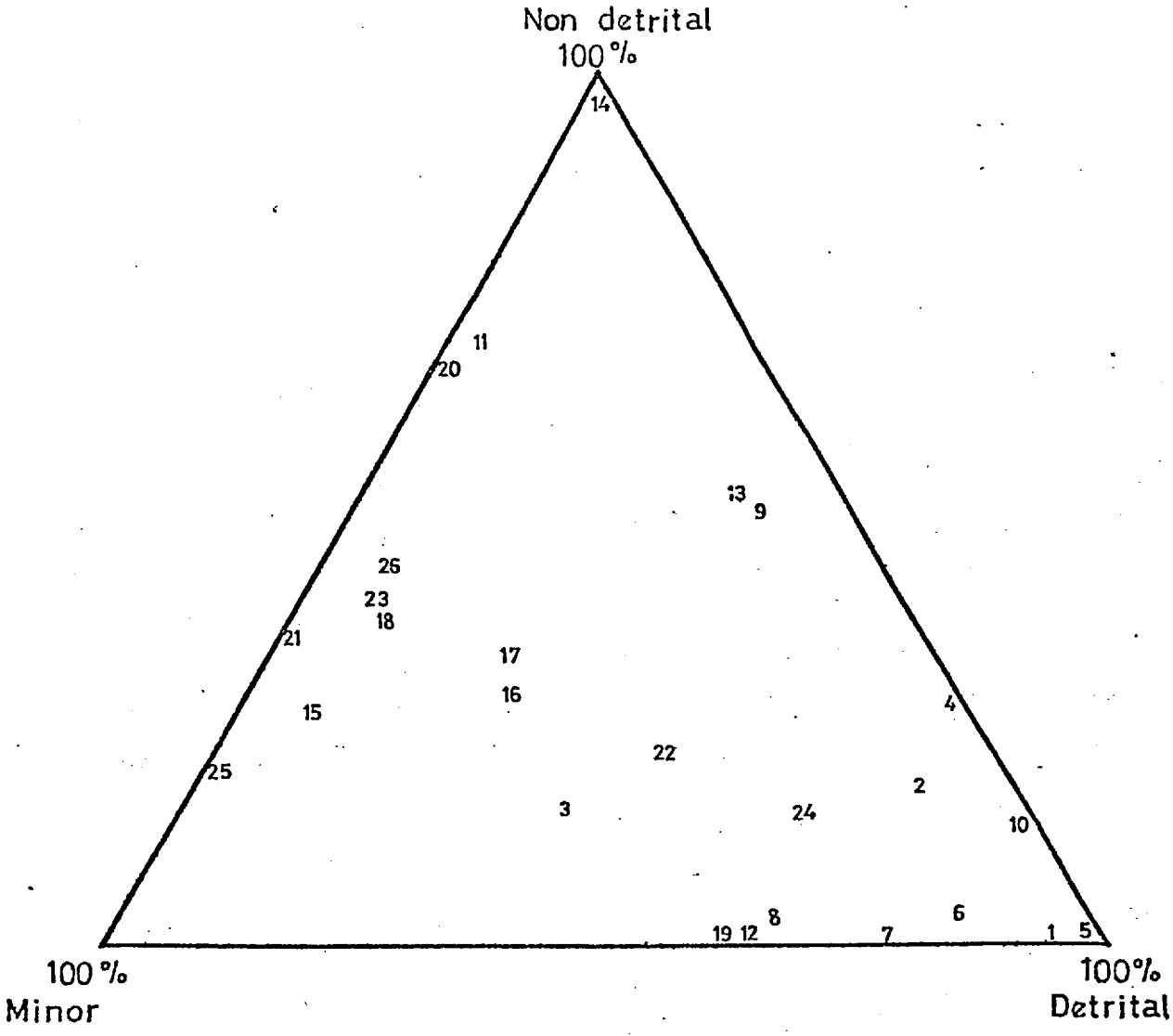


Figure 6.6 Triangulation plot of metal enrichment values for all sets of samples (see identification key, Table 6.4).

TABLE 6.4 IDENTIFICATION KEY FOR METAL ENRICHMENT VALUE GROUP NUMBERS AS SHOWN IN FIGURE 6.6

Location	Geological Age	Group Numbers (metal enrichment values)
1. Culm Measures, Cornwall	E2C	10
	H1	1
	R1	2
	R2	3
	G1	4
	G2	5
	Bideford Shales	6
	Granite Aureole, P2	7
	Granite Aureole R1	8
	Granite Aureole R2	9
2. Bowland, Lancashire	Lower Worston Shales	20
	Lower Worston Shales plus - Pendleside Limestone	23
	P1	21
	P1 - P2 Mearley Clough	22
	E1	24
3. Edale Derbyshire	River Noe, E2	26
	Village, H + R	25
4. Onecote Derbyshire	Dove, E2	15
	Mixon Basal, P1 - P2 (Hamps)	18
	Mixon Dip, P1 - P2 (Grange)	17
	Onecote Shales, P1 - P2 (Mermaid)	16
5. Others		
Garden Cliff, Bristol	Trias	11
Chesterfield	Coal Measures	12
Penarth, S. Wales	Trias	14
Kimmeridge Bay	Kimmeridge Clay, Jurassic	13
Aberystwyth	Valentian, Silurian	19

Location Groups 1 to 4 are all CARBONIFEROUS in age and 'young' stratigraphically from bottom to top in each group.

Of the eleven sets of samples collected of Visean age from the Central Province of England (i. e. Edale, Bowland and Onecote), seven are contained within this group and range petrographically from limestone shales to carbonaceous shales.

The remaining four groups from the Central Province have specimens enriched in all three component groups and these consequentially plot near the centre of the triangular diagram (see Figure 6.5.1). The later stage Bowland groups have an increased presence of detrital enrichment which heralds the appearance of the Pendle Grit (E1 age, group number 24). This trend is diagramatically represented in Figure 6.7.1 and in the triangular diagram Figure 6.6. In the former diagram, the use of the rationalised enrichment index (where each component is represented by 5 variables) shows that a decrease in the detrital index after Lower Worston shales - Pendleside limestone-shale times, (group number 23) is reflected in sharp increases in the non-detrital and the minor-element indicies. Conversely, after P1 deposition, and after minor element enrichment had reached its zenith (group number 22), the strong rise in the detrital index resulted in sharp decreases in the other two indicies. This trend of increasing detrital enrichment continues as E1 deposition commences (group number 24) and results in ever decreasing non-detrital and minor-element enrichment indicies.

In the latter diagram (Figure 6.6) the repercentaged plots of the Bowland sequence illustrate the same evolutionary trend. At the close of P1 deposition (group number 21), detrital enrichment amongst the rock groups is poor, whilst a strong increase in the percentage of minor element enrichments amongst group specimens up to that time produced a progressive decrease in the presence of non-detrital element enrichments. The younging of the rocks through P2 to E1 times

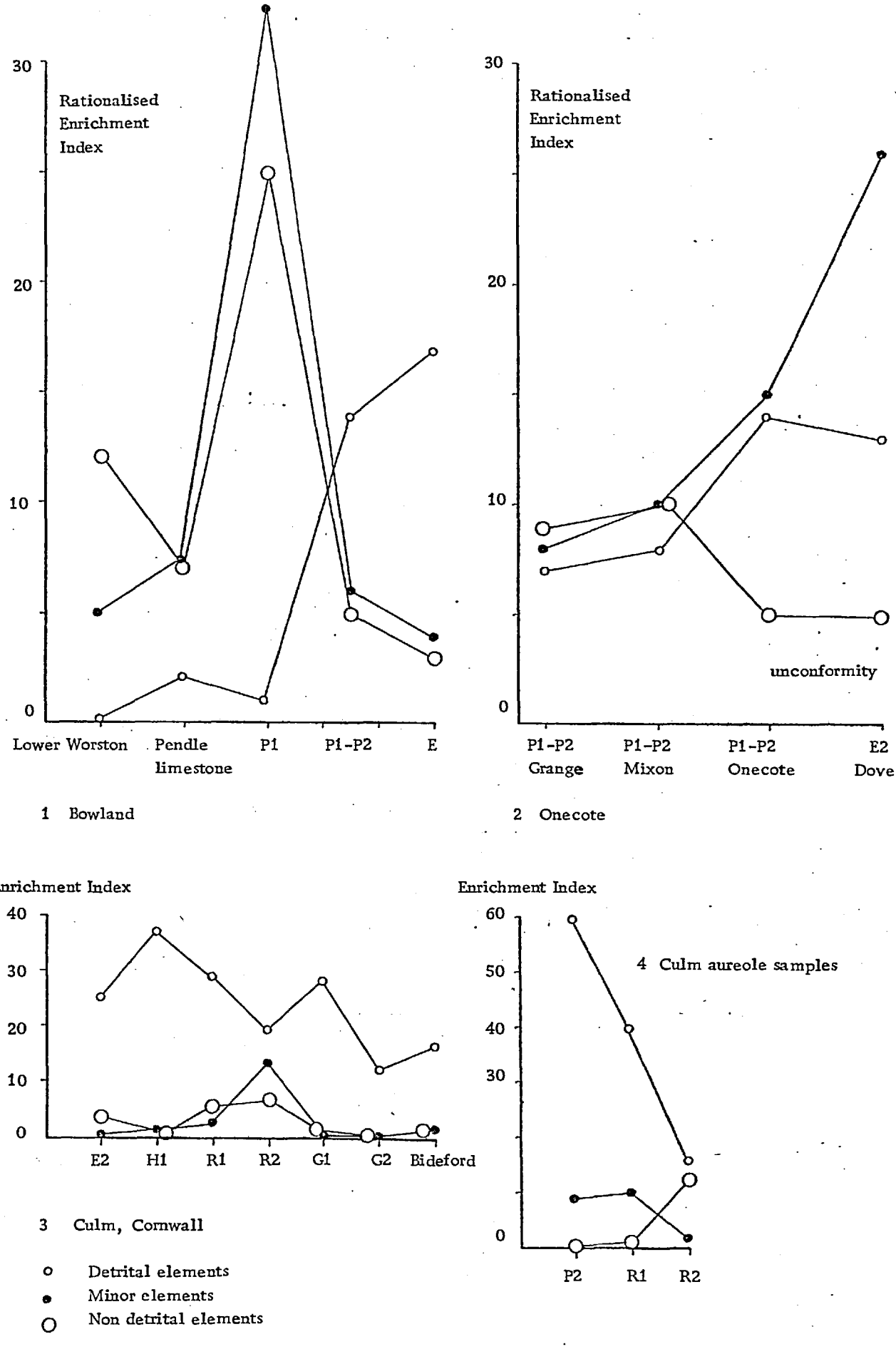


FIG. 6.7 ENRICHMENT INDICES FOR ELEMENT GROUPS IN VISEAN BLACK SHALES

(group numbers 22, 24) is characterized by decreases in both non-detrital and minor element domination and consequently a rapid acceleration towards conditions which typify grit accumulation. Palaeogeographically this trend demonstrates that as the influx of detrital elements starts to dominate, the resultant disturbance of the quiet conditions of the black, calcareous muds, destroys the conditions of enhancement, vital for minor element presence.

In comparison to the strong evolution apparent in the rocks of Bowland, those of the Onecote area are on average enriched in the minor and non-detrital elements. All 4 sets of samples cluster around the 50% minor-element and 20% detrital-element enrichment area in the triangular enrichment graph (Figure 6.5.2). In the plot of the rationalised enrichment indic es (Figure 6.7) the rise in the detrital and minor element indic es results in a decline in the presence of non-detrital elements. The most notable feature of the Onecote rocks is a continual rise in the minor element index and this is also shown in triangular diagram Figure 6.7 where the minor element increase to group number 15 (E2, Dove) is accompanied by declines in both detrital and non-detrital enrichments. The lack of continuity to E2 times between the three component groups is notably different from that which occurred in the Bowland sequence. This may be explained by the presence of an unconformable contact between the Dove and the Onecote shales. The interruption of progressively more reducing black mud deposition may have prevented the subsequent evolution of a stable basin environment which (based on the Bowland model) would be poor in detrital elements and rich in both minor and non-detrital elements. As it is, the rocks of E2 (Dove) age (group number 15) are not enriched in the non-detrital elements, despite the presence of very large minor element enrichments, and hence differ from the rocks of the Bowland area.

As only two sets of samples have been collected from the third Central Province area at Edale, no such trends can be established. It is clear, however, that the younger rocks of H-R1 age (group number 25) are exceptionally highly enriched in minor elements in comparison with the well-enriched older rocks of E2 age (group number 26). The older rocks have a considerably greater percentage enrichment in the non-detrital elements and slightly greater enrichment in the conspicuously near-absent detrital elements (See Figure 6.6).

In conclusion, it can be said that of the three areas in the same palaeogeographical basin, the Bowland rocks achieved full reducing potential relatively early in their collective evolutionary history. Whilst the Bowland rocks were becoming increasingly dominated by the detrital elements, both the Edale and the Onecote sets of samples were progressing towards their peak of reducing power (and corresponding minor element retention capacity). Comparing the E2 age rock groups of Edale and Onecote, the latter set of samples appears to be 'maturing' to maximum minor-element retention capacity most rapidly. Extrapolation of this trend suggests that re-transgression of detrital enriched grits would occur in this area at an earlier date. This conclusion is borne out in the comparitive vertical sections of the three areas (see Figure 5.2 Chapter 5).

The Culm of Cornwall has already been considered above, but some Culm groups occur in two of the other categories. Firstly, that in which the detrital and minor-elements are enriched. In this are included two of the three sets of samples collected within the granite aureole near Okehampton (group numbers 7, 8), and that of R2 age from Crackington Haven (group number 3). The rocks of the latter are noticeably blacker and more pyrite-rich than is usual in the Culm. This is reflected by an enrichment in minor elements and a deficiency in detrital elements, in contrast to the rest of the Culm. The rationalised enrichment indic es (expressed in the order detrital, non-detrital, minor elements) are 19:6:3 for set R2 (group number 3), 60:0:9 for the aureole

group P2 (group number 7) and 40:1:10 for the aureole group R1 (group number 8). These can be compared with the average Culm indic es (group number 1, Figure 6.5.1) of 25:1:1.

The two sets of samples from the granite aureole area are highly enriched in potassium, titanium and silicon and moderately enriched in the minor elements cobalt, lead and chromium. The presence of potassium metasomatism is manifested as biotite introduction in parts of the aureole whilst in addition the formation of tourmaline by the presence of boron metasomatism (Edmonds et al, 1968) is the only mineralogical evidence known regarding the major addition of chemical substances by the intrusion of the granite.

The youngest, R2 set of samples (group number 9) collected near to Okehampton is the poorest of all in minor element content and has the highest non-detrital element content of the Culm samples. With rationalised enrichment indic es (detrital, non-detrital, minors) of 16:12:2 this suggests that there has been no addition of major detrital elements to these rocks. The lack of trace metal enrichment contrasts with the set of samples (group number 3, also of R2 age collected at Crackington Haven, 40 kilometers distant, suggests that either the original element enhancement within the basin did not extend laterally by as great a distance or that some phenomenon of trace element loss under thermal influence, took place. This may be related to the formation of thin veins of pyrite, chalcopyrite and pyrrhotite known within the Culm near the aureole.

The rationalised enrichment variation for the coastal and near-coastal Culm (Figure 6.7.3) indicates that there is a general trend with time towards the detrital-poor element content of an average shale. At all times the non-detrital and minor element enrichment indic es are low, increasing only in R2 times. The trend is also displayed on the

triangular graph Figure 6.6 where the only gross departure from a spiral trend near the 100% detrital enrichment apex is during R2 times. The isolation of the sets of samples from the granite aureole shales can be appreciated in Figure 6.5.B. The marked contrast, which is also displayed in the rationalised enrichment index graph Figure 6.7.4 is undoubtedly related to the suggestion that these samples have come under the influence of metasomatic activity.

6.5 B: CORRELATION-FACTOR INDEX DIAGRAMS

6.5.1 INTRODUCTION AND INDEX CALCULATION

The minimum enrichment values are based on an arbitrarily chosen index. These values have indicated, making a broad generalisation, that as the detrital element enrichment index increases, the indic es for enrichment within the non-detrital and minor-element groups falls. However, when (for example) the minor element enrichment index rises it is clear that not all the elements in the category record an increased enrichment. The metal-poor P1-P2 Mixon limestone and shale group of Onecote (group number 16) has 10 per cent of its 30 specimens enriched in cadmium, whereas the highly metal-rich E2C Dove shale has only 6 per cent of its 47 specimens with cadmium levels above the minimum enrichment value. Therefore a selective enrichment in cadmium would appear to have taken place in the former set of specimens in P1-P2 times which is not apparent in terms of the metal enrichment index. Furthermore, such a selective enrichment would imbalance the correlation which would normally exist between more average levels of this element and any minor element normally related to it. To offset correlation imbalances which occur through selective enrichment the correlation factor index is calculated. This index is not a measure of strict element presence but is a measure of inter-element-stability or,

expected normality. It will be seen that, in the case of the minor-element category the peak of 'normality' is attained, not when minor element enrichment is most marked in the Bowland Shale sequence in P1 times (group number 21), but after this in P1-P2 times (group number 22).

The index is calculated using the following criteria;

$$\text{Index} = 1/6 \lesssim (rij)^2$$

- where rij is the correlation coefficient for each pair of variables.

Each index is calculated using the correlation coefficients between every element in the three basic categories which are made up as follows:

1 Detrital elements: gallium, titanium, potassium, aluminium, silicon.

2 Minor elements: Copper, lead, zinc, cadmium, vanadium, molybdenum, cobalt, nickel, chromium.

3 Non-detrital elements: iron, magnesium, manganese, calcium.

The final indic es are all rationalised in order to make comparison easier; thus using five variables as the norm, the category one index remains unchanged, that for category two is multiplied by a factor of 5/9 and that for category three is multiplied by a factor 5/4.

6.5.2 CENTRAL PROVINCE INDIC ES

6.5.2.1 Bowland Shale Group

The indic es for the Bowland sets of samples are graphed in Figure 6.8.2. Two things are immediately apparent; firstly, the overall domination which the strongly correlating detrital elements have at all times and secondly, the almost total non-existence of all but a token

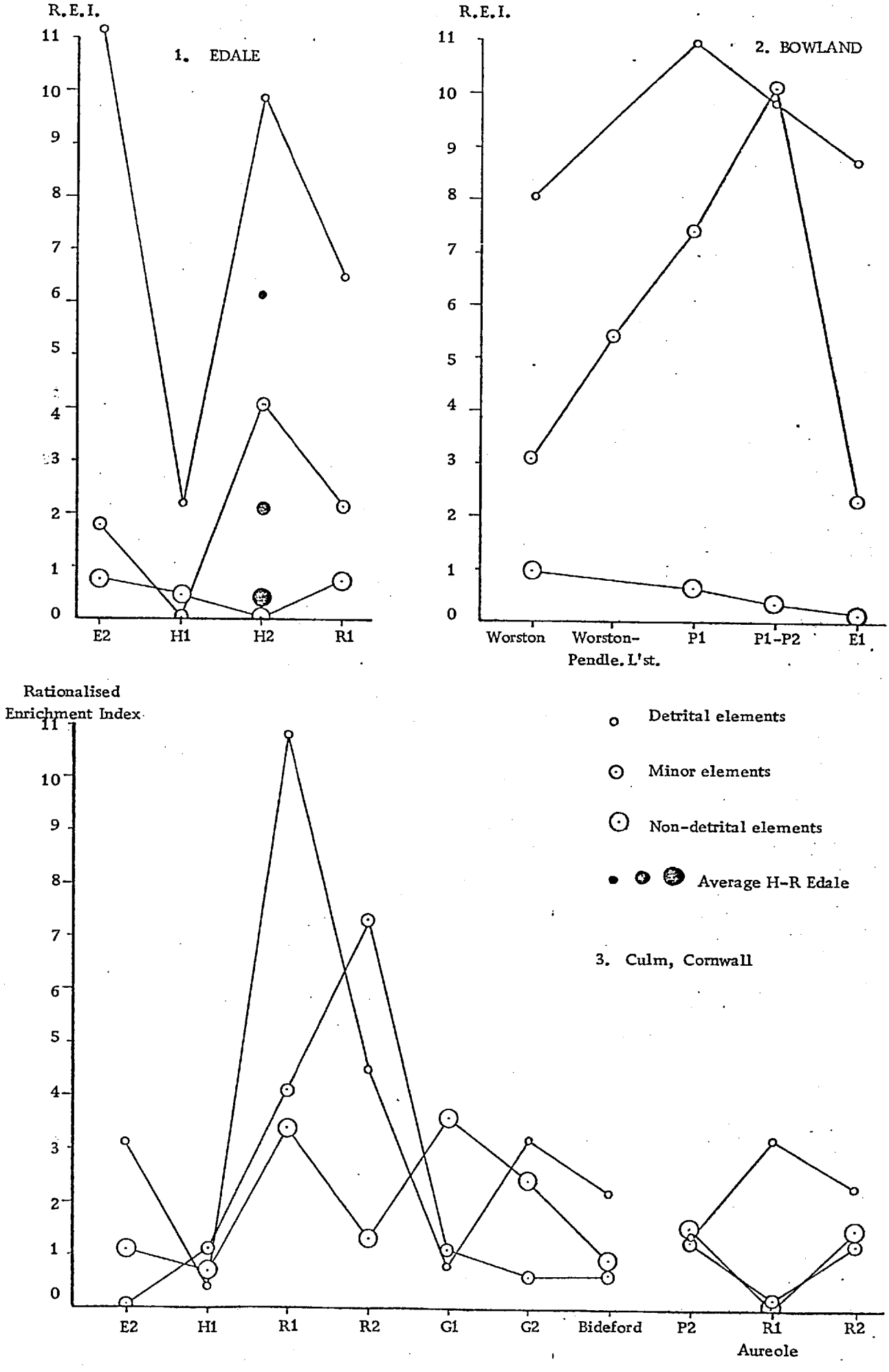


FIG. 6.8 CORRELATION INDEX DIAGRAMS FOR BLACK SHALES

correlation between the non-detrital group elements. This latter group is the only one of the three which actually varies in the same way as that for the enrichment evolution in Figure 6.7. The greatest degree of inter-element normality for the detrital elements shown by the index is not in E1 times (group number 24) when the enrichment is most marked, but in P1 (group number 21). Likewise with the minor element group, where normality is achieved in P1 - P2 times (group number 22) following the P1 period when enrichment is most marked.

The excessive changes in relative enrichments which occur between P1 and P1-P2 times i.e. a 50 per cent increase in detrital enrichment, a 30 per cent minor-element decrease and a 14 per cent non-detrital element decrease, does not reflect a very great change in the correlation index. This suggests a marked series of selective enrichments or depletions in one or more elements in some of the sets of samples (see Figures 6.3-4). This would have the effect of lowering the rationalised correlation factor index for those groups which are imbalanced in P1-P2 and E1 times (group numbers 22 and 24 respectively).

The low minor-element indic es which tend to dominate the minor element index graph are indicative of poor correlations amongst the minor elements and this is caused by the absence of a common linking agent such as excess organic matter presence or the presence of precipitating sulphides. The steady increase in the index through group 23 and 21 to a peak at group 22 (the P1-P2 set of samples) indicates the growing presence of a linking agent such as carbon and this has strong physicochemical connotations.

6.5.2.2 Edale Shale Group

The triangular diagram, Figure 6.7 shows only two plots for the Edale sets of samples, the youngest representing a geological period incorporating rocks of H1, H2 and R1 age.

The correlation indic es averaged for the three sets H1, H2 and R2, comprising group 25, when compared with the indic es for the older E2 rocks (group 26) broadly display the same trends as those identified in the metal enrichment index diagram (Figure 6.8.1) i.e. a decrease in the non-detrital and detrital element enrichment indicies is mirrored by an increase in the minor element enrichment index. However the correlation diagram illustrates scales of change which are by no means similar, the most radical difference being shown by the detrital index which plunges sharply downward. Both sets of samples have unusually low detrital element indic es and it is the especially strong depletion of these elements in the younger group (River Noe, group 25) which has changed the inter-element correlations.

In greater detail, the splitting of group 25 into three separate components in the correlation-factor index graph draws attention to an unusual agreement amongst minor element increases and decreases and those of the detrital elements. This indicates that conditions which had been better for correlation improvement amongst the detrital elements also caused improvement in overall minor-element correlations. A link between the presence of the detrital clay minerals and minor element presence seems possible.

6.5.2.3 Onecote Shale Group

Of the four groups which were considered in section 6.4 as Onecote shales only three represent the shales in this section. Correlation factor indicies for the non-detrital and detrital element categories are not available for the younger set of samples of E2 age from the Dove shales owing to a lack of available analyses.

In the triangular diagram (Figure 6.6) the shales occupy a relatively small minor-element rich area which is slightly more non-detrital than detrital in character.

The evolutionary trend through the P1-P2 age Mixon limestones and shales to the E2 rocks of the Dove shales is marked by a progressive decrease in detrital element enrichment and a progressive increase in minor element enrichment. Little change occurs between the groups 16 and 17 in the Figure 6. , although the reaction to this slight non-detrital enrichment at the expense of the two remaining element categories is very marked in the correlation-factor indices.
Small decreases in the indic es of the non-detrital and minor element groups contrasts with a very large increase in the detrital element index. Thus whilst the former two element categories behave as to indicate a certain deterioration in the conditions of normality, the latter achieves an index high which exceeds any recorded in the present studies. The only differences between the selective enrichments of this group (number 17) and that preceeding it (group number 16) is that whilst the aluminium enrichment of this group rises slightly the silicon content falls slightly. The total aluminium: silicon ratio is conspicuously lower for the high indexed group than for the other and this implies a finer-grained and hence more-balanced sediment.

The large increase in the minor-element correlation index in the youngest group (number 15) agrees well with the trend displayed for the same group on the triangular diagram. A certain inter minor element balance thus accompanies the metal enrichment.

6.5.2.4 Culm Measures, Cornwall

The rocks are all highly enriched in the detrital elements, save one non-aureole set of samples, having more than 75 per cent of samples enriched. The fourth youngest sequence, R2, is comparitively minor element rich and this is demonstrated by its position (group number 3), in some isolation to the other groups of the Culm sequence in the triangular diagram (Figure 6.6). The succeeding set of samples of G1 age (group

number 4) are the most non-detrital element enriched of the sequence whilst the succeeding samples again are enriched solely in the detrital elements (i. e. G2, group number 5).

The correlation factor index diagram, Figure 6. 8. 3 confirms the enrichment patterns for those elements in the minor and the non-detrital categories. The correlation index for the former peaks clearly with the R2 samples, moreover indicating the trend towards the peak with a moderately high correlation index in the preceeding R1 set of samples. This set is sufficiently enriched in the minor elements to isolate it from the bulk of the Culm sets of samples. It is also distinguished by virtue of containing some non-detrital element enrichments, and this corresponds with one of the two correlation index peaks. The second non-detrital correlation index peak corresponds with the set of samples with greatest non-detrital element enrichment, that of G1 age (group number 4). In conclusion, it appears that enrichment in any element within these groups is not selective. Aluminium: silicon ratios are always low and fluctuate only marginally (see Table 10. 1) and detrital enrichment is clearly dominant. The minor and non-detrital elements are supplied in a chemical form which is in a state of equilibrium with the environment and this must have been attained during the long time interval between weathering and final deposition.

Lack of agreement between the time of detrital element enrichment and that when the correlation index reached a peak is due either to selective enrichment or mobilisation of major and minor elements as a result of the metamorphic effects of the intrusion of the Cornish granites. The enrichment in the detrital elements is primarily due to the increased presence of potassium in the Culm rocks, and this can be related to the large amounts of mica and chlorite present in the alumina-rich rocks.

6.5.2.5 Culm Rocks from the Granite Aureole, Cornwall

The three sets of samples collected from the granite aureole near Okehampton show no apparent inter-relationship on the triangular diagram, figure 6.6. The older two of the three groups (numbers 7 and 8) are relatively enriched in the minor elements compared with average Culm rocks, and both are heavily enriched in the detrital elements. The oldest of these two sets of samples (group number 7) of P2 age, has particularly large enhancements in the elements gallium, titanium, potassium and strontium.

All have unusually poor correlation indic es (graph 3, Figure 6.8), although a detrital correlation index peak is present for rocks of the R1 period showing a similarity to the R1 set of samples from the coastal Culm sequence just discussed. Although the minor element enrichment index of the R1 aureole rocks, noted in Figure 6.3, is as high as 94, the corresponding correlation index is practically zero, indicating the gross inter-element imbalance which exists amongst the rock components. This imbalance may have been caused by element removal or enrichment in the granite aureole mobile zone.

6.5.2.6 Other assessments

Five other sets of samples are included in the triangular diagram, Figure 6.6, and these have been considered in section 6.4. Four are represented in Figure 6.5.2. Two (group numbers 13 and 14 of Jurassic and Triassic age respectively) are comparitively enriched in the non-detrital elements although both also have very poor correlation indic es for this category of elements.

Except for the Carboniferous Coal Measures set of samples, the detrital correlation indic es are high, indicating relative stability amongst the detrital elements in each of the deposition basins. The poor correlation indic es for all the element categories in the Coal Measures samples is indicative of completely unsettled inter-element correlations

with none of the categories dominating sufficiently to give any semblance or order. The rocks are only enriched in the detrital elements titanium, aluminium and silicon and in the one minor element nickel.

6.6 A STUDY OF THE SEDIMENTARY ENVIRONMENT

6.6.1 INTRODUCTION

The physicochemical trends which dictated the complexities of the present day geochemistry of several major basins of Carboniferous deposition have already been identified in sections 6.4 to 6.5. A further method which can be used to give additional information on these trends, is to consider a series of inter-related correlation coefficients which can be standardised at strict levels of probability.

The diagrams which follow (Figures 6.9 to 6.18) are arranged in such a way that the single components of the three element categories are equally spaced around an arc of a common circle. The element categories are those which have been used in the previous two sections i.e. the detrital elements, the non-detrital elements and the minor elements. Elements which are positively or negatively correlated at levels of significance of $P = 0.001$ and 0.01 are shown linked by solid or broken lines respectively. Sample sizes have been taken into account when determining the appropriate critical values of the correlation coefficients.

The major disadvantages of this method are, firstly, the increasing complication and hence difficulty in interpretation inherent in such a diagram and secondly the possibility of a false positive or negative correlation being shown to exist incidentally between two usually unrelated minor components which both correlate highly and individually

with a major component. Bearing the second point in mind, the major advantage to such a method is that a visual appreciation of inter-category correlations can be made at a glance, having just been inferred previously. To be certain that the correlation matrix in its entireity has been estimated reliably a sample size of approximately ten times the number of elements would be desirable.

6.6.2 THE REPRESENTATION OF MINERAL GROUPS BY ELEMENT GROUPS

As an introduction to the detailed associations of elements in the different shale groups, two correlation programmes were run in order to assess the level of affinity for a suite of elements with identified mineral groupings. In the first case, eight randomly chosen black shales are correlated against total carbon, total sulphide, total clays, quartz, calcite and iron oxide as identified by x-ray diffraction. The results and significance levels of the results are given in Table 6.5. This confirms the wisdom of choosing the elements titanium, potassium, gallium and aluminium to be representative of the clay minerals and emphasises that the dominant nature of silicon is as free quartz. Only calcium, of the four chosen non-detrital elements, correlates with calcite presence. The remaining three non-detrital elements manganese, magnesium and iron all notably correlate positively with total carbon. Of the minor elements, only lead and zinc appear to be chalcophile in tendency, with vanadium negatively related to sulphide. Molybdenum atomic-absorption cadmium and nickel correlate with total carbon.

In greater detail, in the second programme, the individual Central Province correlations of total carbon with minor element geochemistry reveal only one element with positive tendancies throughout and this is vanadium. Cadmium correlates most significantly with carbon in the Bowland rocks although it does display positive correlations of little

TABLE 6.5 CORRELATION OF MINERALOGY WITH GEOCHEMISTRY

Mineral Group	Sulphides	Clays	Quartz	Calcite	Iron oxides	Total Carbon
	Element Coefficient	Element Coefficient	Element Coefficient	Element Coefficient	Element Coefficient	Element Coefficient
1. Positive correlation coefficients	Ni .74	K .85	Si .89	Mo .82	Zn .91	Mn .74
	Mn .61	Ti .81		V .79	Sn .89	Mo .72
	Pb .62	Ca .58		Ca .77	Mn .89	Mg .71
	Zn .51	Al .57		Sr .69	Pb .86	Ni .69
	Sn .58			Cd .55		Cd .64
						Co .56
						Cu .54
						Fe .50
2. Negative correlation coefficients	Si .69	Fe .88	Mg .59	Ti .57	Sc .72	Si .58
	Sc .60	Mo .62	Pb .55	Al .55	Co .66	
	V .50	Ca .61	Sn .55		Mo .56	
		Sr .56	Mn .54		Cd .53	
		Cd .56	Zn .52		V .52	
		V .56				

1 Mineral group proportions based on x-ray diffraction peak heights

2 All results are of emission spectrometry analyses, apart from Cd, Pb and Zn which are atomic absorption analysed.

Significance Levels	Coefficient Value
P = 0.001	± .87
.01	.76
.05	.63
.10	.55
Number of Samples = 8	

magnitude in the remaining two areas. Aluminium is the only detrital element which correlates negatively with total carbon in more than one area (see Table 6.6).

An inter mineral correlation matrix, simplified in Table 6.7 indicates weak positive correlations between total carbon, calcite and sulphide. The quartz and clay mineral groups correlate positively with no others, but correlate negatively with sulphide and feldspar/calcite respectively. Each of the correlations shown on this table is considered to be self-explanatory.

6.6.3 DIAGRAMS REPRESENTING THE SETS OF SAMPLES OF THE CENTRAL PROVINCE

6.6.3.1 Bowland Shales

It has already been shown that detrital elements correlate well throughout the deposition of the Bowland Shale sequence and that non-detrital element conditions are only marginally present. The lack of contiguity between the times of culmination of minor element enrichment and correlation has been explained in terms of selective enrichments or depletions.

In the lower Worston Shale Group (Figure 6.9) inter category correlations dominate a sediment system which contains an imbalanced suite of elements. The strong negative associations between calcium and the detrital elements indicate the development of a diagenetic calcium mineral, probably the carbonate. Associated with this are the two minor elements zinc and vanadium and possibly a third minor element, cadmium. The minor elements nickel, lead and the major element iron are detrital in their associations. The conditions for minor element retention are poor owing to the unsettled nature of sedimentation, although some carbonate substitution appears to be the cause of the retention of those minor elements which are not detritally bound.

TABLE 6.6 CORRELATION BETWEEN TOTAL CARBON AND GEOCHEMISTRY IN SAMPLES FROM FOUR AREAS

Area	Bowland	Edale	Onecote	Culm (Detrital only)
	Element correlation probability	Element correlation probability	Element correlation probability	Element correlation probability
1. Positive correlation coefficients	V .94 .001 Cd .86 .001 Mo .85 .001 Ba .64 .05	Ba .81 .01 Ti .68 .05 V .56 < .05 Cd .53 < .05	V .72 .05	Ca .91 .001 Mn .90 .001 Ba .82 .01 Fe .77 .01
2. Negative Correlation Coefficients	Al .77 .01 Fe .71 .05 Sn .70 .05 K .66 .05		Al .54 7.05	Mg .56 < .05 Al .50 < .05
Number samples	9	9	9	8

TABLE 6.7 INTER-MINERAL CORRELATIONS

Area	Carbon	Quartz	Clays
	Mineral Group correlation probability	Mineral Group correlation probability	Mineral Group correlation probability
1. Positive correlation coefficients	Calcite .5 .10 Sulphide .44 .10		
2. Negative correlation coefficients		Feldspar .72 .05 Sulphide .64 .05	Calcite .70 .05

See figure 6.19 for key.

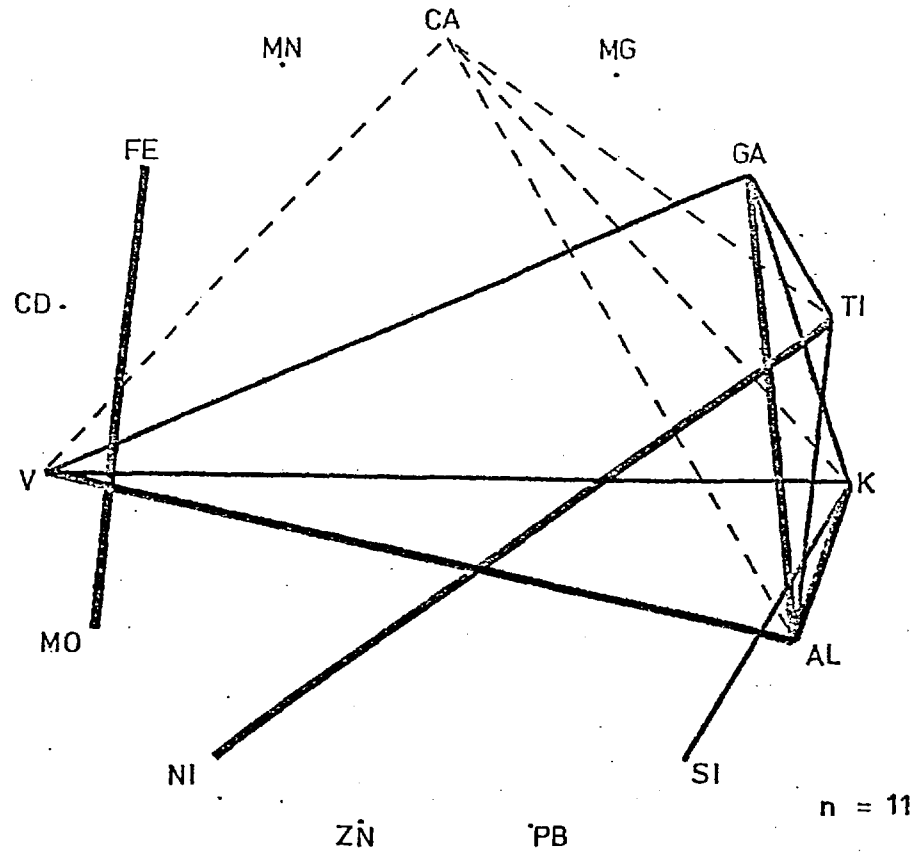


Fig. 6.10 Correlation diagram ; group no. 23

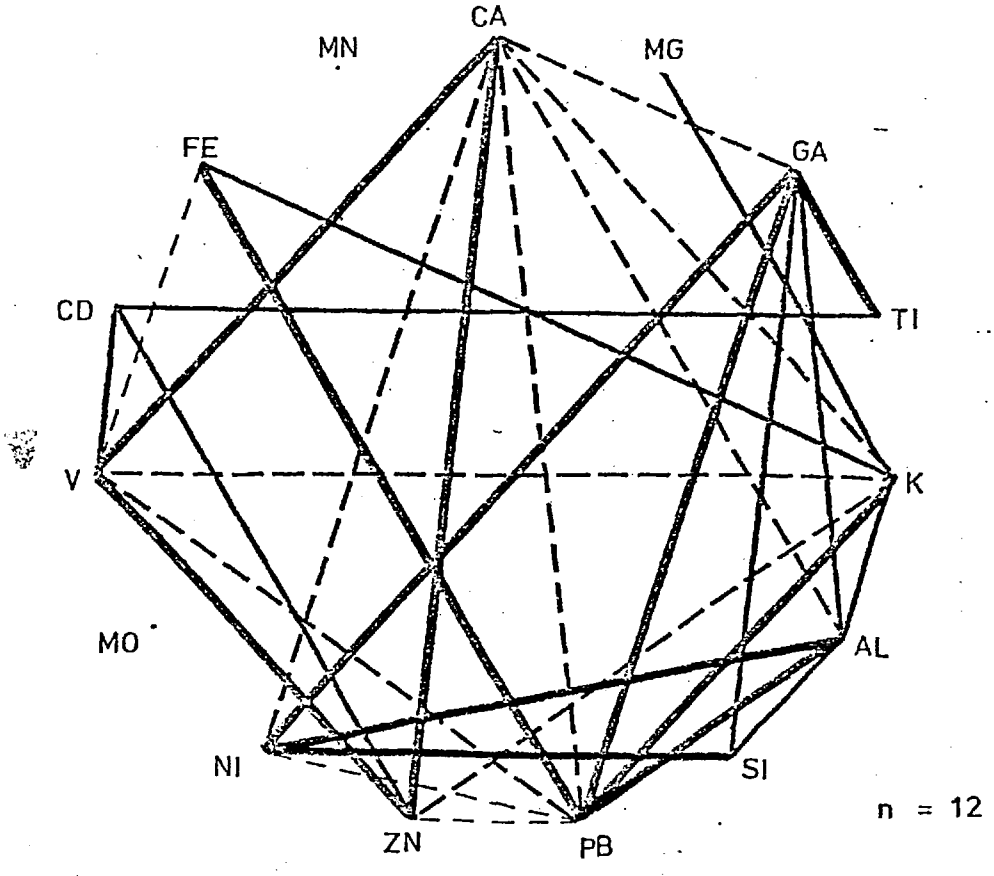


Fig. 6.9 Correlation diagram ; group no. 20

During the periods of shale deposition of the Pendleside limestone which followed the Worston Group (Figure 6.10), the major changes are governed by an overall lull in the chemical richness of the incoming detritus. Enrichments are few and small and this reflects in few positive correlations outside those which link together the clay-mineral elements. The isolation of a strong calcium-rich phase, which characterised the Lower Worston Shale Group has minimized, although it is still present but with a much limited power of retention for the minor elements.

The following P1-age sediments are the most minor element and non-detrital element rich set of samples from the sequence and this is clearly shown on Figure 6.11. Although few inter-minor and inter non-detrital element correlations exist, both categories are conspicuously isolated, not only from the detrital elements, but also each other. The detrital elements, despite an enrichment index near to zero, are excellently inter-correlated, with the notable exception of silicon, representing free quartz. Diagenetic minerals form from the elements iron and manganese and also, calcium and magnesium. The predominantly oxidising environment of formation leads to the formation of oxides and carbonates whilst the influx of free silica as quartz results in a high aluminium:silicon ratio. Of the minor elements, selective enrichment of cadmium, copper (which is represented solely in Figure 6.3) and vanadium are especially worthy of attention.

The cadmium is conspicuous in its complete lack of correlation either with zinc (a detritally biased element in this instance) the clay minerals or with the oxides and carbonates which seem to abound.

Succeeding P1 deposition are the rocks of P1-P2 age from the Upper Mearley Clough (Figure 6.12). The correlation index peak, noted in section 6.5 is attributed to the good correlations existing between the elements cadmium, vanadium, molybdenum and lead. Two of these,

See figure 6.19 for key.

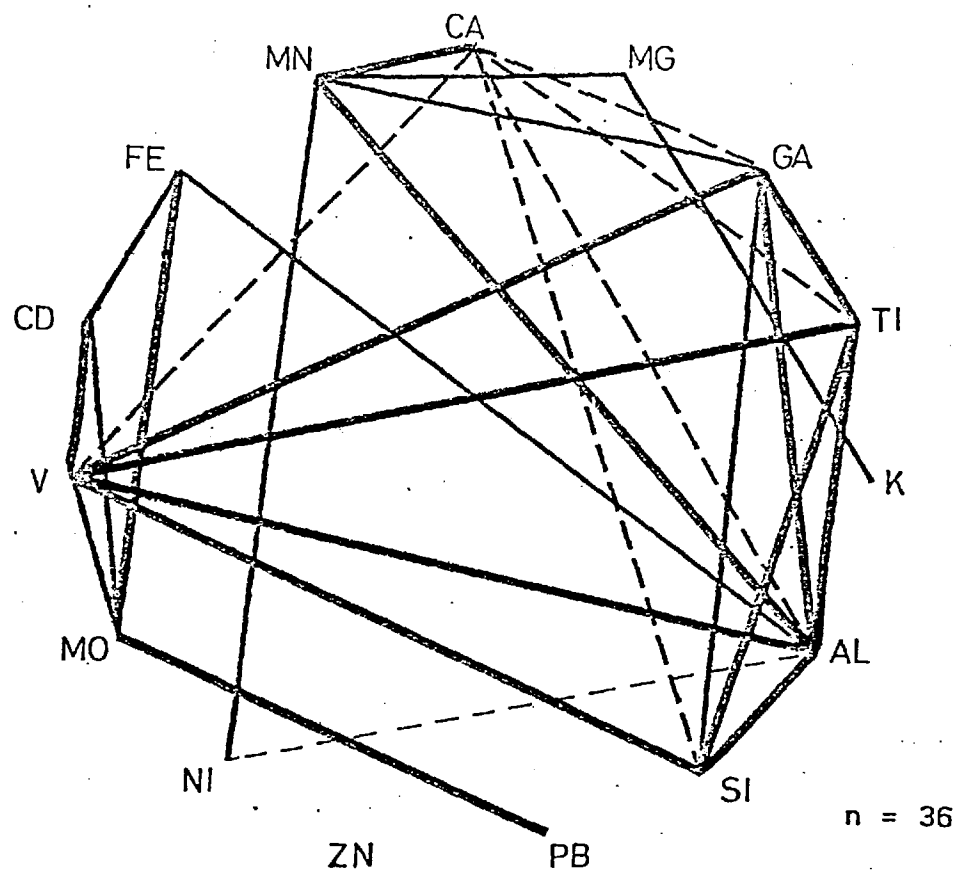


Fig. 6.12 Correlation diagram ; group no. 22

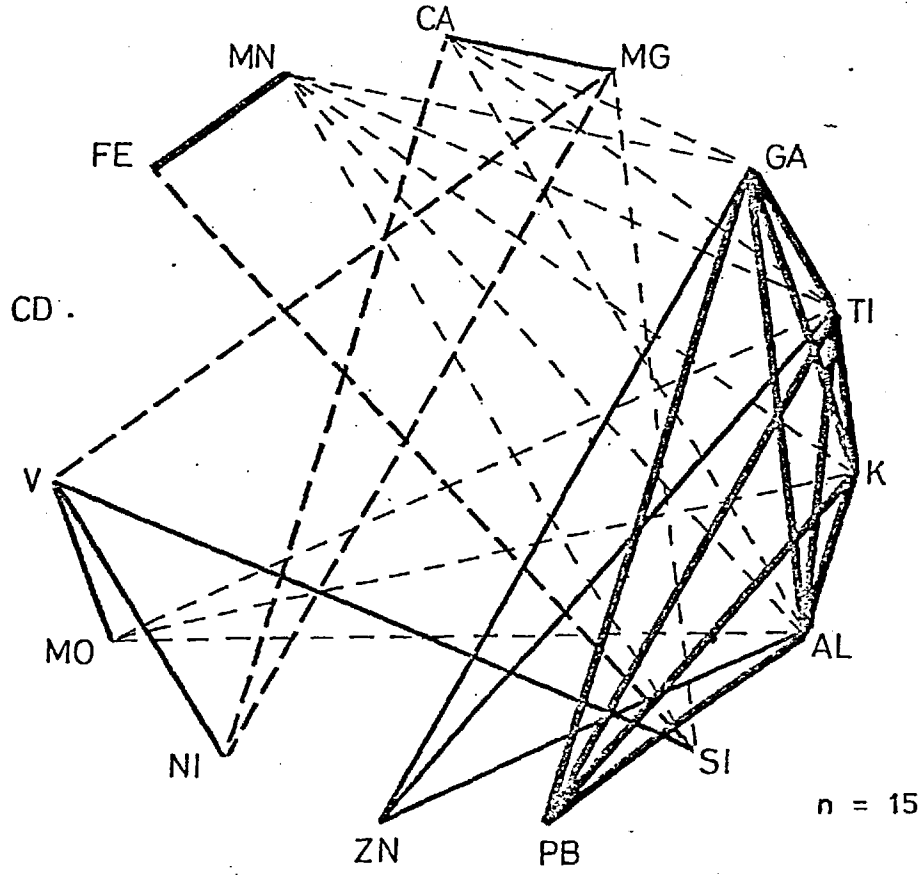


Fig. 6.11 Correlation diagram ; group no. 21

cadmium and molybdenum correlate well with iron. The correlation of silicon with the representative elements of the clay minerals reflects in a revertion, in the samples of this group, to a low aluminium:silicon ratio (see Table 10.1), although potassium, commonly found in the illite mineral group, is unusually isolated. The incoming detritus may be potash defficient as a result of selective loss of the element to the flourishing vegetative land cover. Vanadium is probably included in clay structures. In conclusion the P1-P2 sediments are richer in equilibrated clay mineral elements depositing in an environment where contemporaneous deposition of calcite is still important. Quiet conditions alternating with more disturbed, higher Eh, carbonate environments are conducive to periodic retention of organic matter, which assists in the fixation of the minor elements.

This sequence is brought to a close with the development of a free-quartz rich clay sediment in which increasingly less carbonate presence is recorded. A moderately well-balanced minor element correlation series is present but the only association of note, apart from the detrital nature of molybdenum, is between cadmium and zinc, a relationship which, despite the supposed affinities of one element for the other, is rare in Bowland Shale times. The presence, in the last set of samples, of sulphide minerals may explain the cadmium-zinc association, (group number 24, Figure 6.19).

6.6.3.2 Edale Shale Group

Of the two sets representing this Group in this section, both have strong inter-detrital element correlations which includes silicon and which resultantly contain little free quartz. Both also have low aluminium:silicon ratios, indicative of deposition in quiet waters, some distance from the shoreline. The production of a carbonate phase is especially apparent in the older, E2 shales (Figure 6.13) where the non-detrital elements are strongly isolated from the detrital clay minerals.

See figure 6.19 for key.

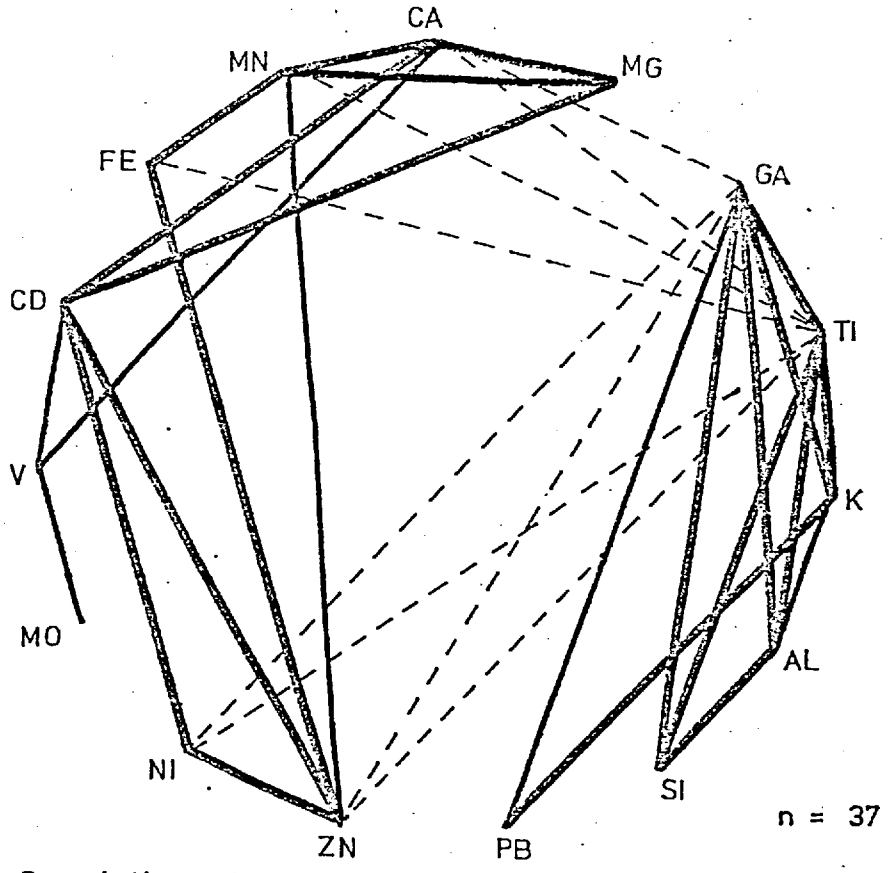


Fig. 6.14 Correlation diagram ; group no. 25

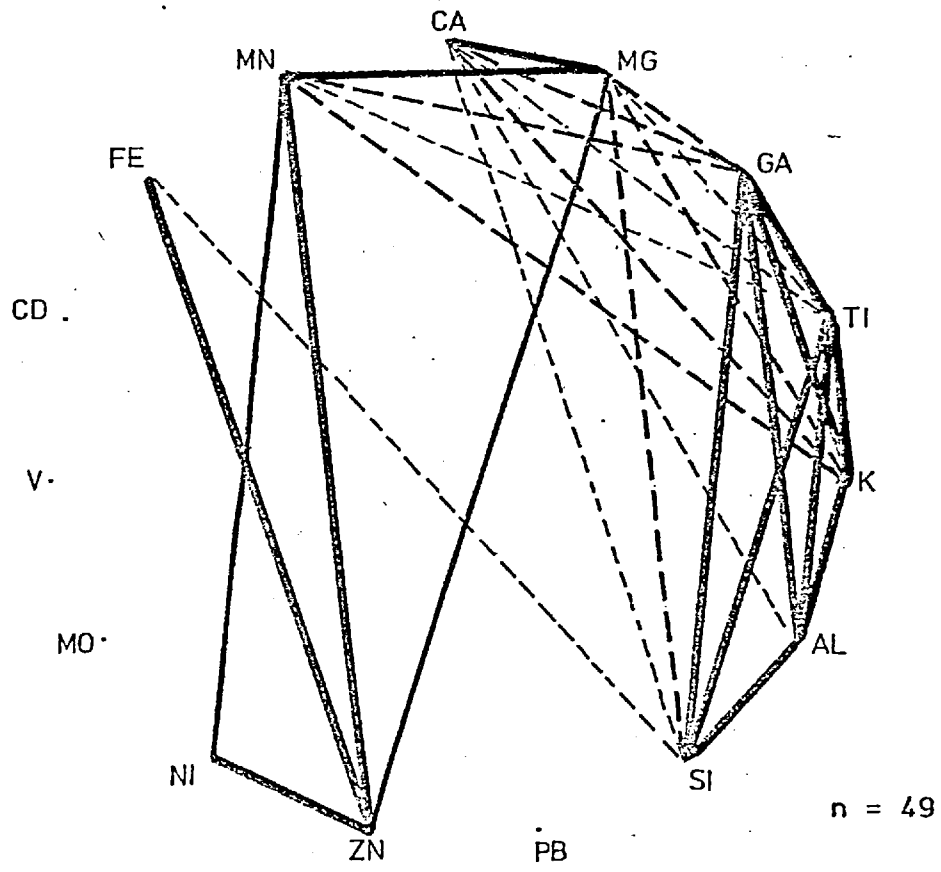


Fig. 6.13 Correlation diagram ; group no. 26

The evolution into H-R age deposition is marked by a reduction in isolated carbonate activity as a result of an oxidation potential rise, following a build-up in residual organic debris. This evolution of a more reducing physiochemical environment has created an environment where minor element redistribution in the sediment can take place within the organic matter and the diagenetically-forming minerals present leading to an enhancement in the minor element content. The hypotheses regarding the mechanics of enhancement are set out in chapter ten.

In conclusion the Edale basin was an environment where warm quiet waters, rich in oxygen and low in dissolved carbon dioxide content favoured the formation of a carbonate-containing, organic, clay-sediment. A decrease in the rate of sedimentation in the H-R period had enabled reducing conditions to dominate whilst correspondingly limiting carbonate production.

6.6.3.3 Onecote Shale Group

The youngest set of samples of the small Onecote Shale sequence has a high aluminium:silicon ratio which is reflected in the isolation of silicon from what is otherwise an almost perfectly balanced suite of detrital elements. These are in turn well isolated from both the non-detrital and minor element categories inside which moderately good correlation conditions prevail. The strong, positive correlations between chalcophile-type minor elements cadmium, zinc and lead to the total exclusion of other associations, is good evidence for sulphide formation. This set of specimens (Figure 6.15) like other Central Province sediments, emphasizes the continued juxtaposed variations in carbonate and sulphide formation in basins where the necessary physiochemical fluctuations are rapid and repetitive.

See figure 6.19 for key.

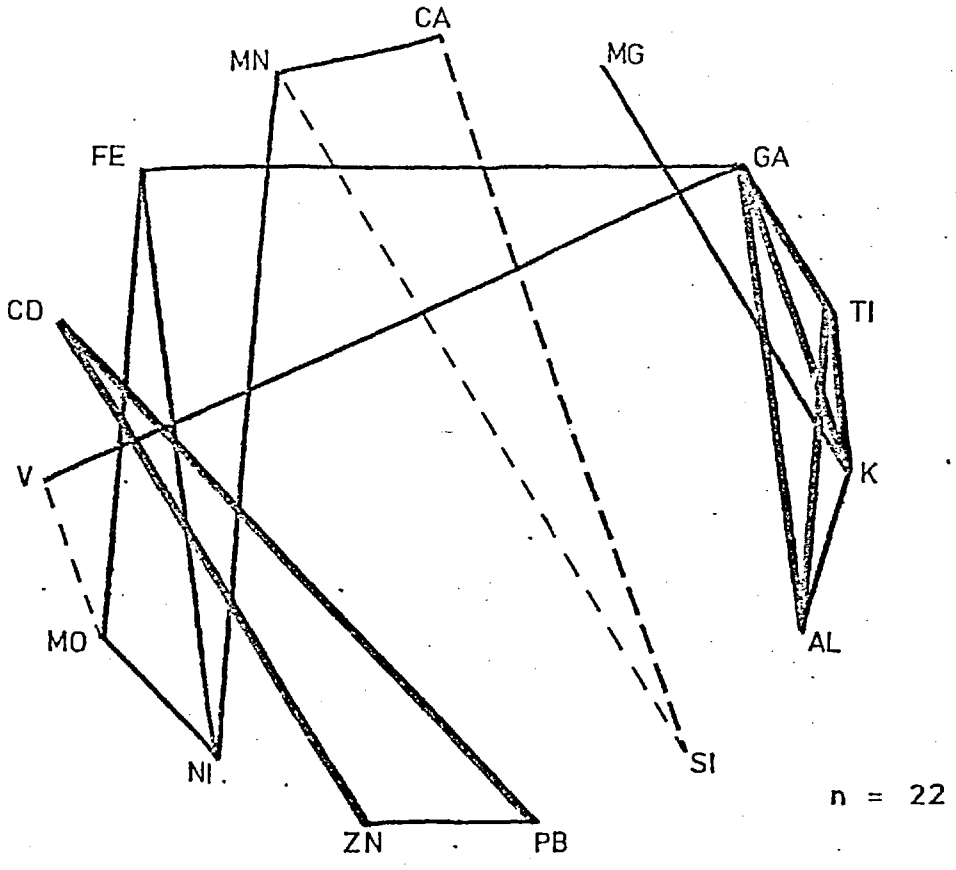


Fig. 6.16 Correlation diagram ; group no. 17

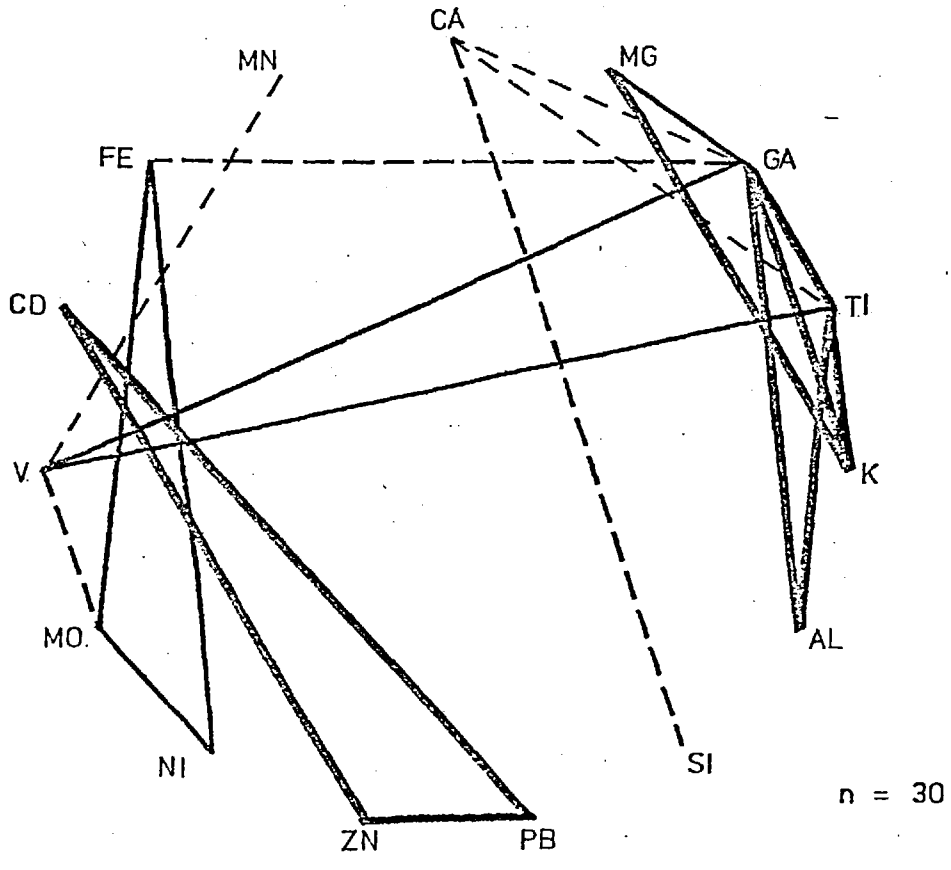


Fig. 6.15 Correlation diagram ; group no. 18

Conditions changed little in the succeeding set of samples collected from slightly younger shales in the Mixon limestone and shale series. Figure 6.16 for this group (number 17) again exhibits sulphide and carbonate precipitation in a set of quartz-rich samples collected over a very small part of the stratigraphic column.

In later times conditions have changed to those which favour the deposition of quartz-poor, well-balanced clay minerals in an environment where carbonate is still forming (i.e. Figure 6.17 for the Mermaid region samples, group 16). It is possible that several of the minor elements are forming sulphides during this stage, but three of them; cadmium, molybdenum and lead, have positive correlations with the detrital minerals. This suggests that the reducing conditions which prevail during times of strong sulphide production are not quite extreme enough to mobilise detritally-held minor elements from the lattices of their hosts.

The rocks of the E2 age Dove Shales (Group 15, Figure 6.18) demonstrate a remarkably clear picture of sediment component segregation. Although the minor elements cadmium and zinc are associated with the free-quartz poor, clay minerals, the remainder of the minor elements are strongly antipathetic to the presence of the clay mineral elements. Of these, vanadium and molybdenum correlate strongly with calcite, and nickel correlates strongly with non-detrital manganese. Nickel which correlates presumablywith oxides of manganese is particularly well-enriched in this set of samples (see Figure 6.3). Overall, the set is the second most minor-element enriched group from the Central Province.

A significantly greater enrichment in aluminium compared with silicon in this set of samples suggests that the quiet, very reducing conditions which characterized the two oldest sets of samples (sets 16 and 17) and which appeared to be lapsing temporarily in the samples of the Mermaid region (group 18), have returned. A strong cadmium-zinc relationship indicates the formation of sulphides.

See figure 6.19 for key.

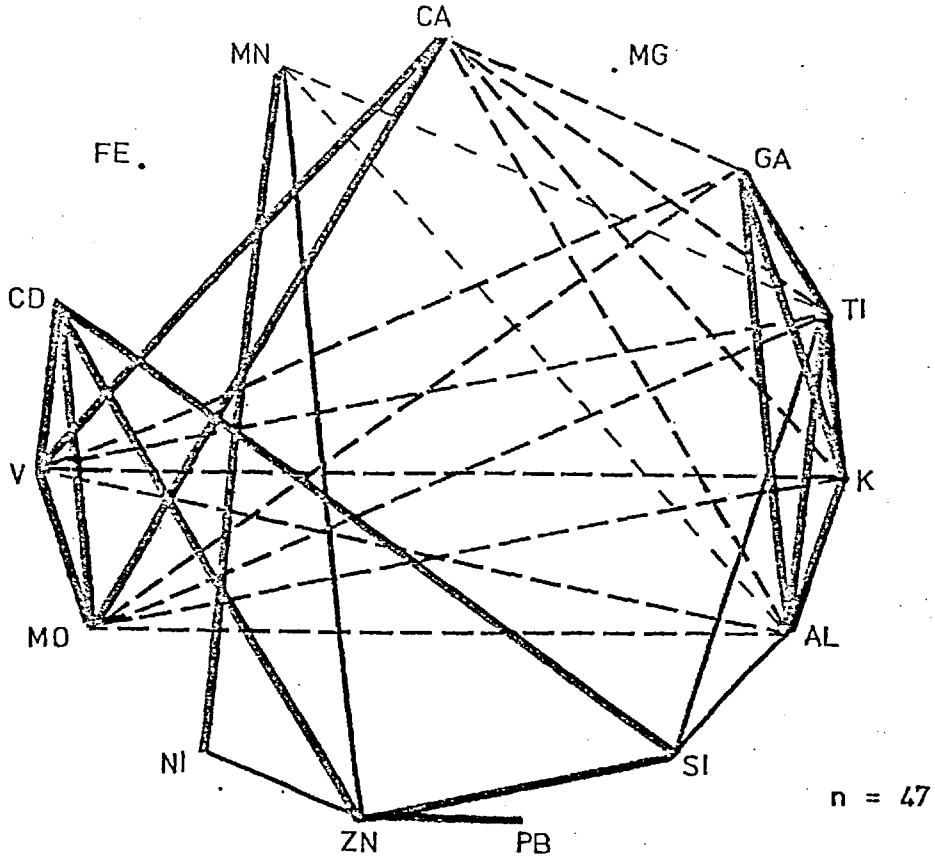


Fig. 6.18 Correlation diagram ; group no. 15.

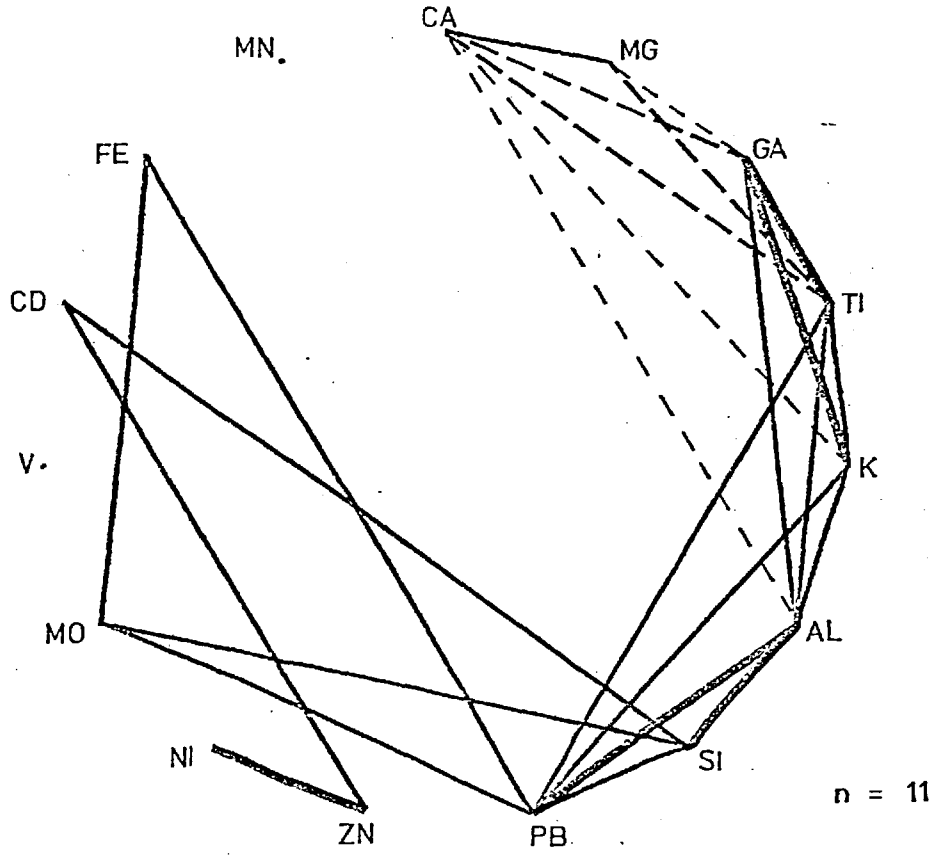


Fig. 6.17 Correlation diagram ; group no. 16.

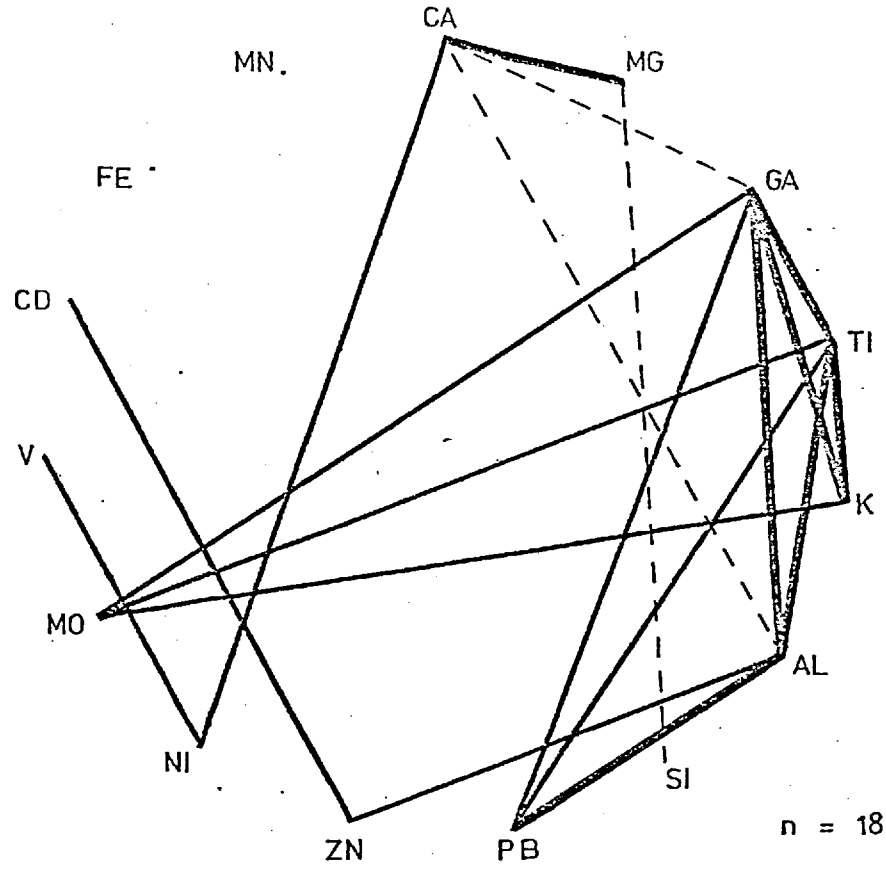


Fig. 6.19 Correlation diagram ; group no. 24.

Figures 6.10 - 6.18

KEY :

Correlation coefficients between pairs of variables expressed as levels of significance.

P = ·01 : - ·01

P = ·001 : - ·001

Identification of group numbers :

15	E2 Dove shales
16	P1 – P2 Onecote shales (Mermaid)
17	" Mixon shales (Grange)
18	" " (Hamps)
20	Lower Worston shales
23	" - Pendleside limestone
22	P1 - P2 Bowland shales (Mearley)
21	P1 "
24	E1 " (Harrop)
25	H + R Edale shales (Village)
26	E2 " (R. Noe)

n = number of samples.

6.6.4 CULM MEASURES, CORNWALL

Correlation coefficient diagrams have been constructed for the Culm sequence. However, owing to the strong possibility of element redistribution which would accompany the reconstitution of the black shales into micaceous black shales caused by the Permian granite intrusion, it has been decided not to include them within a section which is dealing essentially with primary diagenetic change.

6.7 CONCLUSION

The object of this section has been to attempt to pinpoint changes in basin chemistry which affect cadmium retention. Cadmium may enter the basin of deposition in either detrital (within clay lattice) or non-detrital (adsorbed or as free ions) forms. The dominant physicochemistry of the environment at the time of entry will determine the foremost deposited cadmium form. If the environment is reducing enough and sulphide is being evolved, then free cadmium ions may precipitate as sulphides, if the environment is slightly oxygenated then carbon dioxide will be evolved, carbonate may form and cadmium may substitute for calcium within the lattice. If, as is more likely, the environment is neither excessively reducing nor oxidising, then cadmium would flocculate and deposit in colloidal form as organo-metallics, oxides and clays. Cadmium may therefore be associated with, for example, carbon, aluminium and silicon. Re-mobilisation upon diagenesis may lead to the resiting and eventual precipitation of the element. Later chapters will deal with the effect of remobilisation, redistribution and the forms of cadmium resulting from retentative processes. This form should be broadly determined by physicochemical changes in the basin of deposition and within the environment of weathering. Not all black shales, of course, enhance cadmium and although the problem is basically one of concentration, it is also fundamentally dependent on factors of availability and supply.

CHAPTER 7

7 PRESENCE OF MINOR ELEMENTS AND ENRICHMENT PROCESSES IN BLACK SHALES

7.1 INTRODUCTION

The means and ranges of cadmium content detected in black shales by atomic absorption analysis are listed in Table 7.1. Using the minor enrichment value of 11.0 ppm cadmium obtained in Chapter 6, five of the 34 sets of samples were found to be enriched in the element. Three of these were from the Bowland area: P1 age lower Bowland Shales, P2 age Upper Bowland Shales and E1 age Upper Bowland Shales. The fourth was from the H2 age Edale Shales and the fifth was from the P1-P2 age Mixon limestones and shales of the Onecote region.

7.2 VARIATIONS IN CADMIUM PRESENCE THROUGH STRATIGRAPHIC VARIATION

7.2.1 UPPER MEARLEY CLOUGH, BOWLAND

The presence of cadmium in specimens from the Bowland Shale sequence in Upper Mearley Clough was erratic and highly unpredictable (Figure 7.1). Although the presence of cadmium was greater in the Upper Lower Bowland Shales, the overall mean cadmium presence changed little throughout the three main stages of Bowland Shale deposition. A distinct subduing of the oscillating cadmium:zinc ratio takes place at the beginning of the Upper Bowland Shale sequence which implies that there was a measure of increased stability in the formative conditions. In mid P1 times after the G. elegans band the sudden dominance of sandstone facies over shale facies upset the ideal retentive black shale conditions and this resulted in the sudden fall in detected cadmium presence. Following the

TABLE 7.1 THE CONCENTRATION OF CADMIUM IN ALL SETS OF BLACK SHALE SAMPLES AS DETERMINED BY ATOMIC ABSORPTION SPECTROMETRY

Geological Age	Sedimentary Formation	Locality	Age	Number of Samples	Mean Cadmium	Range Cadmium
Silurian	Rheidol Group	Aberystwyth	b5	49	1.2	N.d. - 4.0
Silurian	Stockdale Shales	Lake District	b5	60	1.1	N.d. - 3.0
Silurian	Ludlow Shales	Denbighshire	b7	4	2.0	-
Lower ORS	Middle Devonian	Brecknockshire	C2	6	0.5	N.d. - 0.5
Carboniferous	Limestone	Brecknockshire	d2	3	N.d.	N.d.
	Chatburn Limestone Group		C2	4	0.5	N.d. - 0.8
	Lower Worston Shale Group	Bowland	B1-2	46	4.4	N.d. -32.2
Carboniferous	Lower Bowland Shale Group	Forest	P1	35	16.2	1.0 - 105.0
d2 - d4	Lower Bowland Shale Group	Lancashire	P2	20	16.5	1.0 - 158.0
	Upper Bowland Shale Group		E1	59	16.6	1.0 - 219.0
Carboniferous	Pendlegrit Middle Upper	Edale North	E2	2	2.0	-
d4	Edale Shales	Derbyshire	E2	48	5.2	1.0 - 39.0
Yoredale series			H1	14	6.0	1.0 - 50.0
			H2	25	14.8	N.d. - 91.0
			R1	11	6.0	1.5 - 32.0
	Mam Tor Beds		R2	7	4.2	1.0 - 10.0
	Dove Shales (Namurian)	Onecote-Dove	R1	3	4.7	3.0 - 6.0
Carboniferous	Dove Shales	Southwest	E2	45	6.5	N.d. - 24.6
d4	Mixon Limeston & shales	Derbyshire	P1-2	31	12.8	0.5 - 65.0
	Onecote Sandstone & shales		P1-2	8	9.3	1.0 - 39.0
			E2	12	1.36	1.0 - 2.0
	Crackington Formation	Bude Bay	H1	39	1.3	N.d. - 5.0
Carboniferous		Cornwall/	R1	55	1.74	N.d. - 4.0
d4		Okehampton	R2	29	1.53	N.d. - 3.0
		Devon	91	34	1.0	N.d. - 2.0
	Bude Formation	Bude	92	55	1.1	N.d. - 3.0
	Bideford Formation	Barnstaple	R1-G2	46	1.0	N.d. - 3.0
Carboniferous	Coal Measures	Glamorgan-shire	d5	9	1.0	N.d. - 5.0
Carboniferous	Coal Measures	Chesterfield	d5	15	1.5	N.d. - 3.0
Permian	Marl Slate	Durham	e	35	6.2	N.d. - 73.5
Trias	Rhaetic Beds	Newport	f6	33	0.95	N.d. - 2.0
Trias	Rhaetic Beds	Gloucester	f6	14	1.6	1.0 - 3.0
Trias	Rhaetic Beds	Cardiff	f6	26	0.2	N.d. - 2.0
Upper Jurassic	Kimmeridge Clay	Kimmeridge Bay	g12	36	2.7	N.d. - 7.0

All values in parts per million
N.d. = not detected

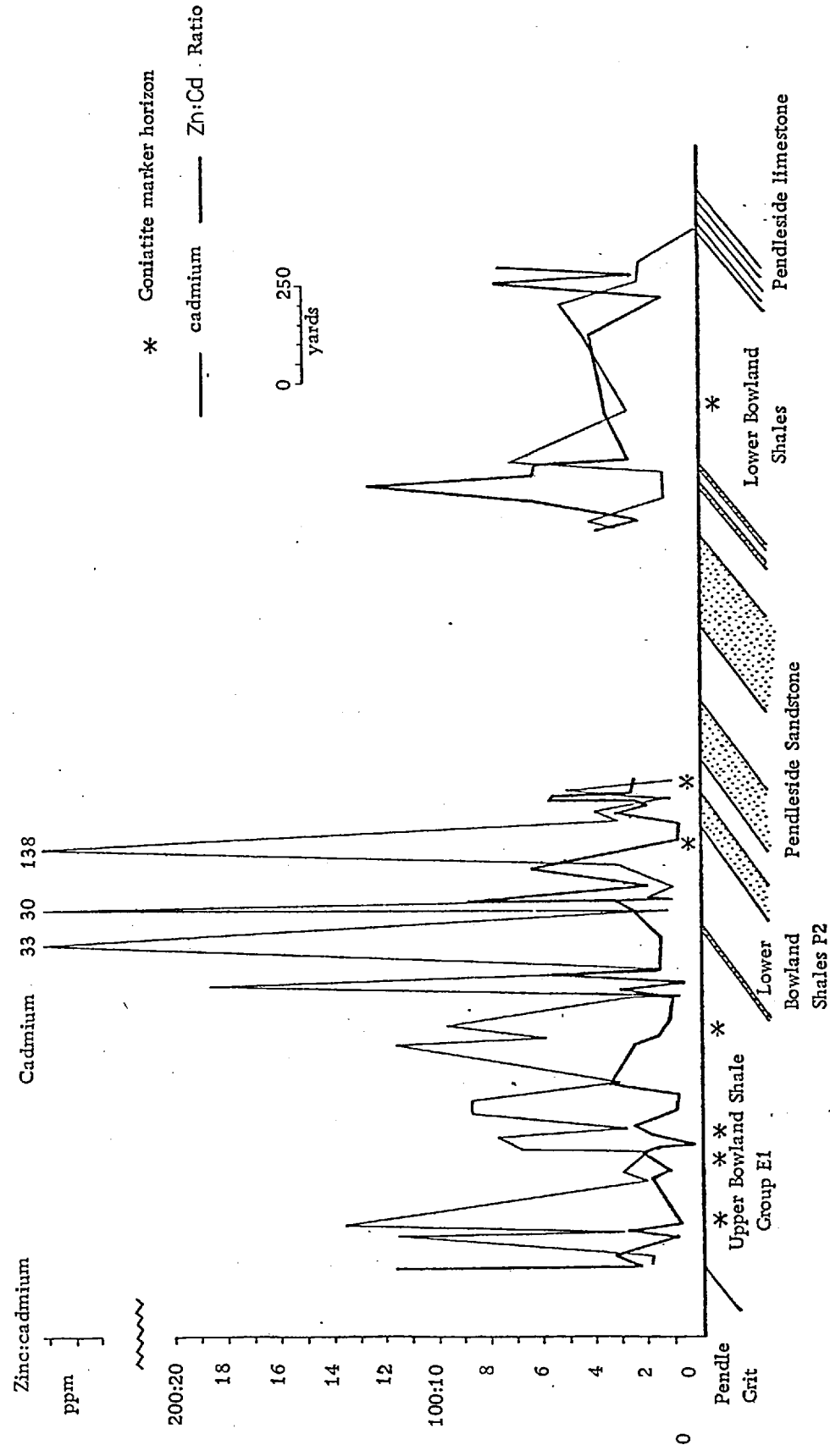


FIG. 7.1 VARIATION IN CADMIUM PRESENCE AND : RATIO IN THE UPPER MEARLEY CLOUGH, BOWLAND

re-emergence of black shale as the dominant facies after the G. granosus band cadmium was once again retained, but erratically owing to the continued incursion of arenaceous detritus. The gradual disappearance of sandy lenses and the total dominance of black shale deposition after the Cravenoceras leion band led to the selective enhancement of cadmium with respect to zinc.

7.2.2 UPPER BOOTH TRAVERSE, EDALE

The variation in cadmium presence through the Upper Booth sequence of the Edale Shales is shown in Figure 7.2. As in the sequence from Bowland, cadmium was not enhanced in all black shale samples in the succession but appeared to be most enriched in those samples collected immediately after and close to marine bands (as in sample numbers 898, 906, 914, 918 and 924). Cadmium did not therefore become enriched during those times when the most stagnant, organic-rich conditions prevailed, but later whenever conditions were becoming more aerated, saline density stratifications were being broken up and metal was once again supplied to the bottom water-sediment contact. Cadmium which had been building up in presence in the less saline and less toxic top waters was subsequently made available for the processes of retention. The behaviour of zinc differed from that of cadmium, since zinc is not as mobile in the secondary environment as cadmium and since it has a greater degree of chalcophicity. Zinc appeared to enter the toxic zone as a sulphide when stagnation was at its height, effectively leaving the topwaters cadmium enriched. Consequently zinc:cadmium ratios were notably depressed during those times when cadmium enrichment was taking place.

7.3 ZINC AND LEAD PRESENCE IN THE BLACK SHALES OF ENGLAND AND WALES

The minimum enrichment value for zinc (as calculated in chapter 6) was 240 ppm and that for lead was 109 ppm.

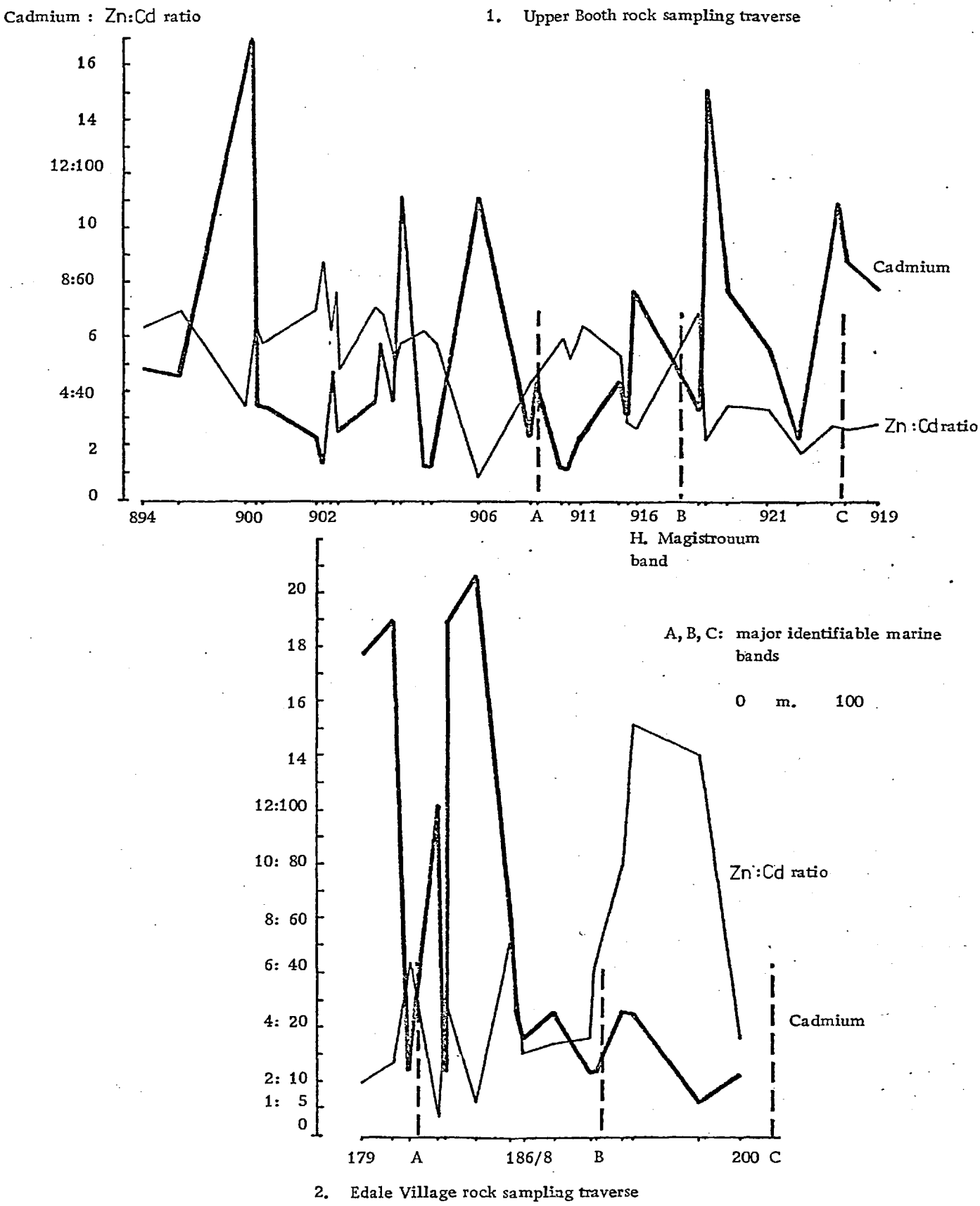


FIG. 7. VARIATION IN CADMIUM PRESENCE AND Zn:Cd RATIO IN THE UPPER BOOTH AND EDALE VILLAGE ROCK SAMPLING TRAVERSES

Four sets of samples listed in table 7.2 exceeded the zinc value of 240 ppm. These were the Lower Worston Shale Group and P2 age Lower Bowland Shales from Bowland, the E2 Edale Shales from North Derbyshire and the R1 age Dove Shales from Southwest Derbyshire.

Zinc was notably more deficient in the remaining two sets of Bowland Shale samples in which cadmium was considerably enhanced. The zinc:cadmium ratio for the P2 Lower Bowland Shale Group, as illustrated in Figure 7.1 ,was erratic and high in comparison with the preceding and succeeding sequences. This was taken to denote a more arenaceous detritus in which zinc, as opposed to cadmium, was more totally retained. The Lower Worston Shale was similarly enriched in arenaceous material and similar processes favouring zinc retention operated.

Strong zinc enhancement within the early E2 age Edale Shales rather than in the later H to R age Edale Shales is reflected in a constantly higher zinc:cadmium ratio as seen in Figure 7.2. Cadmium was enhanced later in the sequence when the increase in the aluminium\silicon ratio denoted a distinct change from a silicon-rich to an aluminium rich sediment (see section 10.1). The preference for cadmium to remain available for retention in the finer grained sediments in comparison to the habit of zinc is again shown.

Zinc was also strongly enhanced in the E2 age Dove Shales which were seen to be only moderately enhanced in cadmium. A study of aluminium\silicon ratios in Table 10.1 again indicates that the zinc enhanced sediments were clearly more silicon (or quartz) rich, than aluminium (or clay) rich.

Mean lead content in shales exceeded the minimum enrichment value of 109 ppm in only three sets of samples: firstly in the Lower Worston

7.2 THE CONCENTRATION OF ZINC AND LEAD IN SETS OF SAMPLES OF CARBONIFEROUS AGE AS DETERMINED BY ATOMIC ABSORPTION SPECTROMETRY

Geological Age	Sedimentary Formation	Locality	Age	Number of Samples	Mean Zinc	Range Zinc	Mean Lead	Range Lead
	Lower Worston Shale Group	Bowland	B1-2	40	240.0	18.0 - 1400.0	152.0	38.0 - 767.0
Carboniferous	Lower Bowland Shale Group	Forest	P1	27	164.0	62 - 510	54.0	29 - 139
d4	Lower Bowland Shale Group	Lancashire	P2	15	359.0	19 - 1685	142.0	29 - 672
	Upper Bowland Shale Group		E1	39	109.0	39 - 221	56.0	29 - 106
			E2	38	406.0	24 - 3000	58.0	19 - 259
Carboniferous	Middle - Upper	Edale	H1	12	82.0	23 - 355	44.0	34 - 53
d4	Edale Shales	North	H2	26	140.0	32 - 662	48.0	29 - 67
		Derbyshire	R1	29	231.0	5 - 1340	64.0	8 - 259
	Namurian Dove Shales	Onecote/	R1	3	183.0	140 - 210	110.0	43 - 190
Carboniferous	Dove Shales	Dove:	E2	41-45	556.0	40 - 4800	51.0	29 - 101
d4	Mixon Limestone and shales	Southwest	P1-2	9	158.0	44 - 350	56.0	38 - 134
	Onecote Limestone & shales	Derbyshire	P1-2	30	165.0	22 - 780	96.0	38 - 317
		Bude Bay	E2	3-12	51.0	33 - 65	32.0	24 - 48
Carboniferous		Cornwall/	H1	26-39	80.0	10 - 125	65.0	10 - 144
	Crackington	Okehampton	R1	30-55	96.0	37 - 220	52.0	29 - 82
d4	Formation	Devon	R2	8-29	82.0	30 - 125	49.0	19 - 91
			G1	32-34	104.0	40 - 160	49.0	19 - 134
	Bude Formation	Bude	G2	55-54	78.0	36 - 185	39.0	19 - 82
	Bideford Formation	Barnstaple	R1-G2	41-46	79.0	19 - 270	67.0	14 - 144

All values in parts per million

Shale Group, secondly in the P2 age Lower Bowland Shale Group and thirdly in the R1 age Dove Shales. In the first set of samples zinc was enhanced in addition to lead, whilst in the second set cadmium was enhanced in addition to lead. Only three samples comprised the third set of samples which had a high range of only 190 ppm lead.

Such a juxtaposition of enhanced elements may be related to their role in sulphide formation and if this is true for the inconsistent enhancement behaviour of lead, then the presence of lead in original diagenetic solutions, which may be correlated with regional factors, may be vital.

7.4 THE REDISTRIBUTION AND ENRICHMENT OF CERTAIN MINOR ELEMENTS DURING DIAGENESIS

7.4.1 AUTHIGENIC ENRICHMENT

The major physical and chemical changes which occur within a sediment undergoing diagenesis were summarized in section 4.6 page 66. For some of these deposits the most significant period of enrichment may have been during the stage of diagenesis wherever inter-stratified black shales were used as traps for mobile elements circulated and expelled during the processes of compaction. For example, authigenic enrichment of the late Permian Kupferschiefer, also discussed in Chapter 4, was brought about by heavy metal rich seepages of meteoric or hydrothermal origins entering the Zechstein Sea and bringing about the early diagenetic replacement of primary pyrite. The antipathetic variation of the elements molybdenum, cobalt and nickel with the rate of deposition suggested incorporation by sorption of dissolved ions on organic carbon and clays to Hirst and Dunham (1963). A fluctuating source for the elements lead, zinc, barium and some copper, apart from normal weathering on the land surface, is accounted for by the intermittent introduction of metals into the lagoon by submarine springs rather than by truly epigenetic mineralisation. The mean cadmium

concentrations in 35 specimens of the Permian Marl Slate from the Sherburn Hill area of Durham was 6.2 ppm with a median of 3.5 ppm and a range of not detected to 73.5 ppm. Zinc ranged in amount from 14 to 29,500 ppm with a median content of 450 ppm and an average ratio with cadmium of 284. After comparison with the average zinc:cadmium ratio of 30 to 50:1 for the metal enriched rocks of the Visean age from the Central Province, there appeared to be a considerable selective enrichment of zinc in the authigenically enriched rocks relative to the syngenetically enriched rocks. In addition a lead content of 21,600 ppm in one specimen which had average zinc and cadmium content indicated that a fluctuating lead source existed alongside a fluctuating zinc source.

7.4.2 DIAGENETIC ENRICHMENT

7.4.2.1 Pyrite

Carroll (1958) showed that iron could be transported as coatings on clay minerals and would be reduced if such minerals encounter a reducing environment. In the presence of sufficient dissolved sulphide ion, precipitation of a primary iron monosulphide may occur whilst the sediment was still in contact with circulating solutions. However, with rather more rapid sedimentation or slightly less reducing conditions iron may escape complete reduction before burial and consequently reduction leading to secondary sulphide precipitation occurs within a foot or so of the sediment-water interface. The monosulphide will eventually be converted to the disulphide either while interstitial waters are being expelled or be delayed until there is little interstitial water movement. Of these three possibilities Nicholls and Loring (1962) claimed that the second (conversion to disulphide at depth) should result in the highest vanadium content in rocks. Since hydrated iron oxides are powerful adsorbants for vanadium, any attached to such oxides would be carried down into the sediment and would be liberated from the iron within the sediment. Some may enter the

monosulphide, some may migrate into the organic matter or clay minerals. Love (1962) wrote, in addition, that the sulphides of the Kupferschiefer were present as spheres enclosing micro-organisms which supposedly caused precipitation of primary pyrite. Pyrite concretions in the Dictyonema Shales in the Baltic basin were analysed for minor element content by Tikhomirova (1961) who detected the following levels (in ppm, levels in pyrite concretions in the rock, in parenthesis) Manganese 160 (30), Nickel 41 (134), copper 26 (61), molybdenum 20 (80), Titanium 4,000 (150), lead 30 (1160), Arsenic not detected (1920), silver trace (2.7).

Several pyrite-rich bands in dark to buff coloured clays have been collected from the H1 to H2 age shales from the Edale Valley. The increased solubility of iron disulphide in the HS^- rich depositional region may have discouraged pyrite from forming in the black shales themselves (strongly reducing conditions tend to delay the conversion of monosulphide to disulphide (Nicholls and Loring, 1962)). The minor element content of the samples (numbers 109046, 109051) was 4.0 ppm cadmium, 18 to 180 ppm zinc, 29 to 58 ppm lead and 264 to 4800 ppm manganese. In a further sample extracted from dark, shaly mud bands the pyrite contained no detectable cadmium, 92 ppm zinc, 29 ppm lead and 480 ppm manganese. The shales immediately above and below the pyrite rich bands had similar levels of cadmium and lead concentration. Although the levels of zinc tended to be higher in the pyrite, the outstanding difference in the chemistry of the nodule was the much increased presence of manganese. Up to three times more manganese was associated with the pyrite than with the rocks immediately surrounding it, but it was noticeable that the manganese content of the average Edale shale was considerably lower than that content of the rocks surrounding pyrites. In conclusion manganese and possibly zinc appeared to have been buried in association with hydrated iron oxides in a sediment which was either depositing rapidly or was not sufficiently reducing enough to cause primary monosulphide precipitation. Subsequently the reduction of the iron and formation of a

secondary monosulphide took place in the topmost sediments causing manganese and zinc to enter into it and also for excess manganese to migrate into surrounding organic matter and clay minerals.

7.4.2.2 Calcareous Concretions

In the H2 age beds of the Edale Shales, the sequence of black mudstones and shales included ironstone lenses and calcareous bullions. The grey, hard nodules were conformable with the bedding and were enclosed in iron-oxide rich spheroidal skins. They were generally small, ellipsoidal or round masses but occasionally bullions attained a thickness of 42 cms. and a length of up to 10m. The small, isolated nodules were formed by the localized precipitation of calcite in the vicinity of an alkaline-rich decaying organism, such as an ammonite. Gad et al (1969) suggested that since carbonate concretionary deposition occurs only in the absence of sulphide, then the sediments must have been sufficiently isolated from the influence of sulphate ions in sea-water, by burial. The elements calcium, iron, manganese, zinc and strontium and high partial pressures of carbon dioxide necessary to stabilize carbonate must have been generated locally at times of comparitively late diagenesis. Fragments of a 42 cm diameter spherical nodule from the Upper Edale Shales at Upper Booth were found to contain low amounts of trace elements with no detectable cadmium, 390 ppm manganese and only 20 ppm zinc. However, the pyrite-rich outer skin of the nodule was found to contain 22.0 ppm cadmium, 537 ppm zinc and 3120 ppm manganese. Within the nodule were considerable quantities of soft, black, opaque crystals which were found to contain 11.0 ppm cadmium, 45 ppm zinc, 2.2% iron and 0.32% manganese and were considered to be hydrous manganese oxides. Siderite nodules from the Margarlatus zone of the Lias analysed by Dunham (1960) were found to contain cracks filled with pyrite, barite and sphalerite which he concluded were probably concentrated from the surrounding shale. The presence of enhanced cadmium levels inside

the concretion and in the surrounding 'skin' demonstrated the ability of solutions to percolate through a sediment during diagenesis. Manganese (which was seen to be the most mobile of minor elements in section 7.5.1) appeared to precipitate as oxide upon initiation of decay and release of carbon dioxide, in addition to ammonia. Before the pH conditions had become sufficiently alkaline to enable carbonate to precipitate, cadmium and zinc rich liquids (possibly in the course of diagenetic expulsion) were scoured by the oxide of their trace element content. After carbonate precipitation had been exhausted, excess mobilised iron precipitated as sulphide as a result of the localised build up of sulphide ions. Gad et al (1969) studied concretions with pyritous rims and observed that in thin section the pyrite was present as anhedral blebs of similar size to and closely inter-grown with, grains of calcite mud. It was in this transition zone rim that cadmium, possibly as the sulphide was most strongly enhanced. A second pyritous rim sampled from another concretion in the Edale Shales was found to contain 25.0 ppm cadmium, 1170 ppm zinc and 3,800 ppm manganese.

In conclusion, it appears that, during the diagenesis process, considerable quantities of zinc, cadmium and manganese are known to have been in a mobile state such that they were available to be concentrated in centres of unusual physicochemistry. The redistribution of manganese in an environment of concretionary formation has been shown by Logrinento and Kosmachev (1960). They also demonstrated the mobile nature of cobalt towards concretionary formations and explained this in terms of the selective adsorptive capacity of manganese hydroxide gels with respect to these elements (see Table 7.3 for summary).

TABLE 7.3 MAJOR AND MINOR ELEMENT CONCENTRATION IN POST-DIAGENETIC ROCK SAMPLES AND IN ASSOCIATED SHALES

Sample Type	Sample Identification Number	Trace Element Content (ppm)				Major Element Content (%)	
		Cadmium	Zinc	Lead	Manganese	Iron	Calcium
Calcareous Concretion	807	16	62	52	221	4.91	0.37
	819B	N. d.	20	48	408	1.1	0.5
	825	3	28	58	8300	2.2	0.55
	827	100	92	58	2500	8.0	0.41
	836	4	136	62	400	2.2	0.48
Siderite Nodule	822	2	118	19	270	45.0	N. det.
Iron rich nodule interior	819A	11	45	67	2976	2.2	N. det.
'Skin' nodule surround	819	22	537	34	3120	9.5	N. det.
	814	25	1170	43	3800	9.6	0.035
Adjacent black shale	816	3	118	43	1392	4.5	N. det.
	817	4	89	43	1800	5.58	N. det.
Pyrite-rich clay band	815	4	180	29	4800	18.0	N. det.
	810	4	18	58	264	24.0	N. det.
Pyritous dark shale	798	N. d.	92	29	480	15.0	0.24

N. d. = not detected

N. det. = not determined

7.5 ENRICHMENT OF MERCURY AND MOLYBDENUM IN BLACK SHALES

7.5.1 MERCURY

Theoretically, mercury content in shales should be about 0.16 ppm or about two times the average for effusive rocks. Saukov (1965) reported the average content in shales from the Akai Mountains (USSR) Germany and Sweden to be 0.153 ppm: Permian and Carboniferous shales from the foremost locality averaged 0.148 ppm. In three samples of Mansf eld Kupferschiefer Stock (1934) reported 0.15 and 0.12 ppm although the mercury content in a composite sample of 36 European Palaeozoic shales was found to be 0.48 to 0.53 ppm. The data presented in Table 7.4 was obtained using a cold nitric acid extraction on black shales followed by atomic absorption analysis. A sufficient range of mercury was observed in each of the sets of samples to warr nt the use of the median value.

Mercury was notably enriched in those sets of samples which were found to be minor element rich by the method of the metal enrichment value explained in section 6.4 page 103. With the exception of the mercury enriched Silurian rocks of the Lake District, which were not included in Figure 6.6, those three sets of samples: E2 age Dove Shales, P1 Bowland Shale and H to R age Edale Shales, which were found to be the most minor element enriched, contained most median mercury. Conversely those sets of samples which were most detrital-rich were found to be most mercury poor. These were the representatives of the Aberystwyth Silurian and the Coal Measures shales from Chesterfield.

It may be concluded therefore, that mercury was slightly enhanced in the carbonaceous shales of the Millstone Grit and that accordingly those processes which led to the enrichment of the minor elements in carbonaceous shales appear to lead to the enrichment of mercury (see Table 7.4).

TABLE 7.4 MERCURY CONCENTRATION IN SETS OF BLACK SHALES

Sample Location	Geological Age	Mercury Content		Number of Samples	M.E.V Group Number
		Median	Mean		
Aberystwyth, Wales	Silurian	.034	.046	3	9
Skelghyll, Lake District	Silurian	.132	.163	6	-
Bristol	Trias	.086	.103	4	11
Bowland, Lancashire	Lower Worston Shale Group	.085	.117	5	20
Bowland, Lancashire	P1, Bowland Shales	.093	.093	5	21
Onecote, Derbyshire	P1-P2 Onecote Shales	.068	.068	2	18
Onecote, Derbyshire	E2, Dove Shales	.170	.143	5	15
Edale, Derbyshire	E2, Edale Shales	.085	.088	3	26
Edale, Derbyshire	H-R, Edale Shales	.140	.162	6	25
Chesterfield, Derbyshire	D5, Coal Measures	.034	.072	4	12

All results in parts per million

M.E.V. = Metal Enrichment Value

7.5.2 MOLYBDENUM

For the estimation of molybdenum in carbonaceous shales, three methods of Molybdenum extraction were used and compared. Experimental details are given in the appendix, page 403. That method of extraction which was considered most consistent for use with organic rich materials involved the use of a nitric-perchloric acid mixture and the following discussion is based on the results so obtained.

In a composite sample of 36 European Palaeozoic shales Kuroda and Sandell (1954) reported 4.5 ppm molybdenum and in an organic shale from Alaska, 9.3 ppm. They wrote that the carbonaceous and pyritic shales were usually much richer in molybdenum, often containing 100 ppm and more. In a study of the distribution of molybdenum in carbonaceous, siliceous shales Razumnaya (1950) estimated that probably 60% of the molybdenum was bound with the organic matter.

One of the Permian Marl Slate samples was found to contain a molybdenum content of 259.0 ppm whilst the four samples of the set contained a median content of 120.8 ppm (see table 7.5). This set of samples was considerably more enriched than any other, although the sets of representative samples from the P1 age Bowland Shales, P1 to P2 age Onecote Shales and H to R age Edale Shales were all notably enhanced in molybdenum. The median molybdenum contents were 47.1, 19.3 and 58.4 respectively. Molybdenum content in the minor element and mercury-rich E2 Edale Shales, was low, with a median of 3.5 ppm. The other notably minor element enriched set of samples from the E2 age Dove Shales also contained a low molybdenum content of median value 3.1 ppm.

A correlation could possibly exist between the presence of organic carbon in the Permian Marl Slate samples, which was found to be

TABLE 7.5 MOLYBDENUM CONCENTRATION IN SETS OF BLACK SHALES

Sample Location	Geological Age	Molybdenum Content		Number of Samples	M.E.V. Group Number
		Median	Mean		
Aberystwyth, Wales	Silurian (Valentian)	-	2.3	1	9
Skelghyll, Lake District	Silurian (Ludlow)	3.4	11.1	6	-
Durham	Permian Marl Slate	120.8	135.9	4	-
Bowland, Lancashire	Lower Worston Shales	7.4	11.7	4	20
Bowland, Lancashire	P1, Bowland Shales	47.1	49.7	6	21
Onecote, Derbyshire	P1 - P2, Onecote Shales	-	19.3	2	18
Onecote, Derbyshire	E2, Dove Shales	3.1	2.7	4	15
Edale, Derbyshire	E2, Edale Shales	3.5	21.1	3	26
Edale, Derbyshire	H-R, Edale Shales	58.4	57.4	4	25
Chesterfield, Derbyshire	D5, Coal Measures	1.2	1.2	2	12

All results in parts per million

M.E.V. = Metal Enrichment Value

14.65%, and the unusually high content of molybdenum and, in addition, the minor elements, cadmium, zinc and lead. No correlation appeared to exist however between the organic carbon content of representatives of the remaining sets of samples and molybdenum presence.

Molybdenum analysed by emission spectrometry was shown to be enhanced in 8 out of 26 sets of samples above the metal enrichment value (see Figure 6.3.1). Those minor elements which were consistently enriched in the same sets of samples apart from molybdenum, were copper, nickel and chromium.

In conclusion, molybdenum was found to be enhanced in the minor element rich and organic carbon rich rocks but exceptions did occur and these cannot be readily resolved (see Table 7.5).

7.6 ORGANIC MATERIAL IN BLACK SHALES

Nearly all sediments contain organic matter, the general average being 2% (Krauskopf, 1955). Black shales grade into oil shales - which contain large amounts of bituminous material, and coal - which is composed of coaly and kerogenous materials. The nature of the products of anaerobic burial and decay of organic matter depends partly on the kind of material buried, such as bitumen from marine organisms and humic material from woody detritus, and also on particular environmental conditions of deposition and the degree of previous and in situ oxidation. The effect of low-grade metamorphism on organic matter of sedimentary origin will be to rearrange the molecules of carbon into the amorphous crystal structure of graphite.

In the H1 age rocks of the Culm Measures of Cornwall, the median carbon content was found to be 2.88%, which is only slightly above the average for sedimentary rocks. The rocks have been subjected to a

metamorphism which has rendered the rock fabric homogenous and has resulted in a high rank measurement. Some very high fusinite and granules of sulphide were seen to be present.

In the rocks of the Central Province the median carbon content was much higher than average, ranging from 3.88 to 7.68% (see Table 7.6).

The onset of Bowland Shale deposition in Lancashire was associated with a massive influx of carbonaceous materials which resulted in an analysed median carbon content of 7.68%. Following the incursion of arenaceous detritus at the close of P1 age deposition, continued unsettled conditions in the environments of weathering and deposition prevented organic matter accumulating beyond an average of 3.88%. The onset of more stable depositional conditions in the E1 age Upper Bowland Shales permitted the retention of 5.15% median carbon. Examination of Bowland Shales has revealed the existence of cellular and broken-cellular fusinite (and semi-fusinite) structures in sparse and small organic particles within a rock with fine-grain size and a moderately pronounced shaly fabric. The rock had a mean reflectance, R_o of 0.936 which was high, but less than that of the Culm samples.

The presence of carbon increased in the younger H1 to H2 age rocks of Edale to a median of 5.34%, from a median of 5.15% in E2 age shales. A distinct shaly, laminated structure was found in the Edale Shales which contained abundant organic particles, abundant framboidal pyrite and considerable amounts of fluorescent materials in ultra-violet light (some of which may be algal). Two main types of vitrinite ranging widely in particle shape and size were identified; stringers, well-rounded and irregular particles as well as fusinite-semi-fusinite with cellular 'bogen' structure and irregular form. A gas chromatogram for a sample of Edale Shale indicated a mature rock with no steranes or tritespanes

TABLE 7.6 PRESENCE OF TOTAL CARBON IN BLACK SHALES

Sample Location	Geological Age	Carbon Content			Number of Samples
		Mean	Median	Range	
Skelghyll, Lake District	Silurian (Ludlow)	2.29	-	-	1
Durham	Permian Marl Slate	14.65	-	-	1
Bowland, Lancashire	P1, Carboniferous	7.73	7.68	6.08-10.48	5
Bowland, Lancashire	P2, Carboniferous	4.27	3.88	3.15- 5.94	5
Bowland, Lancashire	E1, Carboniferous	5.79	5.15	4.39- 7.45	6
Onecote, Derbyshire	P1-P2, Carboniferous	6.39	5.82	5.04- 8.52	5
Onecote/Dove Derbyshire	E2, Carboniferous	7.37	7.41	6.43- 8.21	4
Edale, Derbyshire	E2, Carboniferous	5.79	5.15	4.39- 7.45	9
Edale, Derbyshire	H1-H2 Carboniferous	5.90	5.34	5.31- 7.49	4
Bude Region, Cornwall	H1, Carboniferous	2.94	2.88	2.30- 3.69	4
Bude Region Cornwall	R2, Carboniferous	5.0	-	3.70- 6.29	2

All figures in percent

but which showed a good isoprenoid series. The mean level of reflectance R_o, was 0.684, although two to three distinct rank levels were identified, indicating different source materials or derived materials. The rock contained much low molecular weight material (estimated as 43 mgm. / 100 gm. hydrocarbons) which could possibly be terrestrial in origin.

The presence of carbon in the Onecote and Dove Shales ranged from 5.82 to 7.41%. Further analytical work on specimens of these shales was not undertaken.

To sum up, the relationship between the organic geochemistry of rocks from Bowland, Edale and Cornwall, can be represented as follows:

	↓	Decreasing	i) organics
Edale	↓	"	ii) size of organic particles
	↓	"	iii) 'laminated' shaly fabric
Bowland	↓	"	iv) Fluorescence
	↓	Increasing	i) rank
Culm	↓	"	ii) reflectivity (R_o)

The differences between the Edale and Bowland samples may be due to the increased rank i.e. increased temperature due to greater depth and time of burial and possibly, in part, to different source material and distance from shore. The smaller particle size in the Bowland samples indicates greater distance from sediment source.

7.7 ASSOCIATION OF MINOR ELEMENTS WITH CARBON

The relationship between a selected number of minor and major elements, including cadmium, with total carbon can be seen in Table 7.7.

In rocks of the Central Province cadmium always correlates positively with total carbon. The random association of cadmium in

	TOTAL CARBON EDALE	TOTAL CARBON BOWLAND	TOTAL CARBON ONECOTE
Cd	.53	.87	.14
Pb	-.50	.15	-.17
Zn	-.13	.39	-.40
Mo	.36	.85	.08
V	.58	.93	.77
Ni	.30	.11	.12
Ba	.80	.59	-.04
Ca	-.05	.31	.24
Al	.33	-.77	-.55
Number of samples	9	9	9
Level of significance, P			
.001	.8471		
.01	.7348		
.05	.6021		

TABLE 7.7 Correlation between carbon and other elements

carbonate structures as well as with organic carbon will have the effect of lowering the overall total carbon:cadmium correlation coefficient. The negative relationship between total carbon and calcium in the Edale Shales indicates that carbonate precipitation was not dominant. Consequently, the moderately good correlation between cadmium and total carbon in the same set of samples is a measure of the good association between cadmium and organic carbon. In the remaining Central Province areas, total carbon and calcium correlate positively, indicating that carbonate precipitation was of some importance in the sedimentation process. The lower positive correlation between total carbon and cadmium in the Onecote samples compared with the Bowland samples (0.14, 0.87) is an indication that cadmium is probably associated with both forms of carbon in an indefinite manner. The highly positive and significant cadmium: total carbon correlation coefficient in the Bowland samples (0.87, P=001) shows that cadmium is strongly related to one or other of the carbon forms, in all probability the organic carbon.

7.8 EFFECTS OF CADMIUM PRESENCE ON THE ZINC:CADMIUM RATIO

The ratio of zinc:cadmium calculated from the minimum enrichment values for thirty-six sets of black shale samples is 22. The degree of selective cadmium enrichment in black shales can be gauged by comparing the zinc:cadmium ratio calculated from the contents of metals in the average shale which is 316 (cadmium 0.3 ppm) and the ratio of the average contents of the metals in the earth's crust, which is 420 (cadmium 0.15 ppm, both figures Wedepohl, 1961).

In Figure 7.3 the ratio of zinc:cadmium was plotted against cadmium and was superimposed upon the graphs of cadmium vs. zinc. In order to simplify the thousand or so sample plots which appeared on an unsmoothed graph, each of the points on this figure represents the median value of firstly the zinc:cadmium ratio and secondly (superimposed)zinc, for each cadmium

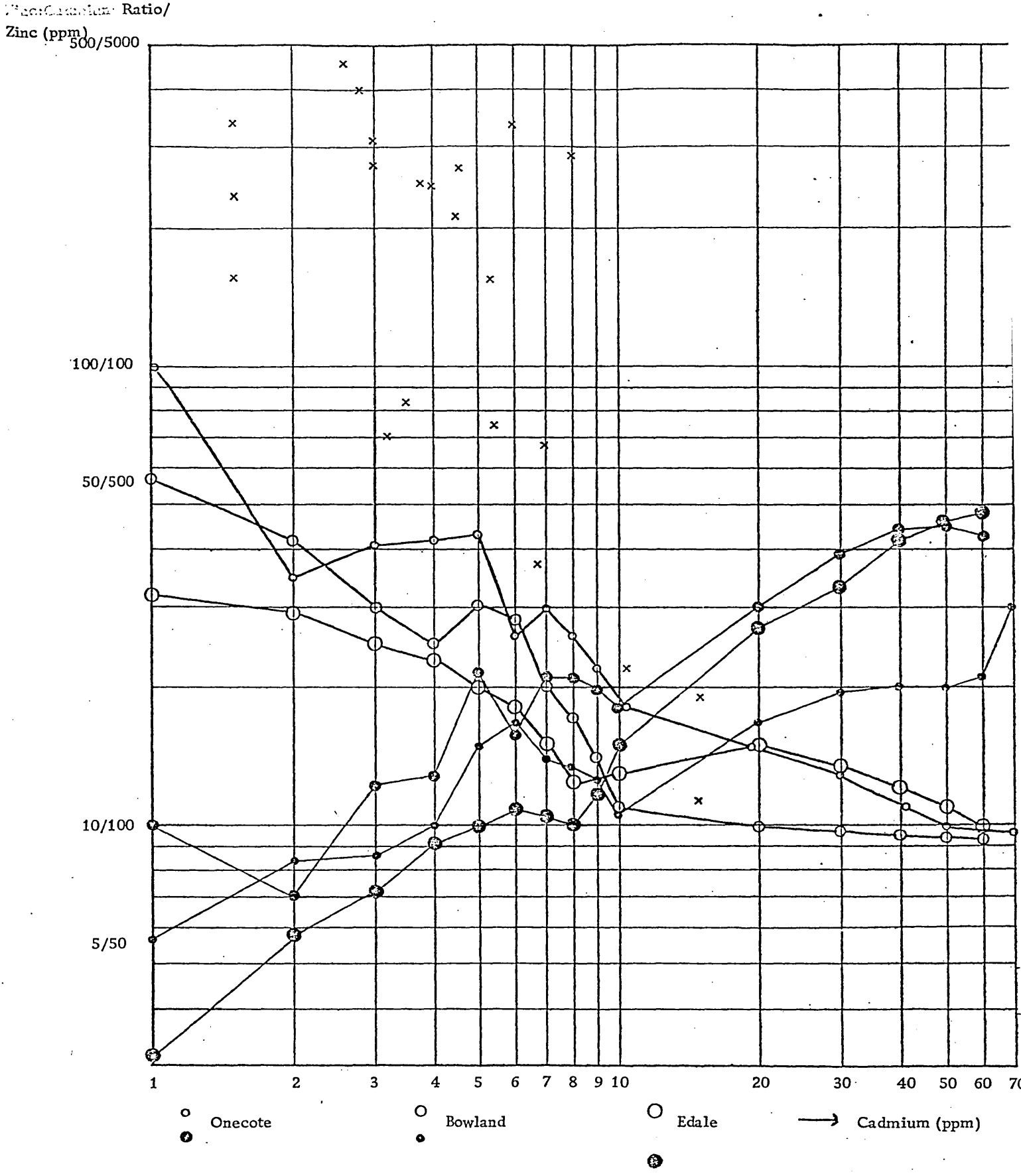


FIG. 7.3 SUPERIMPOSED GRAPHS OF CADMIUM vs ZINC (SOLID CIRCLES) AND CADMIUM vs Zn : Cd RATIO (OPEN CIRCLES) FOR SAMPLES FROM EDALE, BOWLAND AND ONECOTE SHALES

value from 1.0 to 100.0 ppm. Considering the cadmium vs. zinc graph firstly (which is represented by three solid lines with positive gradients) plots of rock analyses from the three areas of the Central Province display remarkable similarities. Apart from some minor fluctuation amongst Onecote and Bowland samples in the region of cadmium content 5 to 10 ppm, the overall gradients are similar. In the region of cadmium concentration 1.0 to 4.0 ppm, the gradient is 21:1, in the region of concentration 4.0 to 10.0 ppm the gradient is 13:1 and in the final region, with cadmium content ranging from 10.0 to 70.0 ppm the gradient is most shallow, at 6:1. Thus in all three areas, irrespective of their geographical isolation from each other, a general enrichment in cadmium content is not reflected in a proportionate increase in zinc content. Cadmium is being selectively enriched in carbonaceous, argillaceous rocks with respect to zinc. In the superimposed trends of cadmium against zinc:cadmium ratio this selective enrichment in cadmium can be seen as a progressive flattening of the smoothly decreasing graph, on cadmium increase. The greater tendancy for cadmium to adsorb onto colloidal materials than zinc may account for cadmium's selective enrichment. The papers by Manheim (1961a, b) discussed in section 4.4 page 58 , drew attention to the fact that in the Baltic Sea, salinity stratifactions perpetuated depletions of trace elements in the most stagnant parts of the basin of deposition and the highest concentrations of elements (precipitated from the water as sulphides) occurred in areas characterized by basal water aeration. Sufficient sulphide to precipitate both zinc and cadmium in the aerated zone may therefore not have been present, excess mobile cadmium would consequently have become widely surface adsorbed and greater quantities of zinc dispersed out of the area. It is also conceivable that after sedimentation and during diagenesis the expelled pure waters rich in mobile zinc and cadmium which had not been in a sulphide or detrital form, were scoured by colloidal materials in the upper shale beds which selectively removed the more susceptible cadmium.

In complete contrast to the graphs of the syngenetically enriched area samples the actual plots of cadmium vs. zinc:cadmium ratio for samples of the Marl Slate, Durham, are also included in the figure. In comparison to the syngenetically enriched rocks which contained between 75 and 123 ppm zinc when cadmium concentrations were around 3.0 ppm, the Marl Slate was found to contain between 850 and 1190 ppm zinc at the same cadmium concentration. Selective enrichment in zinc would appear to have taken place in the Marl Slate. In those four samples in which cadmium was found to be present in amounts more than 10.0 ppm the equivalent zinc presence was only around 200 ppm, implying that during those times of cadmium enrichment in the Marl Slate, zinc was present in comparitive amounts to those which were present in the syngenetically enriched rocks of the Central Province. The highly unusual authigenic enrichment in the sampled parts of the Marl Slate can therefore be said to be solely zinc orientated. The normal processes of syngenetic cadmium and zinc enrichment in the bituminous rock body appears to be similar in nature to those which prevailed in the Visean basin of the Central Province.

CHAPTER 8

8 THE DETECTION OF CADMIUM FORM BY THE USE OF AQUEOUS CHEMICAL EXTRACTIONS

8.1 INTRODUCTION

Investigations of sedimentary depositional environments by the comparative study of sequential correlation diagrams (Section 6.6) drew attention to the ever changing character of sediments during the evolution of the environment. It was found that the chemical composition of incoming detritus for sedimentation was broadly dependent on two factors: firstly, the character of the parent rock body and secondly on the physiochemical conditions which prevailed upon this body during weathering. Upon sedimentation in saline environments the heterogenous detritus would appear to be in a state of mineralogical, and hence chemical, disequilibrium. The resultant potential for early diagenetic alteration within the sediments plays a critical part in the formative history of those mineral species which prove to have an affinity for the minor elements. The behaviour of cadmium in an argillaceous environment where clay minerals are forming alongside organic complexes and sulphide precipitants, shall be further considered in this and the following chapters. Two techniques shall be used to substantiate the circumstantial evidence so far obtained regarding cadmium affinities in the black shale environment. The first, to be dealt with in this chapter, will involve the use of aqueous chemical extractions to identify those species with which cadmium is associated. The second, to be dealt with in the following chapter, makes use of a pyrolysis method of species identification.

The identification of mineral species by the use of chemical extractants is based on a knowledge of the ability of a specific chemical to solubize a single component or set of related components, with their

associated minor elements from within the body of a rock. The choice of chemicals, their optimum strengths and contact periods depends largely on a recognition of the principal minor element-containing components within the natural material in question. Once a set of extractants has been effectively chosen, the relevant rock or soil can by chemically dissected and the presence of a minor element within the mass assessed, according to its loyalties to each dissected part.

8.2 CHOICE OF EXTRACTIONS

Two complementary experiments, each involving the use of five extractants, were carried out. The first, regarded as being the most analytically reliable necessitated the total acid attack and subsequent analysis for cadmium of the residue resulting from partial extraction. The second method required the supernatant liquids from each partial extraction, which contained the extracted components, to be analysed in conjunction with a series of prepared reference standards.

The extractants used and their field of action are as follows:

1 1 NORMAL AMMONIUM ACETATE, pH7

It was discovered by John in 1972, 1973 that amounts of cadmium contained in a soil mobilised by this low strength reagent were significantly related to levels of cadmium in raddish and lettuce grown upon that soil. Consequently the role of this extractant is to determine the amount of readily exchangeable cadmium (and other heavy metals) which is available in the rock and its overburden to the plants grown in the overburden.

2 ACETIC ACID, STRENGTH 25%, COLD

In order to differentiate between the detrital and non-detrital fraction of carbonate rocks Ray et al (1957) noted that dilute acetic acid

would dissolve out all but the dolomite of the carbonates of most rocks. In addition the reagent would remove readily exchangeable metal occupying low-energy adsorbed sites within the matrix of the rock. Arrehenius and Korkish (1959) experimenting with the effects of dilute acetic acid on iron-manganese nodules found that, even after heating for two hours at 100^{o}C the amount of soluble iron oxide was equivalent to less than 15% of the total oxide soluble in hydrochloric acid. Less than 7% of the total manganese oxide was also removed by the same reagent.

3 ETHYLENEDIAMINETETRACETIC ACID (EDTA), STRENGTH 0.05 MOLAR

EDTA is a strong chelating organic extractant which complexes and removes soluble organic material from the sample along with any complexed metal ligands (Hodgson 1960). It has been shown in addition(by Hodgson)that EDTA strips cations from the surface of montmorillonite, although the desorption took ten days to reach completion. The difficulty therefore in accurately quantifying the effects of EDTA on predominantly inorganic sediments pervaded by carbonaceous matter is so extreme that results pertaining to this reagent are considered completely in isolation.

4 HYDROXYLAMINE-HYDROCHLORIDE STRENGTH 25% AND ACETIC ACID, STRENGTH 35% MIXTURE

Known as a reducing-oxidising reagent, the mixture will selectively dissolve out ferro-manganese minerals and associated iron oxides, carbonate minerals and readily exchangeable fractions. The reagents selective preference to dissolve manganese compounds was demonstrated by Chester and Hughes (1967) who showed about 78% of total manganese and about 4% total iron present in a pelagic sediment were soluble in the reducing-oxidising agent.

5 HYDROCHLORIC ACID, STRENGTH 50%, HOT

The most important attributes of this extractant are that it can completely attack the clay minerals and most of the common sulphide minerals (Ray et al 1957). In addition the acid dissolves all carbonates and removes only adsorbed metals. Hydrochloric acid cannot attack the silicate minerals nor can it completely oxidise the kerogenous matter which is common in carbonaceous shales. Several relevant conclusions are drawn in the following sections with regard to the inability of this reagent to attack iron sulphide (pyrite).

8.3 THE ESTIMATION OF ANALYTICAL ERROR

The maximum error which can be expected in any of the results discussed in the following sections is expressed as the percentage deviation of cadmium as estimated by the two extraction experiments from the total cadmium content of the samples as determined by duplicated total acid attacks. The deviations represent cumulative errors in the samples due to sampling, experimental and analytical variability, and appear to increase in value in conjunction with increasing strength of the extractants (see Table 8.1). The extraction reagent however, which determines the greatest deviations from normality, is acetic acid, where the range of cumulated extraction-cadmium deviated from actual cadmium values by a figure ranging from 26% to 44%. In contrast to this, the range of deviation recorded for the hydrochloric acid extractions is 2% to 9% in Central Province samples and up to 24% in the Culm Measures' samples. In conclusion, consideration of the summary values for all samples in Table 8.1 gives the impression that deviation of the cumulated extraction-cadmium values from actual cadmium values is reassuringly low.

8.4 THE IDENTIFICATION OF CADMIUM SPECIES FROM THE ROCKS OF THE CENTRAL PROVINCE

8.4.1 INTRODUCTION

The behaviour of cadmium during the formation of the carbonaceous

TABLE 8.1 PERCENTAGE DIFFERENCE BETWEEN CADMIUM DETERMINED BY EXTRACTION EXPERIMENTS AND AS DETERMINED BY TOTAL ACID ATTACK

Sample Location	EXTRACTANT USED										Number of Samples
	Ammonium Acetate		Acetic Acid		E.D.T.A.		Reducing - Oxidising		Hydrochloric Acid		
	Mean	Median	Mean	Median	Mean	Median	Mean	Median	Mean	Median	
1. Onecote	27	28	26	26	21	18	16	17	9	5	8
2. Bowland	10	5	28	29	13	13	14	13	3	0	9
3. Edale	18	22	44	46	17	9	6	6	2	0	5-6
4. Culm Measures	30	13	34	41	17	17	27	25	24	17	6
5. All samples used	21	17	33	35	17	14	16	15	9	6	29

If Cd_E = extracted Cd and Cd_T = total Cd, tabled values are $((|Cd_E - Cd_T|) \times 100)/Cd_T$ percent.

shales of the three areas of the Central Province studied is, for the most part, remarkably consistent (see table 8.2). The only apparent distinction which can be made between the three sets of samples involves that metal which can be removed from the samples by the two weakest extractants. Thus, whilst the rocks of Bowland are least affected by the action upon them of ammonium acetate, they are conspicuously most affected by the action of acetic acid.

In the shales from Onecote, 70% of the total extractable cadmium is removed by the three strongest extractants and represents that metal which is contained in the iron-manganese oxides, as substitutes in the clay mineral and pyrite lattices, as sulphides and as a constituent of residual kerogen. In the shales of Edale 75% of the total extractable cadmium is so contained and in the shales of Bowland 71% is so contained. In all three areas between 41 to 44% of the total extractable metal forming this 70 to 75% is contained in the lattices of clay minerals and as sulphides. The samples were not analysed for sulphur so consequently no criteria can be applied which could indicate which of the two processes was more important. However, as a result of the work carried out on chosen samples at the Organic Geochemistry Unit at Newcastle-upon-Tyne, microscopic framboidal sulphides and grannular sulphide patches have been positively identified. It will be assumed therefore that the formation of sulphides in the organic-rich reducing environments of black shale sedimentation is the most important of the cadmium retention processes. The formation of cadmium-clay mineral associations in the environment of weathering before transportation and deposition will nevertheless account for the retention of a small proportion of the 41 to 44% of total cadmium which is dissolved by hydrochloric acid.

The detailed breakdown of cadmium into partition categories concludes this section of the chapter.

TABLE 8.2 CADMIUM SPECIES BEHAVIOUR IN BLACK SHALES OF THE CENTRAL PROVINCE AND CORNWALL

SIMPLIFIED CADMIUM ASSOCIATIONS	PALAEOGEOGRAPHIC REGION			
	Central Province			Cornwall
	Onecote	Edale	Bowland	Culm
1. Adsorbed	15	18	5	19
2. Carbonate/clays	15	7	24	19
3. Manganese Specific	24	26	23	21
4. Sulphide/Clay lattice	42	44	41	32
5. Pyrite/Residual Organic	4	5	7	9
6. Organic	29	27	30	33
Total Extractable Metal	35.4	59.4	27.3	32.6
Number of Samples	8	6	10	6

Relationship of Associations with Chemical Aqueous Extractions:

1. Adsorbed: Extracted by Ammonium Acetate
2. Carbonate: Extracted by Acetic acid less that portion extracted in 1.
3. Manganese Specific: Extracted by reducing oxidising mixture less that removed by acetic acid
4. Sulphide/Clay lattice: extracted by hot hydrochloric acid less that removed by reducing-oxidising mixture.
5. Pyrite/Residual Organic: that cadmium content residual after hydrochloric acid attack.
6. Organic: Extracted by EDTA less that removed by acetic acid.

Figures for associations 1 to 6 are the means of 'percent of total available cadmium extracted'.

8.4.2 ADSORBED CADMIUM

In the process of adsorption, elements are retained at the phase boundaries of minerals by physical forces. The governing principles are such that sorption increases as the grain-size of a sediment decreases. Therefore clay-sized particles and amorphous matter are very important as sorbents. Some of the colloidal materials, like syngenetic iron oxides and organic matter will not survive in their original condition on diagenesis and elements enriched in them will be redistributed. Thus, the presence of clay minerals which may be either partly regenerated or unaffected by diagenetic effects will to a great degree control the extent to which cadmium can be seen to be in an adsorbed form. The Bowland samples have only 5% of the total available metal in an adsorbed form (see Table 8.2) which classifies them, with respect to cadmium submission, as the least readily extractable of the shales of the Central Province. The presence of the clay minerals and mica-chlorite groups within these rocks amounts to only 8% of the total mineral content (mineral groups 2 and 3, Table 8.3) which also characterises, perhaps significantly, as the most clay poor of Central Province shales.

In contrast, the shaly rocks of the remaining two areas are relatively clay-mica rich; the samples analysed by x-ray diffraction containing up to 25% aluminium-silicates. Both these sets of samples have up to 15% of the total extractable cadmium within them in a readily exchangeable form.

In real terms, working with the average cadmium content in black shales of the South Pennines area, the amount of cadmium available to weak extracting solutions in soils (with a strength equal to that of neutral ammonium acetate) is between 1.3 and 1.4 ppm. If all this cadmium is retained in the soils it would represent a 3 to 14 fold enhancement in cadmium in comparison to the scientifically accepted

MINERAL GROUP	CENTRAL PROVINCE			CORNWALL	AVERAGE SHALE		SANDSTONE
	ONECOTE	EDALE	BOWLAND	CULM	LEITH & MEAD (1915)	CLARKE (1924)	CLARKE (1924)
1. Quartz	62	43	53	48	32	22	67
2. Clay Minerals	22	13	6	3	28	25	7
3. Other Aluminium Silicates (mica-chlorite)	3	11	2	43	6	0	0
4. Iron Oxides	4	7	2	0	5	6	2
5. Carbonate	12	39	31	0	8	6	11
6. Sulphides	7	9	0	0	0	0	0
7. Carbon	0	4	2	0	1	0	0
8. Feldspar	0	3	2	3	18	30	12
9. Gypsum	0	0	0	0	1	0	0
Number of samples	2	2	2	1			

TABLE 8.3 Black shale mineralogy compared with average shales.

average content of the metal in soils of between 0.1 to 0.5 ppm (John et al 1972). In comparison the amount available to solutions of such power in soils from the black shales of the North Pennines (in Bowland) is only 0.6 ppm.

8.4.3 CARBONATE AND LOW-ENERGY EXCHANGEABLE CADMIUM

Almost a quarter of the total available cadmium in the Bowland rocks adopts inter-layer clay mineral adsorption sites and substitutes in the carbonate lattices. In the rocks of the Bowland Province there is, in addition, more calcite present, on average, than in the rocks of the remaining Central Province areas (see Tables 8.2 and 8.3) and this may be significant. In contrast only 7% of the total available cadmium is known to be present in such associations in the Edale area, and this could reflect either on the nature of the primary detritus entering the basin i.e. the extent to which cadmium is already engaged within the inter-layer clay minerals, or to some manifestation of the specific physicochemical conditions which prevail during the precipitation of carbonate. Carbonate precipitation was relatively common even during the deposition of the Edale Shales, but unless the pH conditions are at the very least mildly acidic, then cadmium will not be available in a mobile and hence potentially substitutable form.

The presence of carbonate minerals in Onecote is comparitively uncommon but the presence of clay minerals is unusually high (see Table 8.3). It must be assumed therefore that the association of cadmium in inter-layer positions especially in those clay minerals of high cation exchange capacity, is the vital retentive process. Studies regarding this problem of the maturity and type of incoming detritus and the physicochemical variations concerned in carbonate precipitation will be made in Chapter 10.

To summarize, the subsequent partitioning of cadmium in these phases is higher in the shales of Bowland then in the shales of the remaining two areas. The action of mildly acidic leaching solutions upon the shales would therefore be to extract 3.6 ppm cadmium from the rocks of Bowland, 2.7 ppm from the rocks of Onecote and 1.9 ppm from the rocks of Edale (see Table 8.4).

TABLE 8.4 ACTUAL CADMIUM CONCENTRATION IN BLACK SHALES CALCULATED FROM AVERAGE TOTAL AVAILABLE CADMIUM AND PERCENT OF TOTAL AVAILABLE CADMIUM EXTRACTED

SIMPLIFIED CADMIUM ASSOCIATIONS	PALAEOGEOGRAPHIC REGION			
	Central Province			Cornwall
	Onecote	Edale	Bowland	Culm
1. Adsorbed	1.34	1.4	0.6	0.2
2. Carbonate/clays	1.3	0.5	3.0	0.2
3. Manganese specific	2.1	2.0	2.8	0.3
4. Sulphide/clay lattice	3.7	3.3	5.0	0.4
5. Pyrite/residual organic	0.4	0.4	0.9	0.1
6. Organic	2.6	2.3	3.7	0.4
Average total extractable Cadmium	8.9	7.6	12.3	1.26
Number of samples	87	105	156	270

All results are in parts per million

8.4.4 ORGANIC MATTER CADMIUM

The effects of EDTA upon the black shales of all areas is to remove a narrow range of between 27 and 33% of the total cadmium from the samples (see Table 8.1). An interesting correlation can immediately be made between the known increasing rank of the black shales (calculated from reflectivity experiments on polished shale surfaces) from the lowest in Edale, where the lowest percentage total cadmium (27%) is removed by EDTA, through intermediate levels of rank and EDTA efficiency in Bowland, to the Culm samples where highest rank couples with the highest percentage cadmium removed by EDTA (at 33%). This would seem to indicate that cadmium adsorption may have taken place after deposition and burial (possibly from connate water) and furthermore that increasing time and temperature of burial accelerates post-burial adsorption. But just how much of the organic matter-cadmium association is primary and how much is secondary?

The willingness of plants to take up cadmium from soils has been demonstrated by John et al (1972, 1973) and such a process may have led to a relative enrichment of cadmium in plants relative to behaviouraly similar elements, like, zinc, before transport into the black shale depositional environment. This enrichment process is shown in the $\frac{\text{zinc}}{\text{cadmium}}$ ratio for all areas, which decreases markedly as cadmium concentration increases (see Figure 7.3, chapter 7). However alterations in organic matter by physical-biological-chemical changes upon lithification may obscure or eliminate chemical patterns characteristic of organic matter of living systems.

The smoothness of the curve joining the Edale plots in the cadmium/$\frac{\text{zinc}}{\text{cadmium}}$ graph (Figure 7.3) in comparison to the erratic nature of those curves for the Bowland area, may indicate the degree to which re-mobilisation due to the humification processes of organic matter had taken place in the latter set of samples. The initial enhancement of cadmium

over zinc caused by preferential plant uptake would tend to diminish as greater depth and time of burial advanced the process of humification. The net result of the humification or maturation processes would be to make the structurally simpler hydrocarbons thus formed more attractive for the subordination of all trace elements available in the connate water and this would confuse any clear-cut primary enhancement patterns. Vine, Tourtelot and Keith (1969) do suggest firstly, that most of the minor elements shown to associate with organic matter are probably fixed or sorbed by decaying organic matter at a short distance below the sediment-water interface and that some may be released, mobilised and recombined in new ways following organic chemical changes after such burial. Secondly, they advance the suggestion that minor element adsorption on organic matter may have taken place from connate water after deposition and burial of the sediment, although the data was not present to prove this. This latter process appears to be what is happening in these sets of samples.

8.4.5 MANGANESE AND FERRIC OXIDE CADMIUM

The proportion of total cadmium which is removed by the reducing-oxidising agent is remarkably uniform in the three Central Province areas; between 23 and 26%. Minor elements are known to be scavenged from dispersive solutions by co-precipitation as a minor constituent of non-detrital minerals. Of the commoner non-detrital minerals hydrous iron and manganese oxides are the most important of those which contain notable levels of minor constituents. Although not well understood, it has been suggested by Hawkes and Webb (1962) that minor element fixation could occur within the crystal lattice, as occluded ions or microcrystals and either as surface or interlayer sorbents.

Between 2.0 - 2.8 ppm of average total cadmium in Visean shales is contained in this category (see Tables 8.2 and 8.4).

8.4.6 CLAY LATTICE AND SULPHIDE CADMIUM

In addition to the probable incorporation of cadmium within growing clay mineral lattices at the site of weathering, the element also participates in charge-balancing substitutions in the fundamental layers of clay minerals. These processes of absorption would possibly result in the existence of positive correlations between the presence of cadmium and the key elements in the detrital and the diagenetic minerals. In addition the formation of sulphides in strongly reducing, anaerobic environments caused precipitation of the dominantly chalcophile elements. The expected association of the other chalcophile elements zinc, lead and iron does occur and will be considered in more detail in subsections 8.7.1-4

The range of detected cadmium presence in these forms is between 41 to 44% of the total available metal and this significantly narrow range of presence again emphasizes the consistency of cadmium behaviour in depositional basins of different character and of wide geographical distribution (see Table 8.2).

The greater overall average total cadmium influx into the Bowland Forest depositional area is reflected in more cadmium being incorporated into the sulphide phases (see Table 8.4).

8.4.7 PYRITE LATTICE AND KEROGEN CADMIUM

Very little cadmium is residual in Central Province samples after attack by hot hydrochloric acid. The narrow range from 4 to 7% of total available metal has, once again, insufficient variation to suggest that any process of retention is prevalent in one area and not in another.

The presence of almost 50% of the total extractable iron remaining in the samples (see Table 8.4) strongly implies that the principal component remaining after hydrochloric acid leach is pyrite and that because of the

strong chalcophicity of cadmium most of the metal will be associated with it. Up to 0.9 ppm cadmium therefore, of a total available content of 12.3 ppm, will substitute in the pyrite lattice (figures for Bowland, see Table 8.4). In more exceptional circumstances, i.e. where cadmium is present in greater total amounts, the participation of cadmium in this phase may be as high as 4.0 ppm, (Onecote sample 1090927). where the total available cadmium metal is 71.0 ppm. The substitution ratio in this sample is 1.0 ppm cadmium per 1.0 per cent iron. The percentage of total zinc which is residual after hydrochloric acid attach is almost exactly the same as that of cadmium, at 6.0 per cent. It is likely therefore, that cadmium and zinc substitute equally into the growing pyrite structure.

No evidence can be presented to suggest that some cadmium is present in the infrastructure of that kerogenous material which is visibly residual after attack by hot hydrochloric acid. However, quantitative evidence has been presented in subsection 8.4.4 which suggested that the effectiveness of the leaching power of the EDTA reagent increased in conjunction with increasing rank (or maturity) or polished shale specimens. This implies that some cadmium is associated with the residual coaly matter.

8.5 SUMMARY OF CADMIUM PARTITIONING IN ROCKS OF THE CENTRAL PROVINCE

Despite variations in physiochemical conditions which must have existed in each of the black shale depositional environments, the behaviour of cadmium during sedimentation and diagenesis is similar in its pattern in each. The element primarily participates in the precipitation of sulphides. Of equal secondary importance are firstly, the association of cadmium in secondary iron and manganese oxide precipitation; and secondly, the formation or retention of stable cadmium-carbon compounds. Thirdly, the element appears to enter the growing iron sulphide lattice. Variation occurs in lower energy sites where inter-layer cation substitution and

surface adsorption have been shown to exist. Conditions can also exist whereby cadmium may substitute into the growing carbonate lattices.

The lowest energy partition sites, where cadmium adsorbs and exchanges in inter-layer clay mineral sites, are those which would have been satisfied last during the sedimentation and diagenetic redistribution processes. However, it is interesting to note that until these categories are considered little differentiation can be made between the three sets of samples. As all three study regions of the Central Province are in a single, large basin of deposition (see chapter 5) it can be concluded that apart from certain minor fluctuations, conditions of deposition were very similar throughout its extent.

8.6 THE IDENTIFICATION OF CADMIUM SPECIES FROM ROCKS OF THE CULM MEASURES, CORNWALL

In comparison with the cadmium-rich rocks of the Central Province the overall average cadmium presence in the black shales of the reconstituted Culm Measures is only 1.26 ppm. Cadmium-rich rocks do exist however, and these were used in the extraction experiments to identify the partitioning behaviour of the element.

The most dominant cadmium forms, as in Central Province samples, were those removed by hydrochloric acid and which have been identified primarily as the soluble sulphides and in addition as clay lattice constituents. However, reconstitution of the detrital clays to micas and chlorites as a result of the localised thermal metamorphic event (see Table 8.3), would have caused mobilisation of cadmium from the original clay lattices. It may be assumed therefore that most, if not all of the 32% of total extractable cadmium removed by hydrochloric acid was contained in syngenetic or diagenetic sulphides. Cadmium presence in the three weakest or readily dissociated phases amounted to almost 60% of total extractable metal (see Table 8.2) which was notably more than combined extractable metal from the same phases in Central Province shales.

Cadmium had been resited, as a result of the metamorphic event, into the adsorbed and weakly absorbed situations made available by the new suite of minerals.

The percentages of total cadmium which were removed by the agent EDTA in the Edale, Bowland and Culm Shales were 27, 30 and 33% respectively and these variations display a trend which is in agreement with tha of increased organic rank amongst them. A correlation could possibly exist between temperature, depth of burial and thermal metamorphism, which leads to the maturing of the organic detritus, and the attraction and stabilisation of increasing amounts of cadmium. On the other hand, the coincident trends could simply reflect the different nature of organic matter in each of the three areas.

As much as 17% of total cadmium was residual after hydrochloric acid attack in the Culm samples in which granular patches of sulphides have been positively shown to exist. An average of 13% total zinc, 29% total lead and 33% total iron was also present in the same category. It is suggested therefore that 1.0 ppm cadmium entered the growing pyrite lattice although in an average cadmium containing Culm shale the substitution would be analytically undetectable. The biggest substitution represented a ratio of 1.0 ppm cadmium to 1.3% iron.

As in Central Province samples, no evidence can be presented to show that any of the pyrite-cadmium is actually associated with residual kerogenous matter.

8.7 SPECIES PRESENCE OF OTHER ELEMENTS IN BLACK SHALES

8.7.1 ZINC

Apart from cadmium the elements zinc, lead, iron and manganese were analysed for during the extraction study and the results for these are illustrated in Tables 8.5.1 to 8.5.4.

TABLE 8.5.1 ACTUAL ZINC PRESENCE

Zinc Associations	Palaeogeographic Region			
	Central Province			Cornwall
	Onecote	Edale	Bowland	Culm
1	5	17	15	2
2	24	19	11	7
3	11	23	17	6
4	276	140	136	60
5	43	56	18	11
6	61	69	65	23
Average total extractable zinc	358	255	196	85
No. of samples	83	105	120	269

TABLE 8.5.2 ACTUAL LEAD PRESENCE

Lead Associations	Palaeogeographic Region			
	Central Province			Cornwall
	Onecote	Edale	Bowland	Culm
1	1	1	1.6	N.d.
2	10	1	10.7	6
3	17	2	12.0	3
4	18	18	32.0	15
5	23	34	31.0	28
6	17	7	22.0	7
Average total extractable lead	69	56	98.0	52
No. of samples	87	106	121	195

TABLE 8.5.3 MANGANESE SPECIES IN BLACK SHALES

Manganese Associations % Extracted	Palaeogeographic Region			
	Central Province			Cornwall
	Onecote	Edale	Bowland	Culm
1	3	6	8	8
2	N.d.	N.d.	10.5	17
3	59	19	44.5	25
4	15	39	24	25
5	23	36	13	25
6	29	29	35	29

TABLE 8.5.4 IRON SPECIES IN BLACK SHALES

Iron Associations % Extracted	Palaeogeographic Region			
	Central Province			Cornwall
	Onecote	Edale	Bowland	Culm
1	N.d.	1.5	N.d.	N.d.
2	2	1.5	2.7	8
3	7	4	9.5	11
4	47	49	44.5	33
5	44	44	43.5	52
6	2	4	3	4

N.d. = not detected

Figures, except those for iron and manganese (in percent) in parts per million

For explanation of associations 1 to 6, see table 8.2 notes.

The most dominant process which has determined the partitioning of zinc in the rocks of all areas was the formation of sulphides (Table 8.5.1). In the Onecote Shales up to 77% of total extractable zinc was soluble in hydrochloric acid alone and in the Central Province Shales an average of 68% was soluble. It has been assumed that the substitution of zinc within the lattices of clay minerals, the figure for which was included in the previous values, was a subordinate process. In contrast, in the Onecote region only 1.4% of total zinc was adsorbed, the average figure for all areas being around 4%. The average zinc adsorbed, cation exchanged in clays, as a substituent in iron-manganese oxides and in carbonates amounted to only 6% of the total which, in real terms was an average of 13 ppm zinc from a total zinc content of 224 ppm.

Between 9 to 13% of total zinc was residual after hydrochloric acid attack for all shales with the exception of the Edale Shales where 22% of total zinc remained. El Shazly (1956) reported that zinc was one of the commonest trace elements observed in pyrite although he further wrote that pyrites of sedimentary origin were notably deficient in this and several other elements. Pyrite was positively identified in the Edale Shales and consequently it seems probable that up to 56 ppm zinc can substitute into the pyrite lattice.

In summary, it is probable that the distribution of zinc upon entering the basin of deposition was controlled by the strong chalcophile tendancies of the element in a sulphide-rich environment. The zinc appeared to provide greater evidence of the richness of the environments of black shale deposition in sulphur than did cadmium; furthermore the smaller ionic radius of zinc compared with that of cadmium (respectively 0.74Å, 0.97Å) make it less susceptible to processes of adsorption and absorption.

8.7.2 LEAD

Between 59 and 94% of total extractable lead was removed by hydrochloric acid alone and was residual after its extraction (see Table 8.5.2). Apart from samples from the Edale and Culm Shales; the proportions extracted by acid and those residual after extraction were approximately equal. In the Edale samples more lead was associated with post hydrochloric acid residues and this is related to the presence of lead sulphide. Lead in the hydrochloric acid soluble phase is associated in all probability, with zinc sulphide.

Of the remaining lead the partitioning characteristics vary markedly from area to area; the only common factor being the presence of tiny amounts of lead from all areas which can be removed by the action of neutral ammonium acetate. Only from 0 to 1.9% lead was in an adsorbed form and hence readily available to soils and plants. In Edale for example, little total lead remains for incorporation either into cation exchange sites in clays, organic complexes or into ferro-magnesian minerals. In Onecote however, by contrast, a quarter of total lead was incorporated in or onto principal secondary minerals.

In conclusion, the behaviour of lead was comparable with that of zinc with the notable exception that lead forms its own insoluble sulphides and its presence in weakly adsorbed forms is marginally less apparent.

8.7.3 MANGANESE

The manganese specific reducing-oxidising agent leached most of the total exchangeable manganese from samples of all areas with the exception of those from Edale where it has been shown that sulphides of lead and zinc were present. Deer et al (1962) suggested that manganese along with cadmium, iron and copper occurred in galena but is probably mostly

present in associated chalcopyrite, sphalerite or other sulphides. In the non reconstituted rocks of Bowland and Onecote, between 44 and 59% of total manganese was removed, probably from the principal secondary oxides, by the use of the reducing-oxidising agent (see Table 8.5.3). Surprisingly little (between 3 to 8%) of total manganese was readily available to neutral ammonium acetate. Rather variable amounts of manganese are associated with the presence of sulphides; a total of 37% total manganese was removed by hydrochloric acid and was residual after its action in Bowland Shales whereas 75% of total manganese responded to the action of the acid in Edale Shales. Such erratic behaviour must have been caused by the presence of highly variable physiochemical conditions in all areas during deposition which affected, amongst other things, the chalcophile tendancy of manganese. In contrast to such erratic behaviour, rather constant amounts of manganese were removed by EDTA. As no great difference existed in total carbon presence between all four areas it can be assumed that manganese colloids were mutually attracted to organic colloids.

In summary, where sulphide presence did not dominate, and where oxidation potential was high enough to allow the formation of oxides, the predominant form of manganese was as the oxide; where conditions of fluctuating Eh were apparent the element appeared to enter into the sulphide phase.

8.7.4 IRON

Like manganese the form of iron which was soluble in hydrochloric acid and residual after acid attack accounted for a high proportion, in this case about 90% of the total exchangeable metal (see Table 8.5.4). In contrast to the regional behaviour of manganese however, the division of iron between these two categories was almost equal in all Central Province

areas. In the Culm Shales iron extracted by and residual after hydrochloric acid attack was 33 and 52% of the total metal respectively. This 85% represented the substitution of iron into the lattices of clay minerals and the growing sphalerite, galena and pyrite minerals. Substitution of iron into the growing pyrite lattice was taken to be that of singlemost importance.

Small proportions of total exchangeable iron were further divided as follows: between 4 and 11% of total iron was included in the principal oxides, between 0 and 1.5% of total iron was adsorbed, between 1.5 and 8% formed carbonates or exchanged into clay minerals and between 2 and 6% was involved with the presence of organic matter (see Table 8.5.4).

CHAPTER 9

9 THERMALLY EVOLVED VAPOUR-PROFILE STUDIES

9.1 METHODOLOGY

Analysis of materials by Pyrolysis, the breakdown of complex materials into simpler units by the use of heat, has been a technique known since the eighteenth century. Developments, primarily in the field of metallurgy, in the USSR and the West since the turn of the present century contributed much to the development of the theory of thermal gas analysis and to the evolution of a wide range of thermo-analytical techniques dependent on weight changes, energy changes, dimensional changes and detection of evolved volatiles. The argon-plasma spectrophotometer system is based upon the principle of evolved gas detection.

A plasma can be defined as a mass of ionized gas in which the concentrations of electrons and protons are in equilibrium. A plasma may be produced at atmospheric pressure by the use of a high-frequency electromagnetic field and, once formed, can be used to ionise molecules channelled into it from a dissociating natural material in a combustion chamber. The following summary of the apparatus used, sample introduction method, means of sample heating and detection system is taken from the paper on the development of the microwave-induced argon plasma emission system by Meyer and Leen (1972). The system is shown diagramatically in Figure 9.1.

The cadmium spectral-line at 228.800 nanometers is selected and the setting is checked by focussing the vertical slit of the monochromator onto the discharge of a cadmium vacuum lamp activated within the microwave cavity. The emission signal thus received is detected by a photomultiplier, amplified, and recorded on one channel of a two-channel

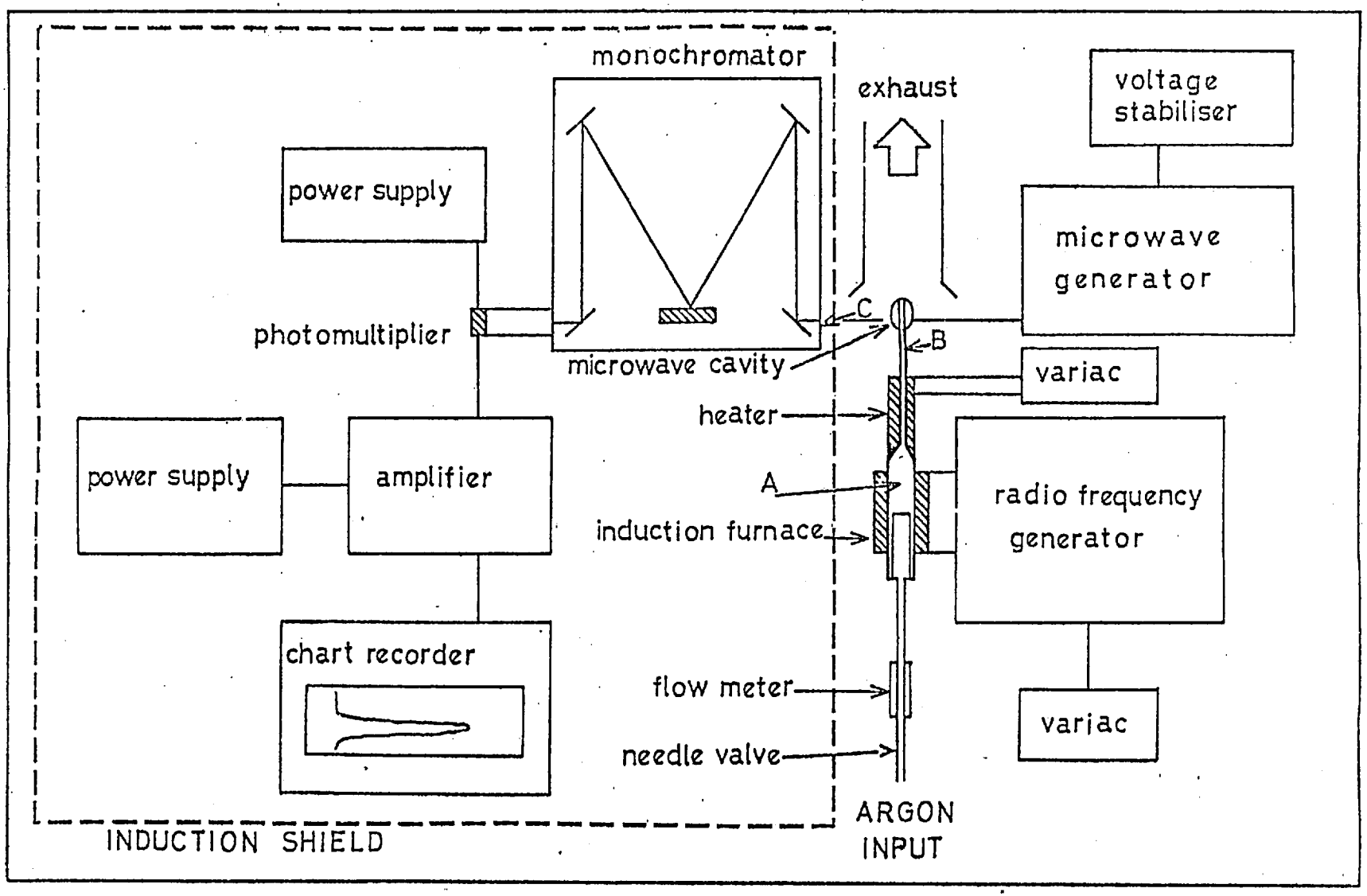


Figure 9.1 Schematic diagram of microwave-induced argon plasma emission system.

Servoscribe chart recorder. Once the cadmium line has been accurately located, a powdered sample of a natural material is manually packed into the conical depression at the end of a graphite crucible of dimensions 27 mm length and 3 mm diameter. This crucible is placed within a sample holder at the base of the furnace pedestal which is then raised into the combustion chamber. The system operates by heating the sample, surrounded by an atmosphere of argon within the combustion chamber (point A in Figure 9.1) to increasingly higher temperatures in a Leco induction furnace operating at a frequency of 14.6 MHz with an output of 1500W. Upon introduction of the argon gas stream (flowing at a volume rate of 1.7 litres per minute) and the subsequent expulsion of any air in the system, the plasma is activated by the spark from a coil vacuum tester and is subsequently stabilised by altering the position of the micro-wave cavity head. The flushing argon flow carries the dissociated sample molecules into a narrow quartz tube at the top of the chamber (point B in Figure 9.1) where the 'tuned' plasma, 25mm long and 1 mm in diameter has been formed. The ionisation of molecules in the argon plasma emits spectral lines which are detected by a plane-grating symmetrical monochromator with bilaterally adjustable slits (point C in Figure 9.1). The sample heating is controlled by steadily and systematically increasing the power to the furnace manually in a stepwise manner using a Variac variable voltage transformer which controls the voltage output to the radio-frequency coil. The transformer is increased at a rate of 10 per cent of total power per thirty seconds and this enables a temperature of 1,100^{o}C to be achieved whenever a graphite crucible is used. In practice the highest useful temperature reached for sample dissociation is restricted to about 900^{o}C as a result of the formation of a radio-frequency 'internal plasma' discharge within the combustion chamber itself at this temperature.

9.2 CLASSIFICATION, CALIBRATION AND PRECISION OF THERMALLY EVOLVED VAPOUR PROFILES

The evolution of gas phases, under conditions of controlled heating, in natural materials takes the form of one of three processes;

1 Vapourization - sublimation

The process of vapourization - sublimation is defined as the transition from the solid to the gaseous state without change in the chemical composition of the molecule. The temperature/concentration curve which is diagnostic of this process rises gradually to the maximum peak height temperature and thereafter declines suddenly. Assuming that the peak area is proportional to the measure of concentration this effectively means that the peak temperature shifts in a positive direction as the concentration increases.

2 Decomposition

Decomposition can be defined as the process of the breaking down of a substance into simpler constituents. The characteristic temperature concentration curve which results from the decompositional breakdown of a substance is symmetrical and the maximum peak temperature is totally independent of concentration. Upon concentration change no shift results either in a positive or a negative direction.

3 De-sorption

The process of desorption is defined as the removal by a physical or chemical action of dissolved substances held or concentrated upon the surfaces of another substance. The characteristic desorption temperature/concentration curve is a steep, sudden rise to the maximum peak height and a prolonged gradual tail-off to background as the temperature progressively increases. Effectively this means that the maximum peak

height temperature shifts to lower temperatures as the elemental concentration increases. Under the physiochemical conditions encountered in clay-rich sediments and in surface geochemistry, adsorption is the most likely process to dominate in the subjugation of metal cations and hence this desorption process is most common during dissociation of geological materials.

Thermally-evolved gas detection is essentially a 'finger-printing' technique. No two materials with marginal differences in chemical composition and crystal structure can give exactly the same temperature/concentration curve, as differing energies will be needed to cause structural breakdown. The practical problem of species identification will be dealt with later in this chapter and it will suffice at present to outline two relevant points; firstly, there is a major problem concerning the ease with which relevant artificial standards can be made, for example, the synthesization of carbonaceous and calcareous rock bases. Secondly, it is therefore necessary to extrapolate the results of other published, thermal analysis methods which differ in technique and in principle from the argon plasma's evolved gas detection method.

Meyer (1973), using a signal to noise ratio of two in determining the limits of detection, heated standard rock powders and solution residues to 800^{o}C and calculated the ultra-sensitive limits of detection of cadmium to be 0.005 ppm in the solid and 0.000009 ppm in the solution. Moreover, the precision of the method on a 1 ppm cadmium standard was found, after repetitive analyses of fifteen sub-samples, to be $\pm$ 10% at the 95% confidence limit. The only pre-requisites to attaining such a good precision in day-to-day use is constancy in the method of preparation, ensuring that the samples are thoroughly crushed and homogenised and that the crucibles for each analysis-run are packed with equal care. The major difficulties in obtaining a better precision are line fluctuations and

wavelength drift caused by such factors as changes in laboratory temperature and humidity. Both of these can be minimised firstly, by the use of a line-voltage regulator and secondly, by the constant readjustment of wavelength settings throughout the duration of experimental use.

9.3 INTERFERENCES FROM OTHER ELEMENTS

The cadmium spectral line used is 228.800 nM. The strongest spectral interference associated with this cadmium line comes from the direct-line fourth order emission of arsenic at 228.810 nM. A series of experiments were carried out by Aldous et al (1971) to determine the possible interference of one thousand-fold molar solutions of the elements arsenic (lines 278.020 nM and 228.810 nM), antimony (lines 206.830 nM and 217.580 nM) and cobalt (line 240.730 nM) added to a 0.25 microgram cadmium ml^{-1} solution. The wavelengths of the significant second and third order emission lines of cobalt and antimony are 228.780 nM and 228.898 nM respectively. It was found that, even in view of the massive excess of these elements over cadmium, there was no interference. However, the rapid heating of the arsenic - cadmium solution to the maximum operating current of 1.9 A did produce a strong, positive interference. On heating more slowly it was apparent that the subordinate arsenic peaks could be easily distinguished from the cadmium peaks, and the dominant cadmium peak vapourized at a temperature between that of the arsenic species peaks.

A comparison of detection limits of the two elements by the same authors in Table 9.1 (alongside flame spectroscopy arc intensities, after Boiteux and Mavrodineanu, 1965) indicates that the concentration of arsenic in the samples to be analysed would have to be at least two hundred times that of cadmium in order to register even insubordinate interference peaks. As a result of the unlikelihood of this being the case in the samples studied here, arsenic interference is thus regarded as being negligible.

TABLE 9.1 COMPARISON OF DETECTION LIMITS OF CADMIUM AND ARSENIC

	Wavelength (Å)	Arc intensity (After Boiteux, 1965)	Order	Detection Limit (After Aldous et al, 1971)	Detection Limit for 0.12 µl solution (ppm)
Arsenic	2780.2	140	1st		
	2288.1	44	4th	4.2×10^{-11}	0.35
Cadmium	2288.0	1500	1st	2.0×10^{-13}	0.0017
	3610.5	360	2nd		

9.4 APPLICATION OF THE THERMALLY EVOLVED VAPOUR PROFILE METHOD

The effects of selective chemical attacks upon rocks described in Chapter 8, have shown that cadmium is present within carbonaceous rocks in a series of forms which pre-supposes that the metal has been freely and completely distributed amongst all the rock components. Although up to 44 percent of the total cadmium in carbonaceous rocks is included within the structures of the clay minerals and as hydrochloric acid - soluble sulphides, the variety of other forms in which it appears to be present is genetically important. In comparison to the other elements studied in the extraction study, cadmium is much more freely available in the rocks to the low strength extractants and hence comparitively less of the total metal present partakes in high-strength bonding associations. These low strength forms will be represented by low temperature vapour peaks.

We may postulate three hypotheses to explain partitioning of cadmium in carbonaceous rocks;

1 Cadmium may be present within the incoming detritus in an adsorbed form for example, (on organic matter) or as a substitute within the lattices of the detrital minerals. In this instance cadmium partitioning would have been determined according to the physiochemical conditions of the weathering environment.

2 Cadmium partitioning may have initially developed as in hypothesis 1 but considerable adjustments resulting in cadmium redistribution may have taken plade during deposition, as a consequence of strong disequilibrium amongst the sediments, or during subsequent diagenesis, when for example secondary sulphides or carbonates may form.

3 The passage of cadmium-bearing solutions through the sediments at some stage late in the diagenetic process may make available the metal to unsatisfied adsorptive or absorptive sites, particularly within 'traps' of clay-grade, organic-rich rocks. The origin of the free cadmium bearing solutions may be in 'connate water' the source of which is in part related to the expulsion of foreign material and waters from limestone and shales during diagenesis.

The identification of vapour profile peaks for cadmium over a wide range of temperatures can provide the factual background from which the behaviour of cadmium during the historical evolution of a sediment can be mapped. A similar use may be made of soils. Meyer (1973) noticed that a high temperature form of cadmium could be identified in the weathered rock and overlying till and soil in the zones beside mineralized faults in the Keel zinc-lead-cadmium prospect, County Longford, Eire. Above the mineralized faults however, the high temperature cadmium form was absent. The use of a readily volatile technique, where samples are rapidly heated up to only a moderately high temperature of 500^{o}C, showed that the volatile cadmium fraction reached a maximum concentration over the area of the mineralised faults, whereas a simple total cadmium analysis using atomic adsorption methods did not exhibit the high anomaly to background contrast of the volatile method (Figure 9. 3). The plasma technique had been used to discover cadmium enhancement in the adsorbed phase representing the epigenetic anomaly above the mineralised faults.

In the diagramatic figures which follow, the temperature intervals used correspond successively with 10 percent increments in total power input to the system. Temperature calibration was based on a graph (Figure 9. 2) which was plotted by Meyer and his associates during an early stage in the use of the system.

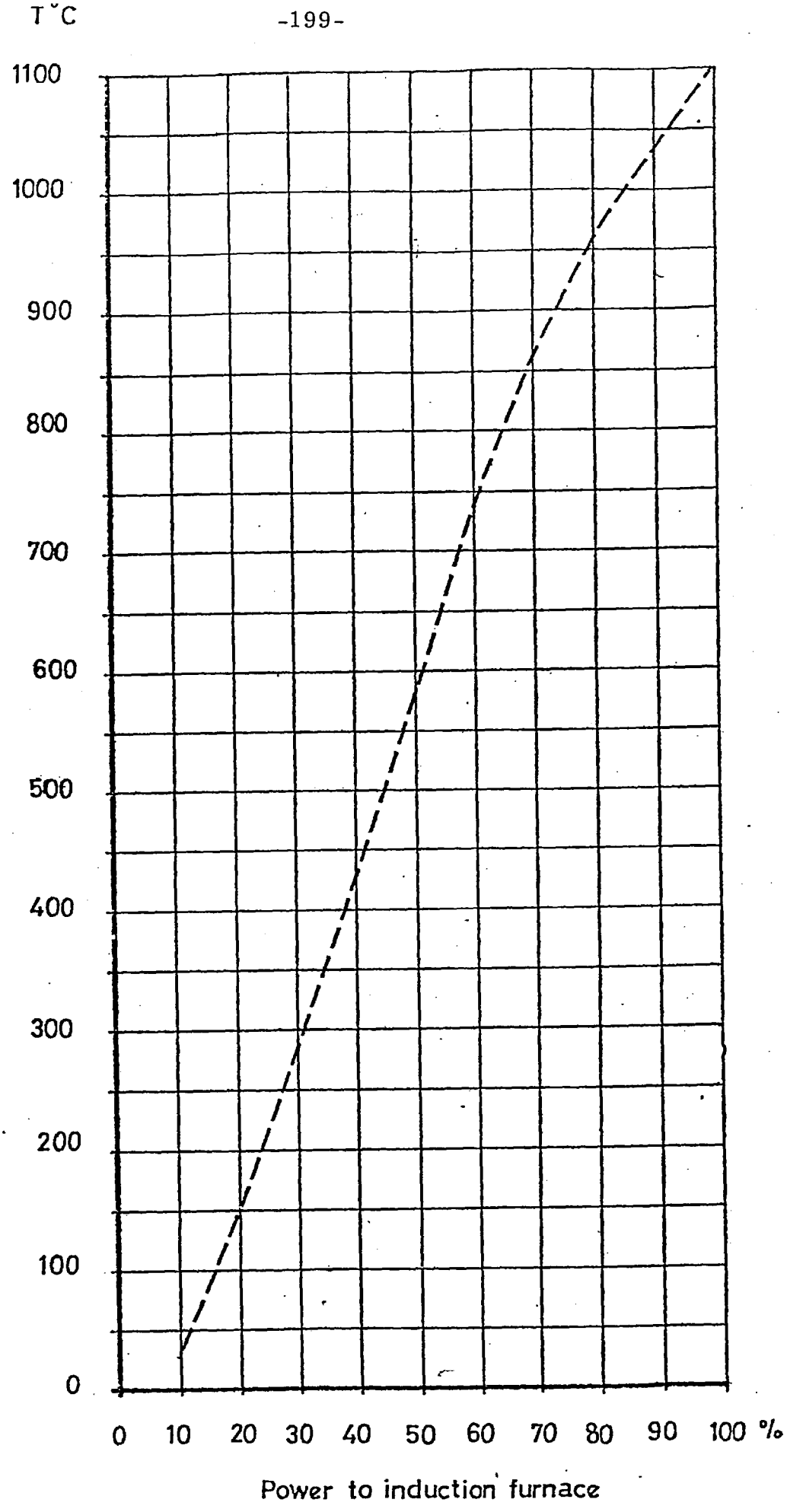


Figure 9.2 Calibration of carbon crucible for use with the slow heating method on the induction furnace.

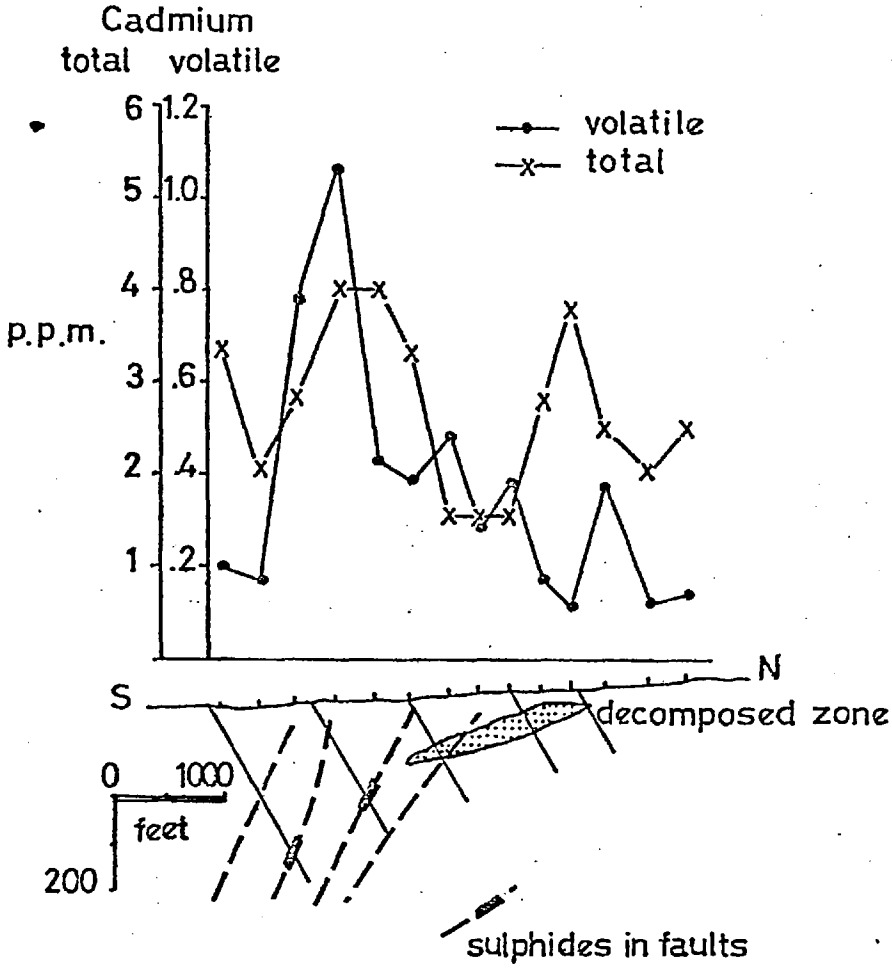


Figure 9.3 Volatile cadmium (<500°C) in soils from Keel determined by plasma emission compared with atomic absorption total cadmium.

9.5 ANALYSIS FOR CARBON AND SULPHUR

In the carbonaceous shales of the Carboniferous and Lower Palaeozoic the black colouration of the rock results from the inclusion of carbon (which may amount to over 6% by weight) and of finely disseminated iron sulphide. Much smaller amounts than 6% of total carbon will suffice to give a black pigmentation to the rocks and the presence of fine pyrite at low levels will also encourage a blackness.

The early stages in the maturation of organic material in a sediment undergoing diagenesis involve the expulsion of hydrogen, oxygen and nitrogen from the rocks leading to a proportionate increase in total carbon presence. The carbonaceous matter takes the appearance of residual, finely divided coaly material which is resistant to all but the most oxidising of chemical attacks. This study aims to determine the relationship between the metal present and the organic and sulphur-rich phases of carbonaceous and sulphurous shales.

The emission line formed subsequent to the breakdown of organic material and dissociation of carbon from carbonate minerals, is strongly received at 247.8 nM. Since the stronger Sulphur emission line at 469.6 nM has a strong carbon-line interference, the actual line used for sulphur detection is 190.1nM.

At the outset temperature/concentration curves for sulphur in rocks were poorly reproduceable and indicated insensitivity, consequently only a few graphs are reproduced in this section (Figure 9.4). Of these, graph 1 (Figure 9.4) is the best example with two sulphur peaks at 240^{o}C and 600^{o}C coinciding well with the first and fourth peaks of the superimposed cadmium curve for the same sample and the two distinctive superimposed carbon peaks. The thermal dissociation of pyrite takes place in oxidising

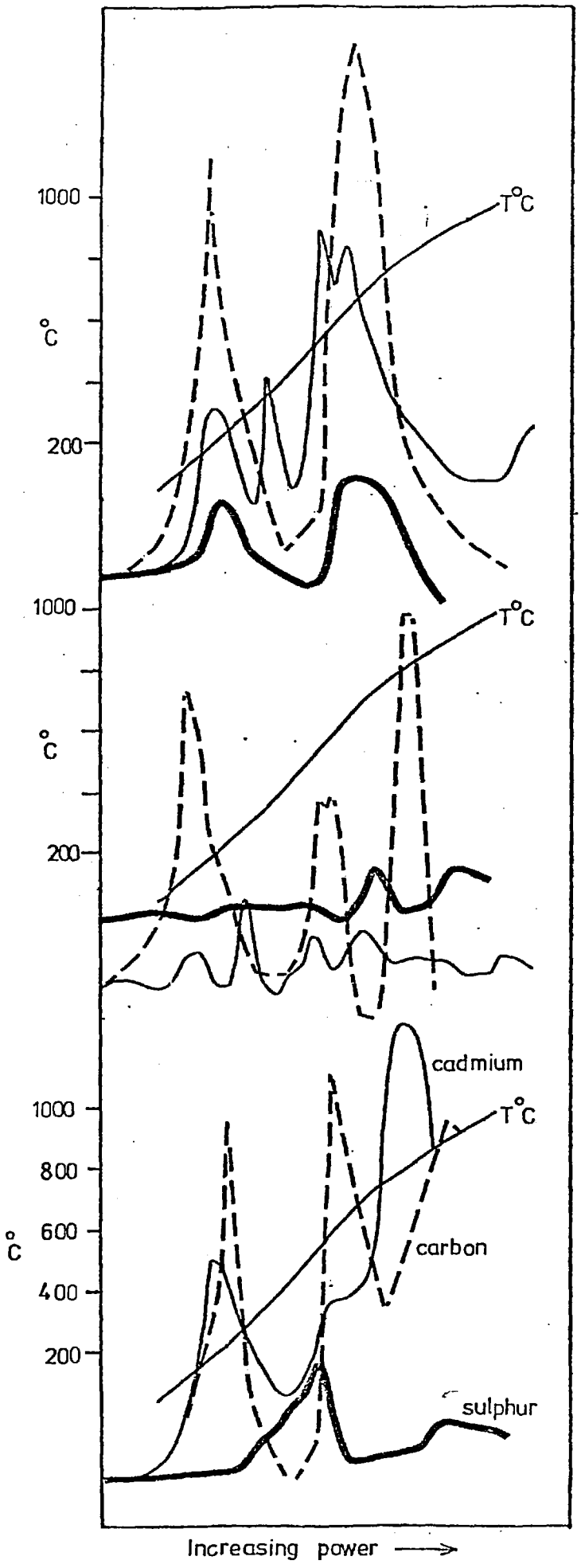


Fig. 9.4 Juxtaposed cadmium, carbon and sulphur profiles.

conditions at 550°C, with the release of sulphur dioxide and examination of natural compounds in the argon-plasma suggests that the 600°C peak may be caused by the release of an oxidation product of pyrite. Peters (1974) suggested that a higher temperature well-defined peak at 735°C was due to the release of sulphur from finely ground pyrite and he further suggested that a peak at 230°C is due to thermal release of native sulphur occurring in soils or sediments containing organic matter. Higher temperature emission peaks were closely related to the presence of sulphides, since this peak in particular became enhanced over sulphide zones during soil-traverses of mineralized veins.

The strong relationship between the low temperature peaks of the carbon, cadmium and sulphur graphs confirms that this peak forms as the result of the first stage in the carbonization of metal-containing organic matter (graphs 2, 3 Figure 9.4).

The moderate temperature sulphur peaks at 485°C and 515°C in graphs 2 and 3 correlate respectively with pronounced peaks in juxtaposed cadmium graphs and they are, in all probability formed by the early release of sulphur and cadmium from the lattice of the pyrite mineral.

The higher temperature sulphur peaks in the graphs 2 and 3 (Figure 9.4) are caused by the release of sulphur from non-pyritous sulphides (see Figure 9.9) and in graph 3 the similar peak temperature of the cadmium graph indicates that the cadmium is sulphide bound.

9.6 REGIONAL ANALYSES OF THERMALLY EVOLVED VAPOUR PROFILES FOR CARBON AND SULPHUR

In the Edale rock graphs (Figure 9.4 graphs 1, 3) carbon compounds Thermally Evolved Vapour Profiles (hereafter referred to as TEVPs) reveal

two strong peaks at 230° and 590° to 600°C, both correlating with cadmium peaks. The lower temperature carbon peak, with dissociation commencing between 120° and 150°C may be attributed to intramolecular changes which are synonomous with the normal first stages in the in situ maturation of coal - loss of moisture and oxides of carbon. The higher temperature peak between 500° and 600°C is formed by the loss of most of the aliphatic side-chain structures and other 'amorphous' carbon attached to the aromatic nucleii of kerogenous material. The cadmium and sulphur with similar release temperatures seem to be related to this carbonaceous material and may actually be biogenic in origin.

In the Bowland sample (Figure 9.4, graph 2) a third peak at 810°C is formed by carbon dioxide release from the dissociation of the carbonate minerals present. The thermal dissociation of dolomite is known to commence before 800°C in an inert atmosphere (see Figure 9.6). However, no high temperature carbon peak is recorded in a second Bowland sample (Figure 9.5, graphs 1 and 2), although a more complex series of peaks is recorded between 490° and 605°C. All these peak positions correlate well with the cadmium peaks at 490°C and 570°C and all represent successive increments into the second stage in the carbonization process (Berkowitz, 1967) which is conventionally designated 'active decomposition' and generally involves severe molecular disruption. This phase, like the low temperature phase, is characterized by the release of predominantly peripheral molecular stages.

The two samples from the Culm Measures of Cornwall reflect the maturity of the carbonaceous material within them (see Section 8); 'phase one' is completed by 240°C and 'phase two' lasts from 600° to 610°C (Figure 9.5 graphs 3 to 6). In each case the carbon peaks coincide with the cadmium peaks, although in sample 532, graph 5, the dominant peak at about

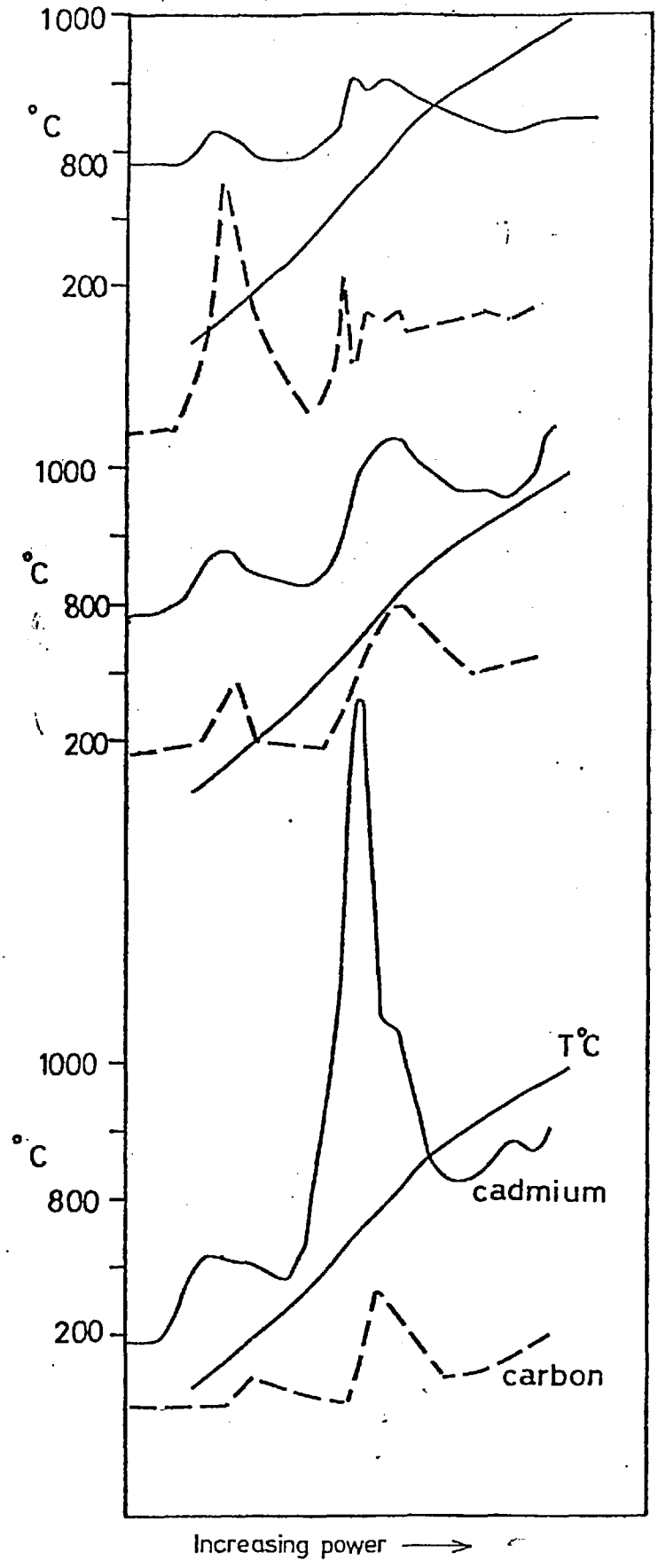


Fig. 9.5 T.E.V.P. graphs for three samples showing juxtaposition of cadmium and carbon peaks.

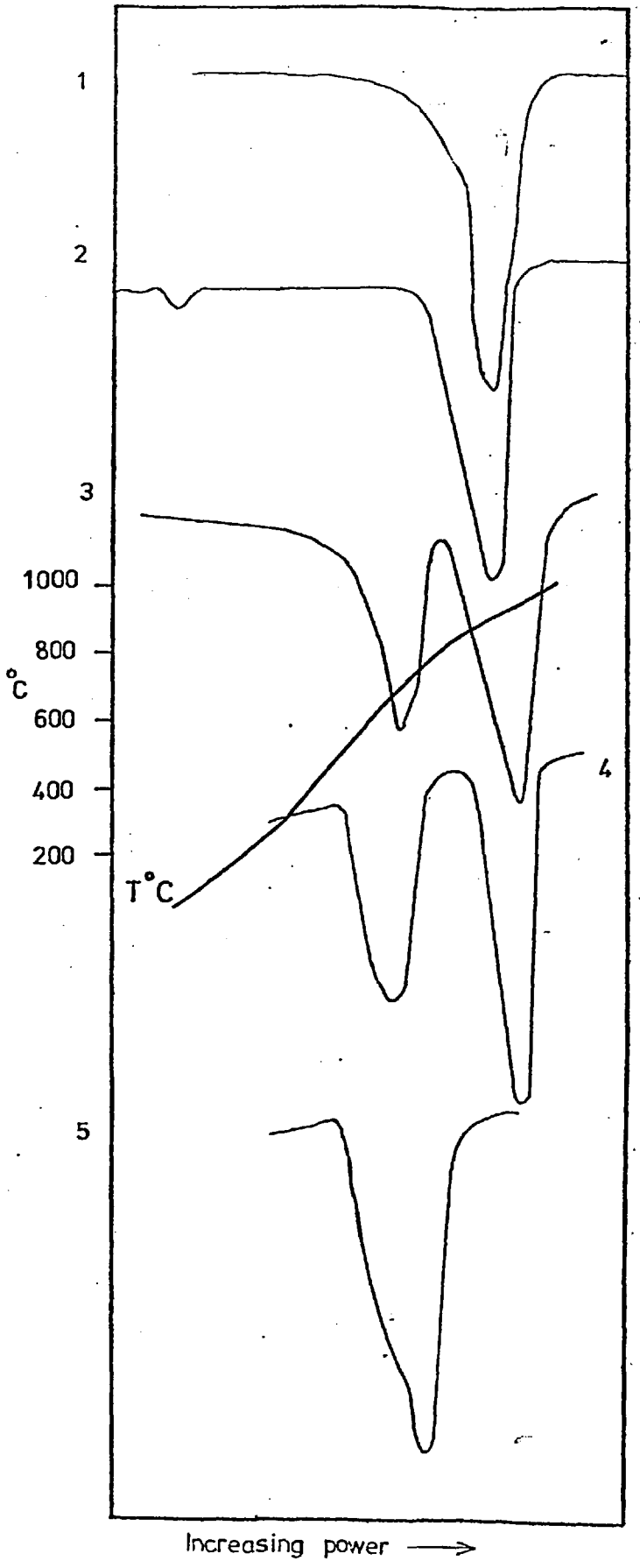


Figure 9.6 D.T.A. curves for carbonates.

550°C is conspicuously lower in temperature because a classic heterogenous desorption (see Section 9.2) has caused a negative temperature shift.

In conclusion, it can be assumed that in the Culm Measures, cadmium peaks at temperatures of 190° to 240° and 600° to 610°C are carbon correlated. In Edale, peaks at 180° to 220°C and 580° to 610°C are carbon and sulphur dominant, whilst any peak at around 880° to 900°C is likely to be sulphur controlled. In Bowland, three carbon peaks are characteristic; one around 150°C, another representing severe molecular carbon disruption occurring between 490° to 605°C and a third, not always present, representing carbonate carbon, dissociation at 810°C. The first two peaks strongly correlate with cadmium volatilization whilst, in this instance, none correlates with the carbonate-carbon peak. The higher temperature cadmium peak at 720°C correlates well with a strong sulphur peak at the same temperature which, in all probability represents a sulphide breakdown.

9.7 DIFFERENTIAL THERMAL ANALYSIS AND THERMALLY EVOLVED VAPOUR PROFILE CURVES FOR KNOWN MINERALS AND ORGANIC GROUPS - A CALIBRATION STUDY

This section deals with the previous work which has been carried out in the field of thermal analyses of mineral groups by Differential Thermal Analysis (DTA) and by the argon plasma Thermally Evolved Vapour Profile (TEVP) methods and it is intended to supplement the following sections on peak identification.

The DTA technique is one in which the difference in temperature between an unknown substance and a reference material, both subjected in a chosen atmosphere to the same controlled temperature regimes, is recorded. The curve produced shows a series of peaks whose position is

determined by the chemical composition and crystal structure of the substances in the samples and whose area is related to the energy involved in the reactions (assuming that the substance under consideration is thermally active in the temperature range used). Most of the DTA peaks illustrated in the graphs of this section are examples of endothermic reactions.

In attempting to estimate the composition of natural geochemical materials using the TEVP method by reference to the more precise curves of DTA or even EGD (Evolved Gas Detection), care must be taken not to over extrapolate conclusions made on experiments conducted in air and even more oxidising atmospheres. Several of the samples illustrated in the next sections have been thermally activated in oxidising atmospheres but most chosen for comparison have been heated in reducing or inert atmospheres in order to duplicate plasma experimental procedure as much as possible.

The study with selective chemical attacks indicated that sulphides, clay minerals, organic matter and carbonates were all important in the processes of complexation of cadmium in a rock and reference curves of these minerals have been selected from Mackenzie (1970) to feature alongside curves of cadmium containing minerals analysed by TEVP as part of this project.

The dissociation of calcite in air (see Figure 9.7 graph 1) reaches a maximum at a temperature of 900^{o}C, whilst dolomite generally forms two clear peaks at 780^{o}C and 920^{o}C, graphs 3 and 4. The dissociation of dolomite in carbon dioxide at low pressure, in graph 5 commences at 700^{o}C, reaches a maximum at 820^{o}C and is complete before 920^{o}C.

A selection of clay minerals have been included in Figure 9.6 and all show a marked endothermic peak at temperatures ranging from

100°C (illite, graph 6) to 170°C (vermiculite graph 5). The vermiculites related to smectites (montmorillonite group) and micas show specific peaks between the temperatures of 280° to 300°C (see graphs 4 and 5 Figure 9.7). Montmorillonite's low temperature endothermic peak system is markedly influenced by the nature of the exchangeable cation as the mineral group is strongly susceptible to isomorphous substitution. Graphs 1 to 3 all exhibit saturated smectites, the mid-temperature peak varying according to the substituted cation, between 500° to 600°C.

As the kerogenous matter of carbonaceous shales, like coals, have been subjected to the effects of carbonization the thermal breakdown of the material in shales is assumed to be similar to the thermal breakdown of coals. In Figure 9.8 graphs 3 to 5 two strong endothermic peaks are consistently displayed at between 60° to 130°C and 410° to 450°C for coals of various ranks. The graphs 1 and 2 show how the normal DTA curves for coal can be suppressed by the addition of mineral impurities, as in both these instances the peaks for the substituted kaolinite are clearly expressed.

The breakdown of the cadmium-containing minerals in the inert atmosphere of the plasma discloses that sphalerite or blende releases cadmium at temperatures between 865° and 1035°C. The release of cadmium in zinc carbonate, graph 3 took place predomenantly upon dissociation of the carbonate lattice at 450°C. This is in agreement with Mackenzie (1970) who reported that the main endothermic peak for zinc carbonate lay within the range 420° and 525°C (see Figure 9.9 for the cadmium mineral graphs).

9.8 IDENTIFICATION OF CADMIUM SPECIES WITH THE AID OF SELECTIVE CHEMICAL ATTACK RESIDUES

9.8.1 INTRODUCTION

The work summarized in Chapter 8 is of great assistance in the identification of the forms in which cadmium is present in rocks in which

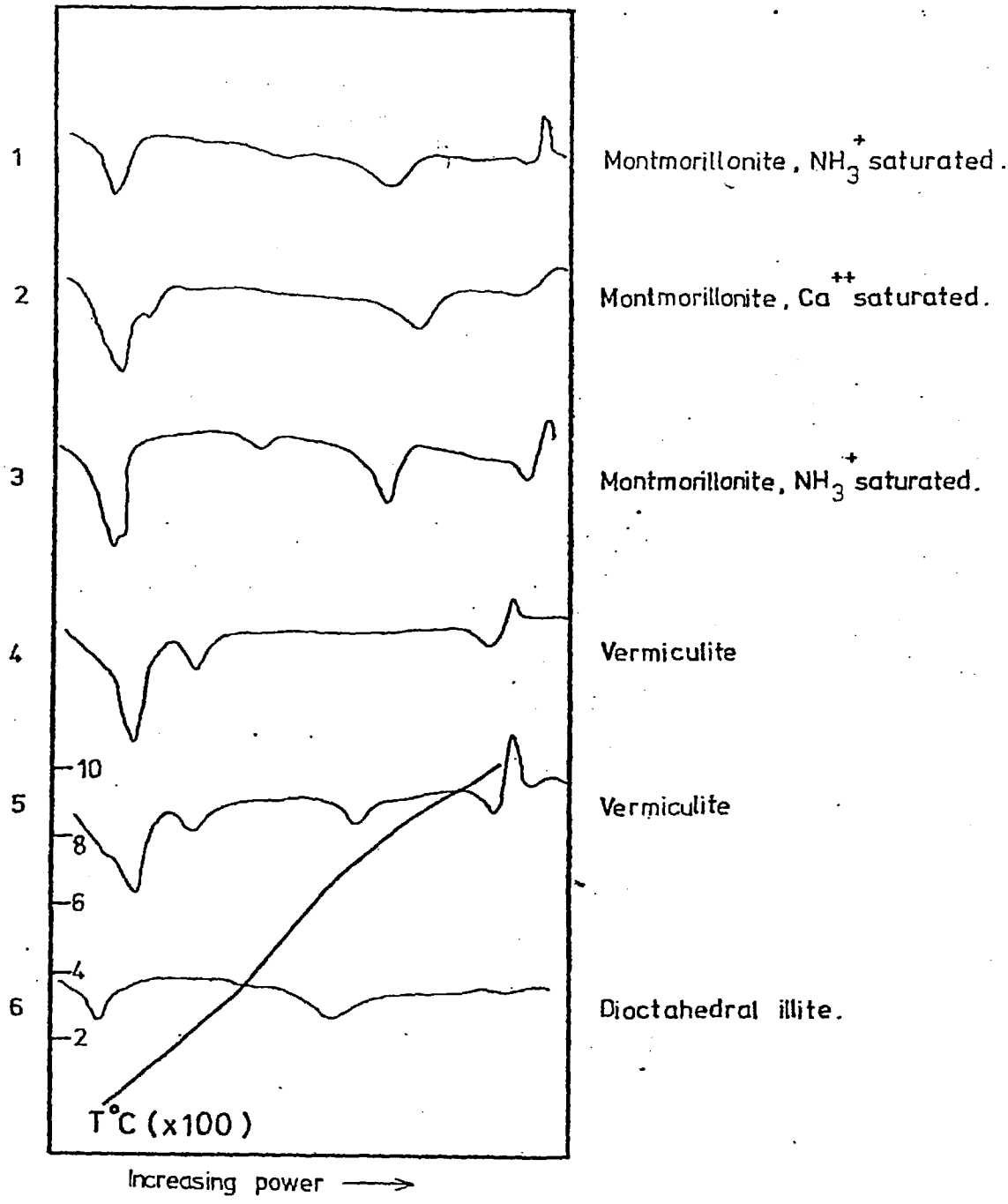
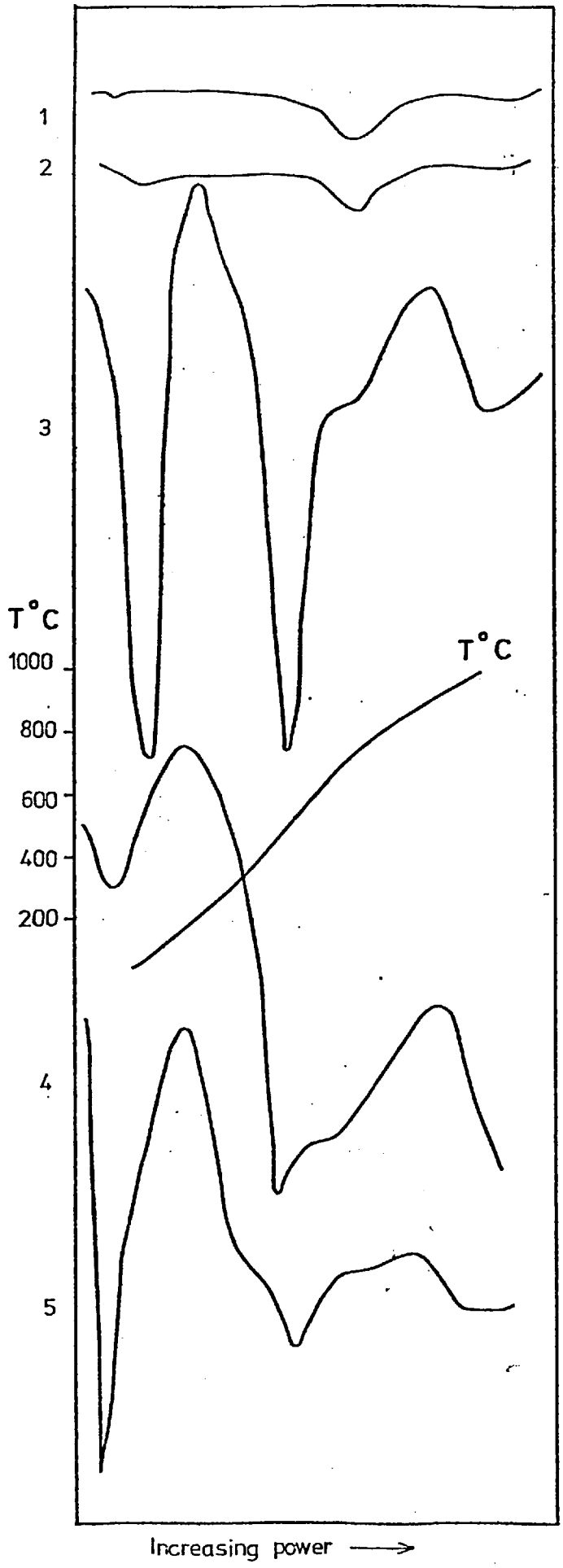


Figure 9.7 D.T.A. curves for clay minerals.



Kaolinite–coal mixture in an inert atmosphere. 1. 25% kaolinite
2. 25% kaolinite +5% coal

Sub–bituminous coal, 51.5% volatiles

European black coal, 90.7% carbon.

European brown coal, 72.7% carbon.

Figure 9.8 D.T.A. curves for organic compounds.

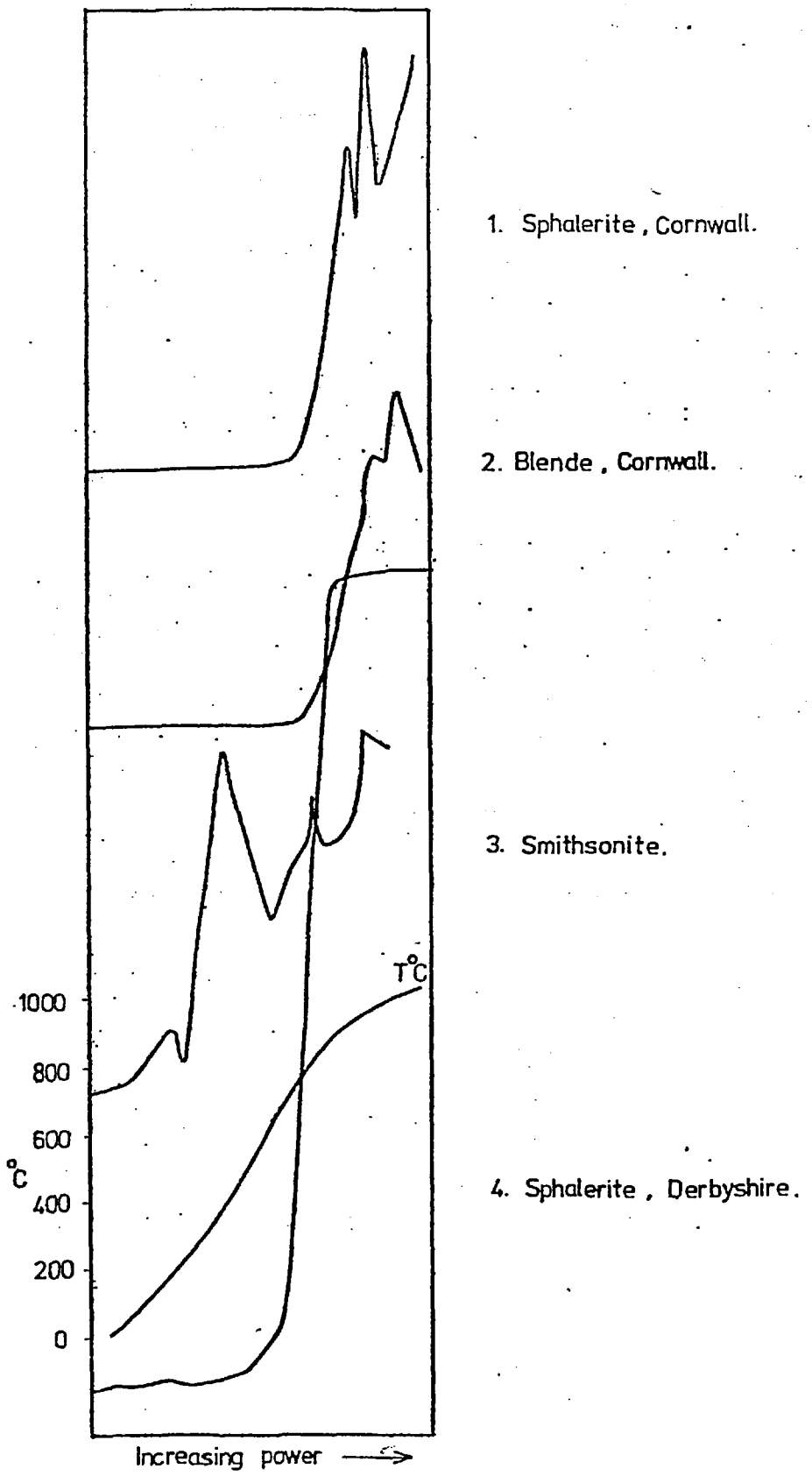


Fig. 9.9 Argon plasma curves for common minerals.

it is enriched but one of the most accurate ways to identify them is to thermally dissociate the post extraction residues of the rock samples utilised in the selective chemical attack experiments.

Each post extraction graph for the same extractant residue retains the same suffix throughout the figures (Figures 9.10 to 9.17) of this section, thus:-

1 represents the TEVP graph of the original rock powder,

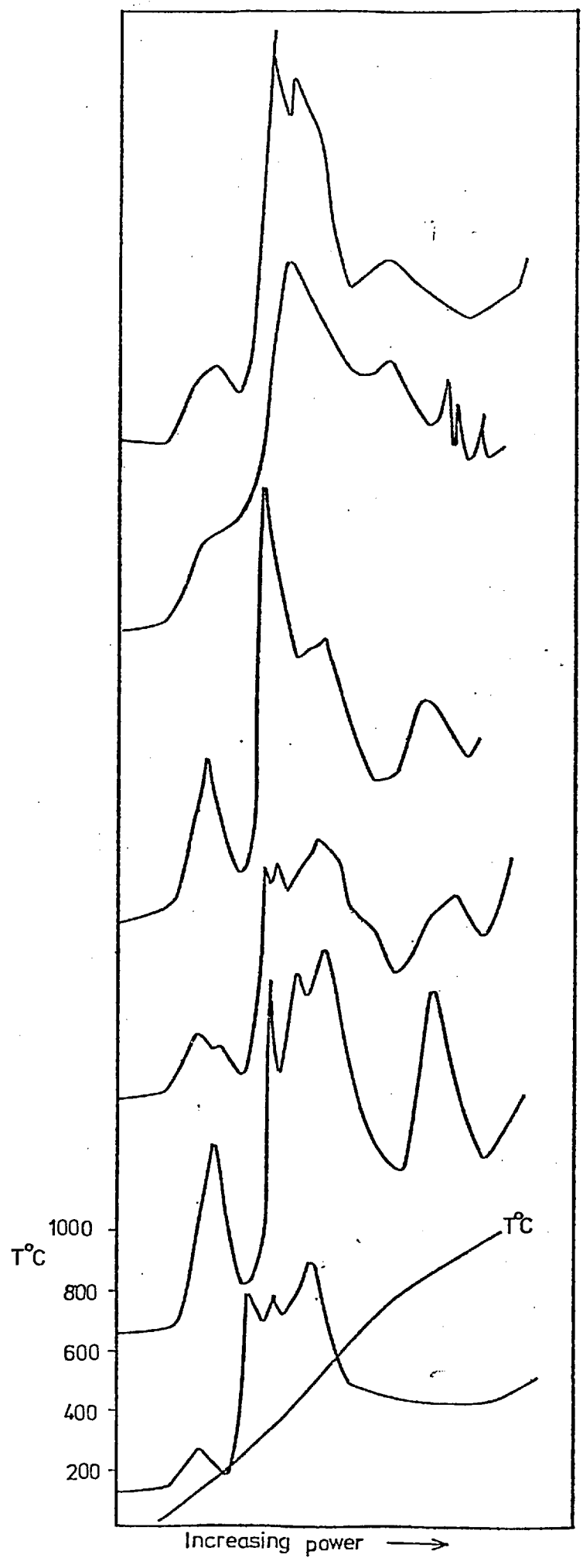
2 to 6 represent the TEVP graphs of the same rock powder after extraction with: 2.neutral ammonium acetate; 3.25 percent cold acetic acid; 4. hydroxylamine hydrochloride-acetic acid mixture; 5. EDTA; and 6. 50 percent hot hydrochloric acid.

For an understanding of the theoretical behaviour of each of these extractants upon the varied components of rocks, Chapter 8 should be consulted. Experimental details of the use of selective chemical extractants, are summarized in Appendix I.

9.8.2 CADMIUM SPECIES IN A BLACK SHALE OF SILURIAN AGE FROM THE LAKE DISTRICT

Sample number 1090178; locality ^{NY}E410N030, Skelghyll, Cumberland. Geological age: Skelghyll beds, Silurian.

The thermally evolved vapour profile has four distinct peaks at 150^{o} 340^{o}, 410^{o} and 740^{o}C (figure 9.10 graph 1) and a fifth 'shoulder' peak at 510^{o}C.



Sample no. 178 from the Skelghyll beds, Silurian, Lake District.

1. Original
   (Cadmium 1.5 p.p.m.)

2. Post ammonium acetate.

3. Post acetic acid.

4. Post reducing-oxidising agent.

5. Post E.D.T.A.

6. Post hydrochloric acid.

Fig. 9.10 Post chemical extraction T.E.V.Ps. Silurian sample.

The 'residual' cadmium remaining in the rock after the strong leach of 50 percent hot hydrochloric acid is represented by a profile area only half that of the original (compare graphs 9.10,1 and 6) implying that 50% of the total cadmium present (up to 3 ppm on average) in a rock of the Skelghyll beds is in a form resistant to attack. The two low temperature peaks are those which probably formed as the result of the breakdown of mixed-layer minerals, for example the vermiculitic-type of Figure 9.7 graphs 4 and 5, which would be composed predominantly of micas weathering to montmorillonites. The low temperature peak is formed by the thermal expulsion of loosely absorbed cadmium and this is confirmed by the habit of Cd^{++} ions which, when released, from the remaining phases successfully attacked in the other residues, into solution in the extractant, for example, the removal of the 740°C peak by acetic acid in graph 3, reabsorb into unsaturated surface and edge clay-complex sites. This causes an extension of the low temperature peak and emphasises the potential capacity of such sites for adsorption scavenging.

The residual nature of the 150°C peak may be partly due to the fact that the cadmium is involved within mica structures, as the common micas are insoluble in hydrochloric acid. However, the peak also appears to be related to the presence of coaly material. The metamorphosis which these rocks must have undergone since Silurian times will have removed all the volatiles from the organic matter present and completely carbonized it into kerogen or coaly matter. The DTA curve of a 90% carbon coal (Figure 9.8, graph 4) included strong peaks at about 100°C and 400°C with a double 'shoulder' peak at about 500°C, agreeing almost exactly with the pattern of residual cadmium peaks in the post hydrochloric acid graph of the Silurian rock (graph 5, Figure 9.10). The graphs 2 to 5 in Figure 9.10 indicate that with the exception of the extractants hydroxylamine hydrochloride and hydrochloric acid, each of the four extractants have little effect on strong, organically-bound cadmium. The effectiveness of the hydroxylamine hydrochloride (or 'reducing-oxidising' reagent) implies some correlation

of cadmium with manganese. A relationship may exist between manganese oxides, associated cadmium and organic material.

The high temperature peak at 740°C is destroyed by acetic acid, the acetic-acid based reducing-oxidising agent and hydrochloric acid. The DTA peaks of magnesium-iron carbonate (which has been identified in x-ray diffraction traces of Skelghyll beds rocks) show decomposition commencing at about 700°C in air, and in all probability this 740°C peak formed in the inert atmosphere of the plasma results from the release of cadmium from decomposing carbonate.

The presence of a notable increase in peak areas in graphs 2 to 5 at temperatures exceeding 850°C is the result of the decay of a cadmium complex which has been formed during the course of the extraction experiments. If the peak was caused by the decay of auto-reduced cadmium oxides (formed from the non-residual cadmium) then a similar peak would be expected in graph 1 but this does not occur. There are two possible explanations for this:

1 The removal of the more easily acid soluble siderite from the magnesium-iron carbonate structure will leave only magnesium carbonate behind and will increase the DTA temperature necessary to cause complete carbonate dissociation. The observed temperature increase of 120°C is however, considered somewhat excessive, ruling out magnesium carbonate as a cadmium host.

2 The peak is possibly a sulphide which has formed in the sample during the extraction process. All the samples, except for the hot hydrochloric acid extraction, were leached during a

period of exceptionally cold weather and all evolved much hydrogen sulphide and carbon dioxide during the course of the experiment. Settling could conceivably have taken place during the agitation stage and any hydrogen sulphide build-up in the body of the sediment may have raised the pH locally and sufficiently for cadmium sulphide to precipitate. Provided that acid liquids did not disturb the inner sediment during the centrifuging stage of sample preparation, then the sulphides may survive, only to be thermally dissociated by TEVP heating.

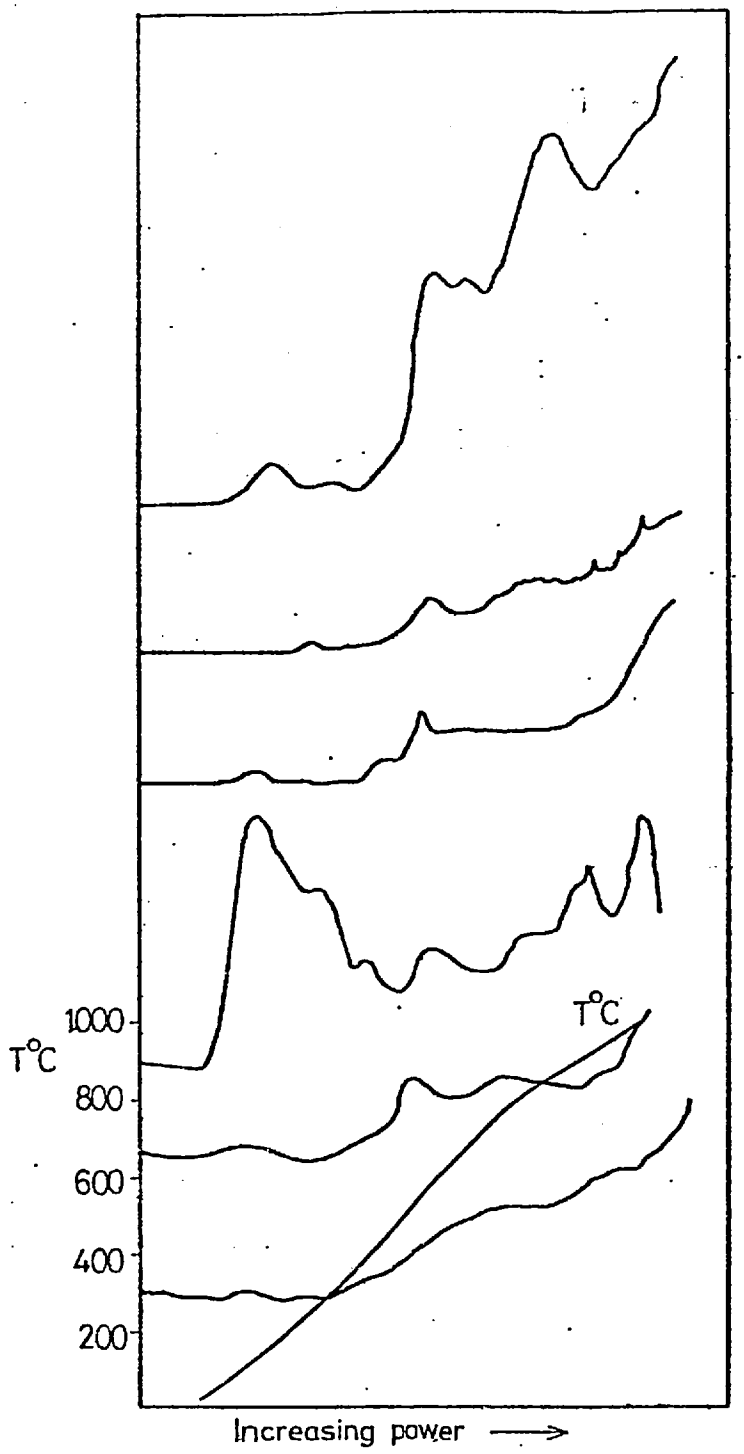
The two main conclusions from this set of samples are firstly, that so much cadmium is in a residual organic form that none of the extractants removed more than half of the total extractable and that secondly, the only positively identified cadmium association with inorganic minerals is with a magnesium-iron carbonate.

9.8.3 SPECIES IDENTIFICATION IN THE BLACK MICACEOUS SHALES OF THE CULM MEASURES, CORNWALL

Sample numbers: (1) 1090656, (2) 1090533; Locality: (1) E2460, N0967(2)E2138, N0966.

The rocks of the Southwest Peninsula are even more mica-rich than the Silurian black-shales and although no schistosity has been recognised, the rocks have undoubtedly been metamorphosed by the intrusion of the Cornish granites.

1 In the older of the two rocks studied (sample number 1090656) of P2 age, Carboniferous, ammonium acetate removed all but 5 percent of the incorporated cadmium from the original rock (compare Figure 9.11,



Sample no. 656 of P2 age from the Culm Measures near the Dartmoor granite.

1. Original
   (Cadmium < 2 p.p.m.)
2. Post $NH_3.COOH$
3. Post $CH_3.COOH$
4. Post reducing-oxidising agent.
5. Post E.D.T.A.
6. Post Hcl

Fig. 9.11 Post chemical extraction T.E.V.Ps. Culm measures.

graphs 1 and 2), suggesting that none of the peaks (which are present in the original rock, graph 1) represent positive intracellar cadmium associations. The peaks in graph 1 have been identified as follows: the peak at 180°C and the smaller peaks at 330°C and 865°C are all formed as a consequence of cadmium release from the lattices of the mixed-layer minerals, collectively termed vermiculites. 43% of the minerals identified in this sample were aluminium silicates (see Table 8.3). The 180°C peak also involves the presence of organic matter, as does the peak at 590°C (see EDTA graph 5) although the latter is considerably more prominent and is more closely related to coaly matter alone. The peak at 670°C immediately following the crest of the cadmium-carbon peak, is thought to be the release curve of cadmium associated with a manganese oxide such as pyrolusite (MNO_2) which dissociates in air at 625°C.

The massive readsorption displayed in graph 4, which represents the post reducing-oxidising agent TEVP, is probably explained in terms of the reducing component used in the extraction mixture, which created reducing conditions of sufficient magnitude to prevent total removal of cadmium from the system.

2. Sample number 1090533 of H1 age was collected from the North Cornwall coast, at Crackington Haven, more than 40 kilometers distant from the present-day Dartmoor-granite/Culm unconformity. In contrast to sample 1090532, of the same age and locality, which was analysed for cadmium and carbon and illustrated in Figure 9.5 (graph 5), this sample has a much less prominent peak at 550°C (see figure 9.12). This peak, which does not appear in the older Culm rock (see sub-section 9.8.3) is present as a consequence of the substitution of cadmium within the pyrite lattice. This peak, together with a mica peak at 180°C remains after hydrochloric acid extraction (graph 6). Although EDTA has little effect on it, the peak at 630°C is likely to be formed by the release of cadmium

Sample no. 533 from Culm Measures of H1 age.

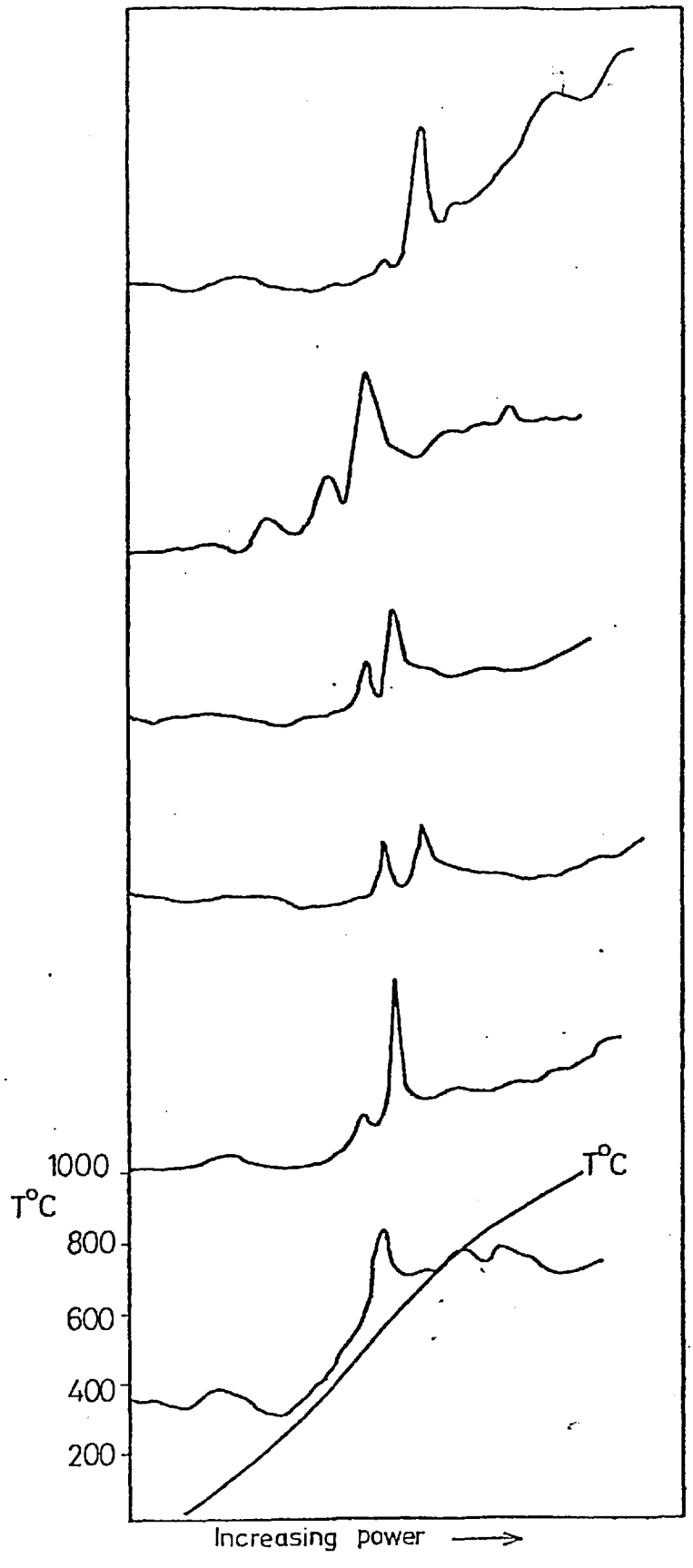


Fig. 9.12 Post chemical extraction T.E.V.Ps. Coastal Culm Measures.

from dissociating residual organic complexes. Apart from a peak at 180°C which forms on release of cadmium from a mica-carbon matter association, the trace as a whole is uninteresting. However, the small peak area of the profile suggests that the total cadmium content of 1.0 ppm determined by atomic adsorption, is correct.

In conclusion, the cadmium is known to be associated in the Culm rocks with organic material, in all likelihood as biogenic metal, and also within as well as adsorbed on the mica minerals and their weathering products. The presence of sulphide is not known in these particular samples but sulphides in similar samples are discussed in sub-section 9.9.3

9.8.4 EVIDENCE FOR METAMORPHIC ALTERATION IN THE CULM MEASURES

Sample number 1090656 of P2 age in the Culm sequence was collected four miles (6 kms.)from the Granite-Culm contact near the town of Okehampton, whilst sample 1090533 of younger, H1 age in the Culm sequence, was collected on the Cornish coast at Crackington Haven, twenty-five miles (40 kilometres) distant from the present-day Granite-Culm unconformity.

The former sample (1090656) has lost the residual carbon-cadmium complex peaks at about 150° to 240°C and 590° to 630°C which are so characteristic in the post hydrochloric acid extraction profiles of all carbonaceous shales (compare Figure 9.11, graph 6 and Figure 9.12 graph 6). In addition the points noted earlier (in Section 9.8.3) concerning sample 1090656 must be raised again; although the peaks in graph 1 appear to reflect progressively stronger cadmium component associations on temperature increase, they are almost completely removed by neutral ammonium acetate solution, implying that the cadmium adopts equally weak associations in all cases. This can be explained by hypothesizing

that the total rock components have been stoichiometrically weakened in some way (for example, by the thermal metamorphic effect) exposing the included trace metals to easy chemical expulsion. This implies either that no emanating 'front' formed by the granite (with an attractive capacity greater than that of neutral ammonium acetate) actually came in contact with these rocks, because if it did the cadmium (by virtue of its 'thermal realignment' amongst the rock components) would have mobilised or that the clay-grade, organic-rich rock acted as a 'trap' for cadmium enriched solutions emanating from the granite, allowing the metal to adopt adsorption-type positions within a previously cadmium deficient sediment. Interestingly enough the TEVP graph for sample 1090533 from the coast (Figure 9.12, graph 1) looks distinctly similar to that for the older rock (1090656) following treatment with ammonium acetate solution (see Figure 9.11, graph 2), since in both cases the only significant peak falls at 590^{o} to 630^{o}C. However, sample 1090656, from the granite contact, appears to be the exception to the rule, judging by the graphs of Figure 9.5 in which the classic carbon-cadmium peak at about 600^{o}C always predominates, to the extent that the remaining peaks are almost insignificant. It is not clear to what extent the 600^{o}C peak is enhanced by post-diagenetic, metamorphic redistribution of cadmium to the components from which this cadmium peak originates, although destruction of the old mineral suite by metamorphism in favour of a mica-dominant composition must have been accompanied by a metal redistribution. There is no direct evidence for metal expulsion bar the circumstantial evidence that the Culm Measures are very cadmium-defficient compared with other black shales of the Carboniferous and that the South-West England mining region has yielded significant quantities of lead and zinc. However, extended discussion of whether or not the source of the heavy metals known in the fracture-belts within the Culm Measures is from the Carboniferous Culm Measures is not appropriate here.

9.9 COMPARATIVE SPECIES FROM THE SEDIMENT OF THE ENGLISH CENTRAL PROVINCE - A STUDY OF EDALE, BOWLAND AND ONECOTE SHALES OF THE LATE VISEAN ERA

9.9.1 ONECOTE, DERBYSHIRE

Sample number: 1090270; Locality: E4044, N. 3555, Onecote Grange; Geological age: Visean, P1-P2 Mixon limestones with shales.

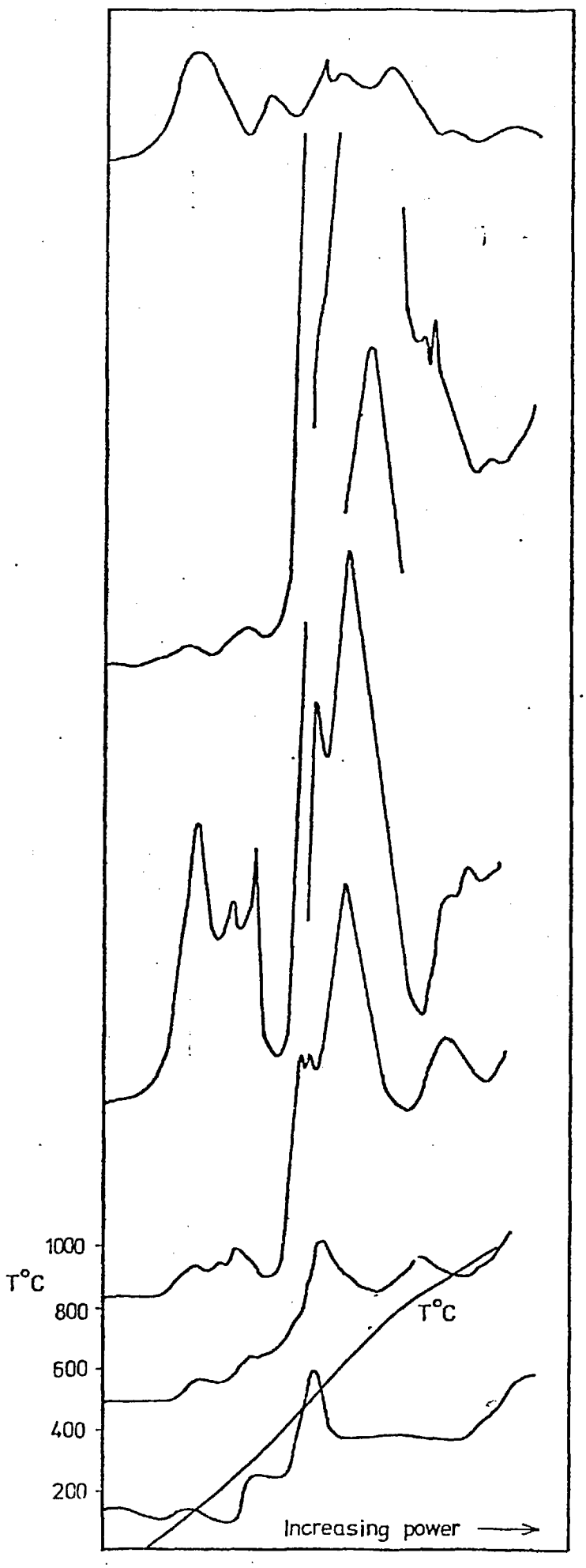
Only hot hydrochloric acid has any significant effect upon the cadmium peaks of the Onecote rock, removing all those save that at 515°C which is formed by the release of cadmium from the pyrite lattice (Figure 9.13 graph 6). A significant proportion of the total metal evolved by 1000°C is in the form of a complex with kerogenous organic matter (shown as a peak removed by EDTA, compare graphs 2 and 5). A small peak at 865°C (which is removed solely by HCl) is thought to be caused by the release of cadmium from the lattice of a sulphide mineral, such as sphalerite.

9.9.2 BOWLAND, LANCASHIRE

1 Sample number: 1090784; Locality: E3785, N4412, Upper Mearley Clough; Geological age: Visean E1 shales.

2 Sample number: 1090118; Locality: E3950, N4567, Flasby Beck near Skipton; Geological age: Visean P1 shales.

In the post-extraction TEVP study, carbonate associations with cadmium are known from the Carboniferous, only in Bowland. The possibility of a calcium-cadmium association was first realised on studying



1. Original sample no. 483345 from P1-P2 Onecote shales.
Cadmium 55ppm.
Scale = 200 mV.

2. Post NH_3.COOH on original sample no. 178. Horizon similar to 1.
Cadmium 9.3 p.p.m.
S. = 100 mV.

3. Post CH_3.COOH (178).

4. Post reducing-oxidising agent (178).

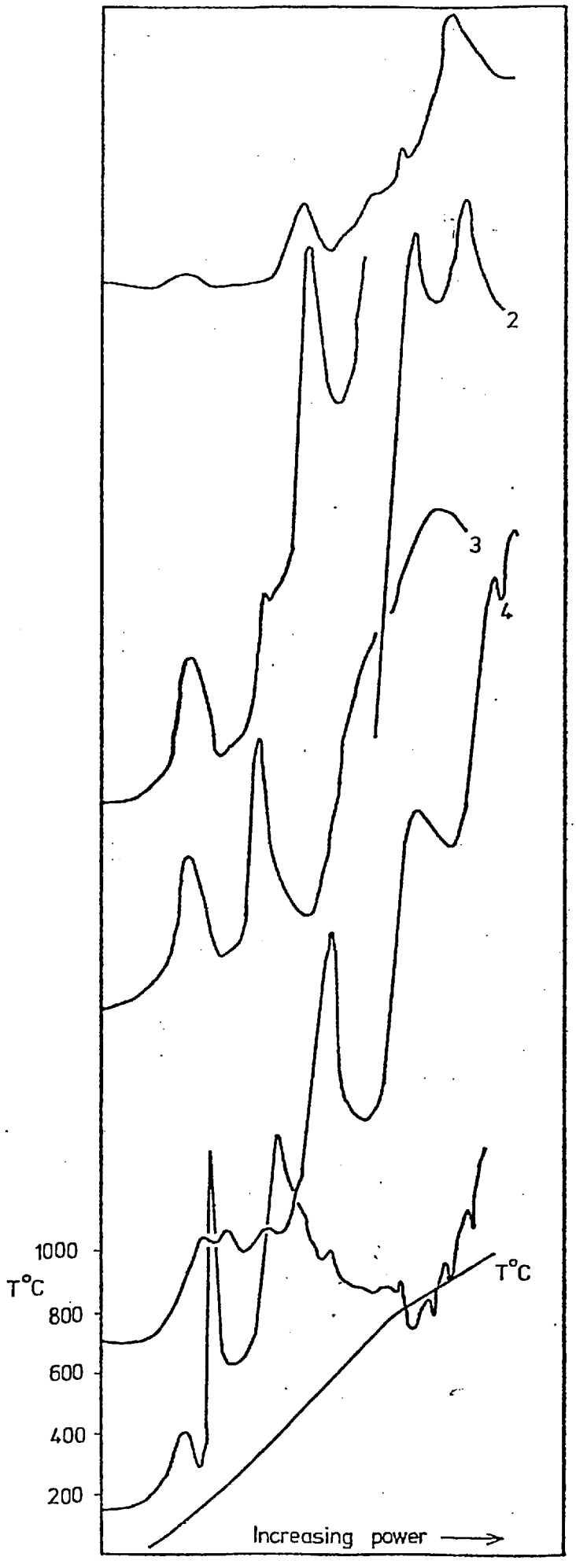
5. Post E.D.T.A. (178)

6. Post Hcl (178)

Fig. 9.13 Post chemical extraction T.E.V.Ps. Onecote Shales.

the carbon graphs of Figure 9.4 where the carbon release curve for Bowland samples revealed three, unlinked peaks at 140°, 560° and 820°C (graph 2) - in contrast to the usual double peaks (such as graphs 1 and 3 in the same figure). In graph 1, Figures 9.14 and 9.15, peaks approaching 800°C occur and these represent cadmium escaping from the dissociating carbonate structure. The inability of acetic acid to remove or even partially attack, the carbonate peaks in both samples suggests that dolomite-associated cadmium predominates, although calcite exceeded dolomite by a factor of eight in the minerals identified in Bowland rocks by x-ray diffraction. Palitsyn (1938) correctly identified the first of the twin DTA dolomite peaks as being due to the decomposition of the carbonate ions associated with magnesium (see dolomite graphs Figure 9.6, 3 and 4). The presence of cadmium in the magnesium-calcium carbonates and not in pure calcium carbonates may be the result of the dolomitization process, whereby cadmium carbonate is restricted to the calcium fraction of the dolomite and expelled from the magnesium dominant phase. Although since secondary dolomitization is a very selective process (with the magnesium derived in part, in some way, from sea water) one might have expected little room for cadmium in the dolomite structure.

In both figures, the high temperature peaks in graph 1, at 910° to 970°C, are formed by the release of cadmium from the sulphide lattice. In E1 and earlier P1 Bowland black shales, sulphide peaks tend to dominate the remaining cadmium peaks, whenever the total cadmium in the rocks achieves a suitably high level, around 12.0 ppm and more. The significance of high temperature peak dominance and high total cadmium contents will be explained in section 9.11. It has been concluded that sphalerite dissociates in the argon-plasma system between the temperatures of 865°C and 1035°C forming peaks at temperatures around 930°C to 980°C.



Sample no. 784 of E1 age Bowland Shales.
Cadmium 16.6 p.p.m.

1. Original.
   Scale = 200. mV.

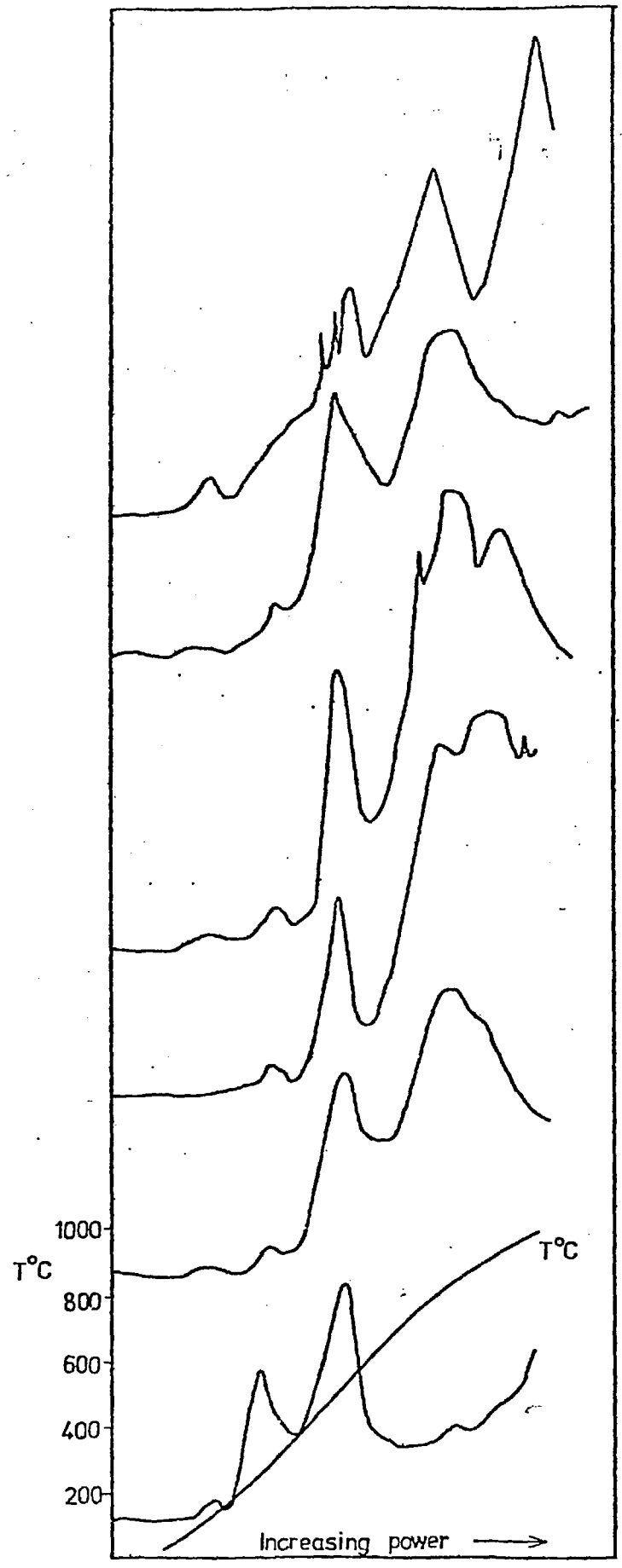
2. Post $NH_3.COOH$
   S. 2-6 = 100mV.

3. Post $CH_3.COOH$.

4. Post reducing-oxidising agent.

6. Post Hcl

Fig. 9.14 Post chemical extraction T.E.V.Ps. E1 Bowland Shales.



Sample nos. 128 (1) and 118 (2-6). Both of P1 age Bowland Shales.

1. Original
   (Cadmium 49ppm.)

2. Post $NH_3.COOH$
   (Original Cd 40ppm.)

3. Post $CH_3.COOH$.

4. Post reducing-oxidising agent.

5. Post E.D.T.A.

6. Post Hcl

Scale at 200mV.

Fig. 9.15 Post chemical extraction T.E.V.Ps. P1 Bowland Shales.

As regards the other peaks in the Bowland rocks:

1; that which forms between 460°; and 570°C formed as a consequence of the active molecular decomposition of carbon compounds containing cadmium. Partial dehydroxylation and elimination of carbon and oxygen bound CH_3 groupings from cadmium - containing organic material associated with or adsorbed on to manganese-containing mica minerals, results in the formation of the peak at 150°C in both figures.

2; the peak at 340°C (barely visibly in Figure 9.14 graph 1, and visible on graphs 2 to 4 and 5 of Figure 9.15) is caused by the release of cadmium from the lattice structure of vermiculite-like, mixed-layer minerals such as montmorillonite and mica. The appearance of this peak in Figure 9.15 is the result of astrong surface readsorption within the sample in the extraction vessel, on the mixed-layer mineral adsorption sites unsaturated by the action of the extractant.

Although the carbon related cadmium peaks are almost invariably present, it is to be expected that the simultaneous presence of the sulphide and the carbonate forms is highly unusual considering that the two anionic groups are essentially environmentally antipathetic. The detrital provenance of one of the two forms swept into an environment where the other is momentarily forming is conceivable and this hypothesis is accepted at this juncture, but only on two occasions out of thirty-four in the Mearley Clough traverse (see Section 9.11.1) and coincidentally in both samples chosen for the residue TEVP study. It seems most probable that cadmium was being incorporated into the carbonate lattice outside the realm of the excessively reducing environment where sulphide precipitation was taking place, and was being subsequently washed in. If this process caused a rise in the local oxidation potential and arrested the furthered continuance of sulphide-forming, reducing conditions, then the carbonate forms may have survived more easily. In Section 10, this issue will be reconsidered using further evidence.

9.9.3 EDALE DERBYSHIRE

Sample number: 1090939; locality: E4123, N3857, Edale Valley Derbyshire, Geological age: Visean E2 shales.

The original rock TEVP (Figure 9.16, graph 1) reveals an unusual pattern of cadmium enhancement with only one peak (at 515°C) truely isolating itself from the strong background levels. Comparison of the residue graphs with that for the original rock, shows that the expected 'distinctive' peaks exist beneath the unusual background, and what is more, several of them are not removed by hot hydrochloric acid - which is reminiscent of the hydrochloric acid residue graph of the Silurian rock (Section 9.6.2, Figure 9.10). In a rock where over 5.0 ppm total extractable cadmium is known to exist this is highly unusual and it must reflect the post depositional diagenetic processes which took place. In the Silurian rock (Section 9.6.2) the conclusion was reached that the majority of the 'residual' post hydrochloric acid peaks were caused by the release of cadmium from organic matter but in this Edale specimen the carbon graph (Figure 9.4, graph 1) for a similar E2 shale (sample number 1090900; locality: Edale Valley) shows two strong and distinct peaks at 165° and 645°C, the latter appearing to be too high to be responsible for the 495°C peak present in the hydrochloric acid residue graph. However, 490°C carbon peaks have been identified (in Bowland) and it seems reasonable to assume that all the peaks shown in the hydrochloric acid residue graph for 1090939 (Figure 9.16, graph 6) are formed, in the absence of pyrite, by the release of cadmium from dissociating carbon compounds.

The diversity of carbon compounds within the Edale shales of the same period is problematical. Following the discovery of an intimate association of solidified hycrocarbons with such gangue minerals as pyrite, marcasite and flourite at topographic Carboniferous limestone 'highs' below

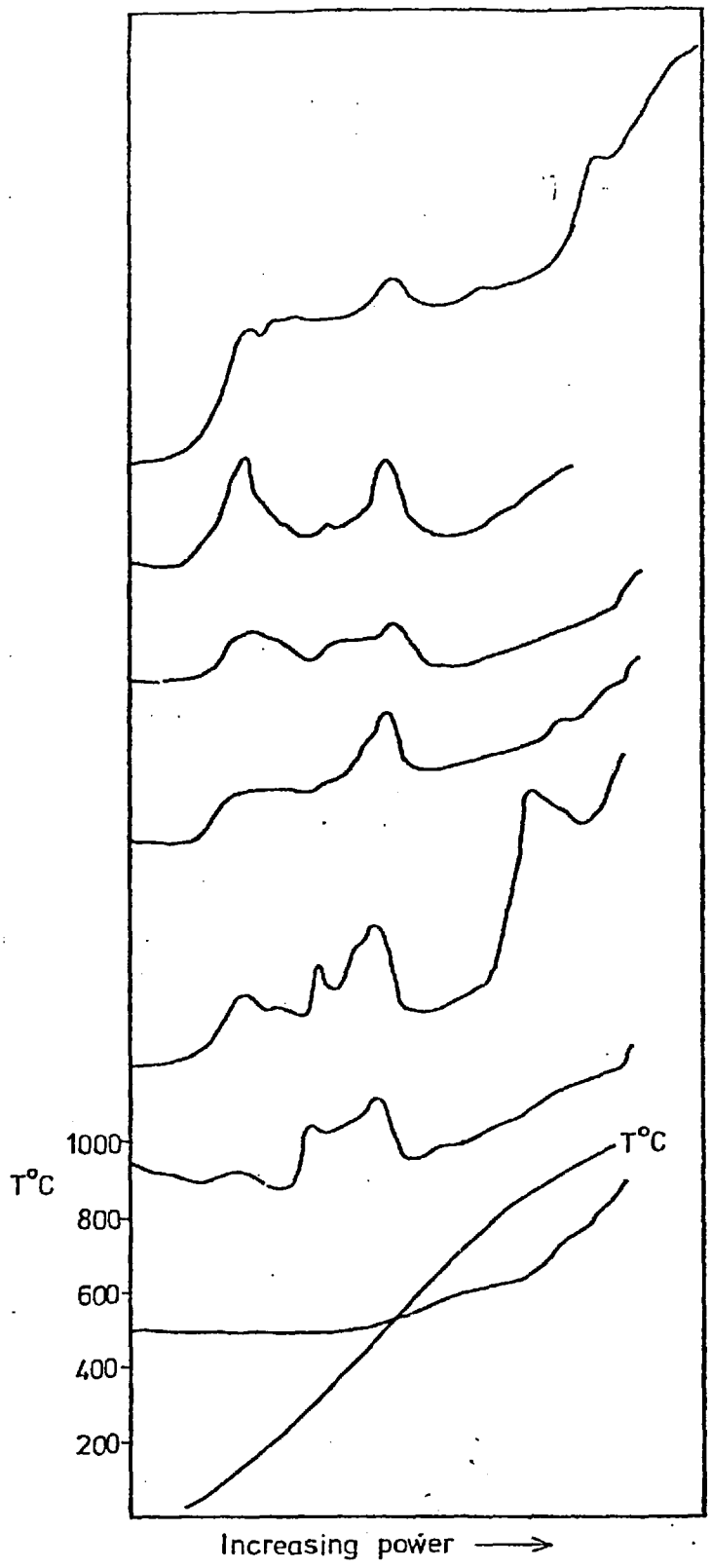


FIG. 9.16 TEVPs OF EXTRACTION RESIDUES, E2 EDALE SHALES

the Edale shale, Pering et al (1973) studied the possible parent sediments of the bitumen in order to learn something about the effects of processes associated with ore deposit formation on the origin and character of the organic matter. The Edale shale is considered, along with other units in the Millstone Grit series to be the source of the small reservoirs of crude oil occurring in Central England (Kent, 1954) and recent studies on fluid inclusions within the bitumens suggests that the temperature of ore-bearing distilling solutions was around 150°C or even as low as 100°C. The distribution pattern of the brown bitumen hydrocarbons according to Lovely (1946) closely resembles that of its postulated source rock - the Edale shales, and the material released when the bitumen is heated yields an infra-red spectrum similar to, and as complex as, that of the material extracted from the shale. The apparent release of asphaltic compounds in at least some of the Edale rocks and the thermal 'smearing' of cadmium forms (Figure 9.16) suggest the occurrence of events which are unusual for black shale formation.

The effect of ammonium acetate upon the original TEVP graph is to remove the 'background' and leave remaining those peaks which are hydrochloric acid residual and in addition, a large peak at 150°C. The latter is almost totally removed by the manganese specific reagent (graph 4) suggesting that the cadmium is also strongly related to manganese-containing mixed-layer minerals. The efficiency of the weak acetate solution in removing almost all the original cadmium was also discussed in the earlier Section (9.6.4) concerning the rocks of the Culm Measures. The possibility of a thermal event stoichiometrically weakening a heavy metal bonding and making it potentially available to the mildest of extractants is important since it is conceivable that quantities of cadmium have already been removed from the rocks as the result of the passage of such a solution and deposited alongside other gangue minerals in favourable environments (e.g. in the vicinity of solid hydrocarbons). The possibility of the shale having acted

as a 'trap' for cadmium enriched migrating solutions (as mentioned in Section 9.6.4) must also not be overlooked as a reason for the existence of readily removeable cadmium.

9.10 IDENTIFICATION OF CADMIUM-SPECIES IN AN ANOMALOUS STREAM SEDIMENT WITH THE AID OF SELECTIVE CHEMICAL ATTACK RESIDUES

The original TEVP graph for the cadmium rich stream sediment displays no clear cadmium peaks and consequently this indicates that the metal is so diversified in its form that no clear metal component association exists (see Figure 9.17, graph 1). In graphs 2, 3 and 5 readsorption occurs, but the extraction of manganese oxides from the sediment system by the manganese specific reducing-oxidising agent effectively removes all cadmium from the sediment (graph 4). This indicates that the cadmium association with manganese oxides dominates. Small peaks remain, even after the manganese-specific reagent has been used on the sample, at 470^{o} and 615^{o}C. The former is effectively removed by EDTA and is untouched by hot hydrochloric acid whilst the latter is more or less untouched by all of the remaining reagents. The former probably results from the release of cadmium from dissociating carbon compounds, whilst the latter appears to be caused by the thermal release of cadmium from the lattice of unweathered pyritous minerals.

9.11 STUDIES OF THERMALLY EVOLVED VAPOUR PROFILE MODIFICATIONS THROUGH STRATIGRAPHIC VARIATION

9.11.1 UPPER MEARLEY CLOUGH TRAVERSE, BOWLAND

To recapitulate on the geology of the Bowland Shales, the Group can be divided up into two distinct series based on broad lithological differences. The Lower Bowland Shale comprises black shales and

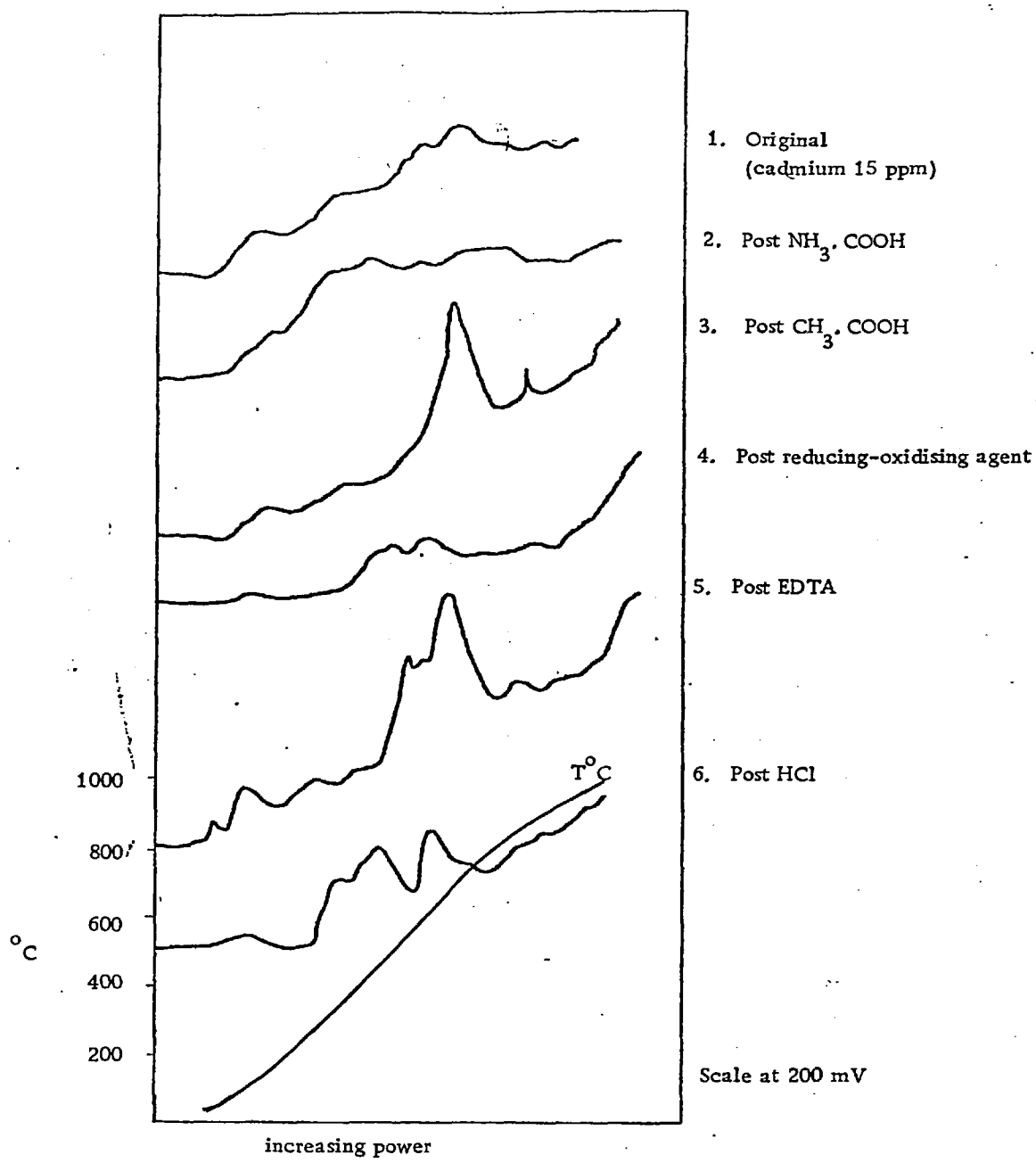


FIGURE 9.17 POST CHEMICAL EXTRACTION TEVPs STREAM SEDIMENT, TAWE VALLEY, SOUTH WALES

mudstones, usually calcareous in nature, interbedded with dark limestones and bullion beds. A large intercalation of sandstones within the lower group is known as the Pendleside Sandstone, a thick series of dark, medium-grained arenites which are especially well developed in late P1 times. The Upper Shale Group comprises papery and pyritous black shales, less calcareous in form and containing less limestone bands than appear in the Lower Shale Group.

The lithological differences between the rocks of the two groups are reflected in the change from the commoner presence of high temperature cadmium-species in the pyritous Upper Shale Group, to that of low temperature species in the Lower, more calcareous Shale Group. The diagramatic representation of cadmium-species peaks in the Mearley Clough traverse of Figure 9.18 reveals that of all the species types present, those involved with the presence of organic matter are most recurrent and persistent, i.e. those peaks between 100^{o} and 150^{o}C and 500^{o} and 600^{o}C. The carbon-cadmium species peaks occur so repetitively that there is no indication, from their consideration, of the fluctuating depositional conditions which must have occurred within the basin of sedimentation. There appears to be no possible way to predict impending depositional change within the shaly components of the sequence by extracting and examining the two cadmium-carbon components.

The interrupted presence of the cadmium peak at 300^{o}C is due to the discontinuous actual existence of the vermiculitic mixed-layer minerals, in which the cadmium is included. No relationship seems to exist between the presence of these mixed-layer minerals and that of zonal fossil bands, although their occurrence is especially apparent at the close of P1 times whenever sandstones, sandy shales and shales alternate in rapid succession. The weathering of mica minerals within these more energetic environments could accelerate the production of mixed-layer, montmorillarite rich minerals which could be ideal pre-diagenetic scavengers of any cadmium still available after the erstwhile inorganic precipitation of minerals.

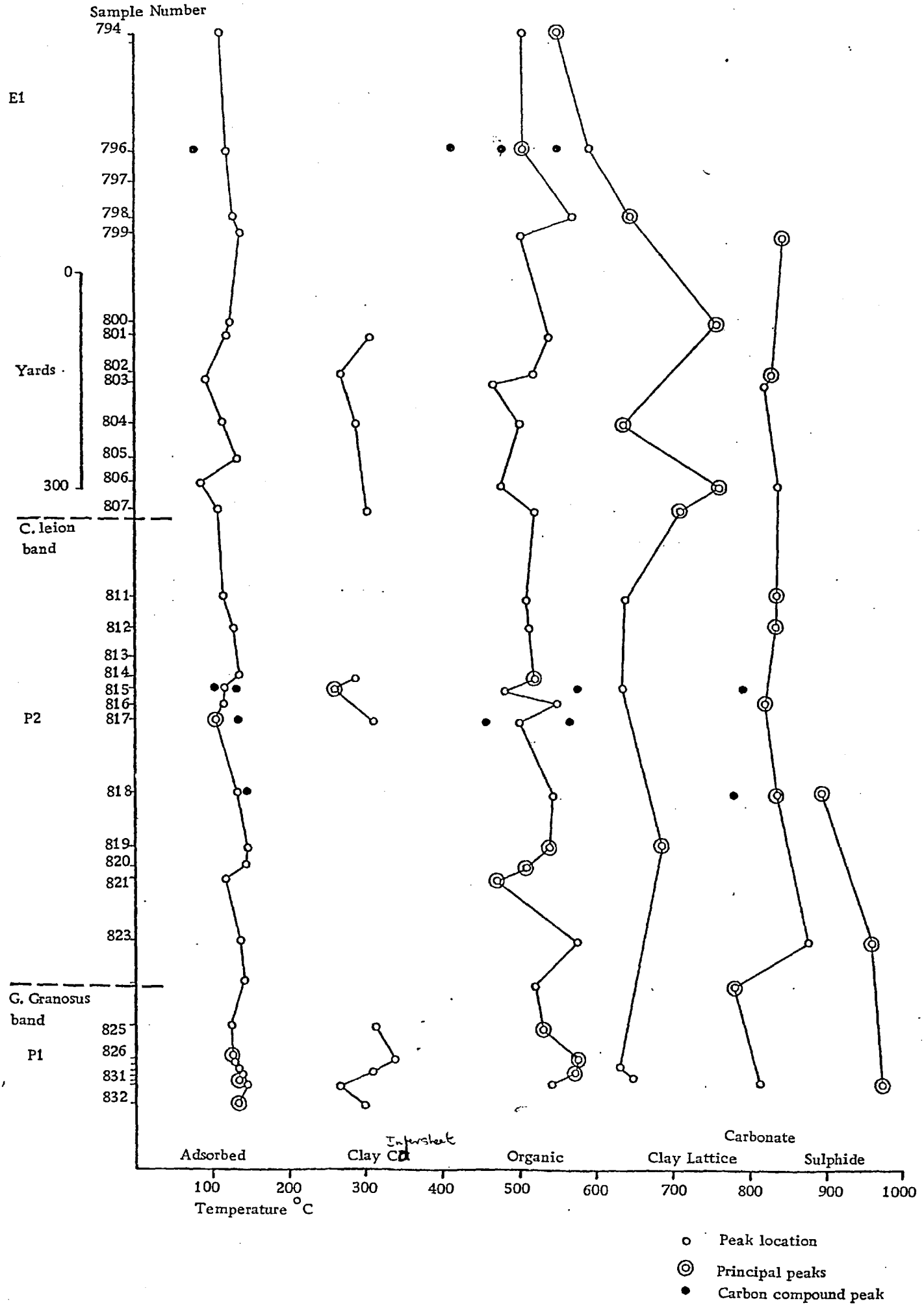


FIG. 9.18 BOWLAND SHALE GROUP. TEMPERATURE LOCATION OF CADMIUM-SPECIES PEAKS FOR CONSECUTIVE SAMPLES FROM THE MEARLEY CLOUGH TRAVERSE

The presence of the high temperature minerals again does little to indicate fluctuating physiochemical conditions. Although carbonate and sulphide forms, as a rule do not appear in the same sample the two forms appear alternately, each almost equally spaced amongst all the samples. The difference in the three sample groups, P1, P2 and E1 does become apparent from the position of the principal peaks per sample (see Figure 9.19). In the Upper Bowland Shales the principal peaks are always high temperature, whereas in the topmost P1 samples the most dominant peaks are low to medium temperature. The P2 shales, between these two series show great fluctuation of principal peak temperature, although high temperature sulphide peaks dominate.

It may be deduced that sufficiently little disturbance in carbonaceous mud sedimentation took place in Upper Bowland Shale times to upset the process of sulphide precipitation or the processes involved in incorporating cadmium into the carbonate structure. In P1 times influx of organic matter was on a similar level to that in Upper Shale times, resulting in the formation of similar organic-cadmium products. However, the fluctuation of environmental conditions with the arrival of sandstones produced sufficient instability within the black muds to prevent the domination of high temperature precipitated cadmium forms. The constant alteration of Eh and pH generally prevented the growth and stabilisation of the carbonate and sulphide forms. This would help explain the usual extreme oscillation of dominant peak temperatures amongst samples in P1-P2 times. The damping of this oscillation in E1 times is simply a measure of increased stability of formative conditions. In none of the three groups is actual cadmium presence especially dominant, indicating that metal supply, like the organic matter supply, was not fluctuating excessively. It is notable however, that when high cadmium contents do occur in the rock samples, the sulphide form is dominant and is the species which has 'precipitated' the excessive

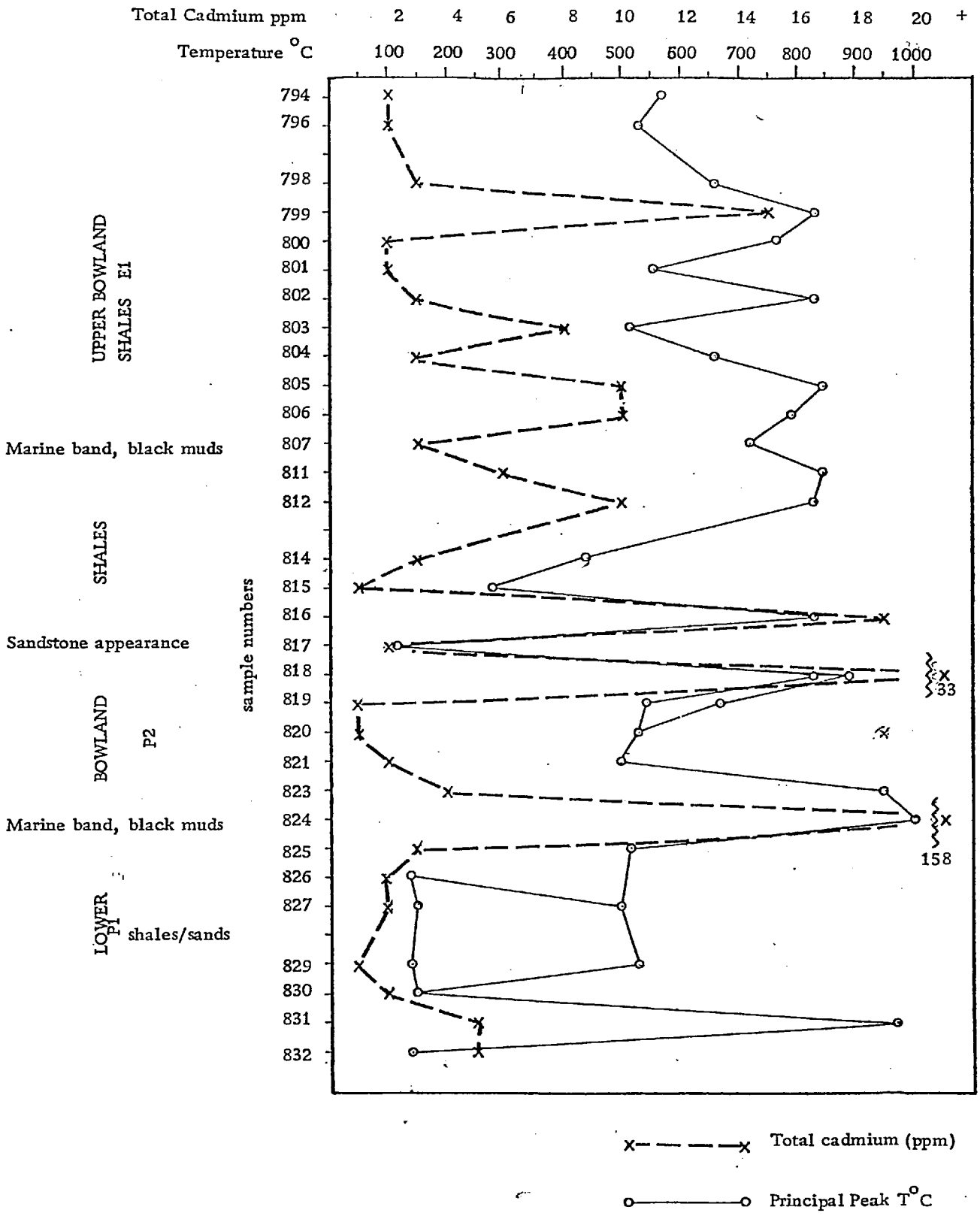


FIG. 9.19 SIMPLIFIED REPRESENTATION OF PRINCIPAL PEAKS OF MEARLEY CLOUGH SAMPLES, BOWLAND

cadmium presence. As more oxidising conditions follow excessive reducing conditions, implying that a cyclic sedimentation occurs, the same supply of metal will be bonded into lower energy associations as adsorbed and lattice-site cations instead of forming sulphides. But as reducing conditions return the increased acidity of the water in contact with the black mud (pH 5.5-7) will aid in the removal of any simply adsorbed ions and make them available for sulphide precipitation when sufficient hydrogen sulphide has been formed on decomposition. This explains why in any of the TEVP graphs for ammonium acetate solution very little cadmium is usually removed from the unweathered samples, implying that surface adsorption is unknown. Only cadmium which is strongly organically complexed or is strongly absorbed into clay mineral lattices will escape remobilisation and ultimate precipitation as sulphide.

Carbonates are formed in environments of high pH, low carbon dioxide partial pressure and moderate temperature. Where organisms flourish and hence where carbonate is readily available for shell production, inorganic precipitation might be expected. In Bowland this process takes place outside the realm of black mud formation and appears to include cadmium. The presence of the carbonate-cadmium phase as the principal form in the Mearley traverse is noted as commonly occurring immediately before samples where the sulphide form dominates.

The implications are that cadmium is only completely removed from the system by sulphide and carbonate and that cyclical recurrence of sulphide precipitating conditions occur seven times in the Mearley section. Cadmium released from its complexed forms on arrival in the slightly acidic black mud environment, will be partly adsorbed, partly scavenged and partly mobilised. The mobilised compliment may escape from the black shale basin towards the environment of limestone production in the

nearby reef, (see Figure 5.1) where it may substitute into the carbonate structures of precipitates or growing micro-organisms and eventually be redeposited back into the black shale basin. When euxinic conditions reach excessive proportions, more of the biogenic cadmium is released as bacterial decomposition of the organic matter increases, and this, along with any remaining mobile cadmium, will precipitate as the sulphide, this being the ultimate stabiliser of cadmium in the black mud basin.

9.11.2 UPPER BOOTH TRAVERSE, EDALE

The Edale shales are predominantly deposited in quiet marine environments and are known to show cyclical sedimentation with a repetition of formal phases. The geochemical study involved the sampling of the succession, on average, once every 300 feet (90m) and hence any small-scale cycles may have been overlooked.

The diagramatic peak locations shown in Figure 9.20 indicate that there exists a predominance of medium to high temperature peaks in the earlier samples of E2b age and a predominance of low to medium temperature peaks in the following E2C rocks. In the principal peak diagram (Figure 9.21) the rest of the Upper Booth series is shown and apart from a sporadic high temperature dominant peak in early H2 times, the medium temperature peaks dominate in H1 and H2 times.

The presence of high temperature peaks does not, in every case, reflect a higher than average total cadmium content, as it does in the Bowland sample, although on average a 7.0 ppm cadmium sample has a generally higher release temperature than a 2.0 or 3.0 ppm cadmium sample.

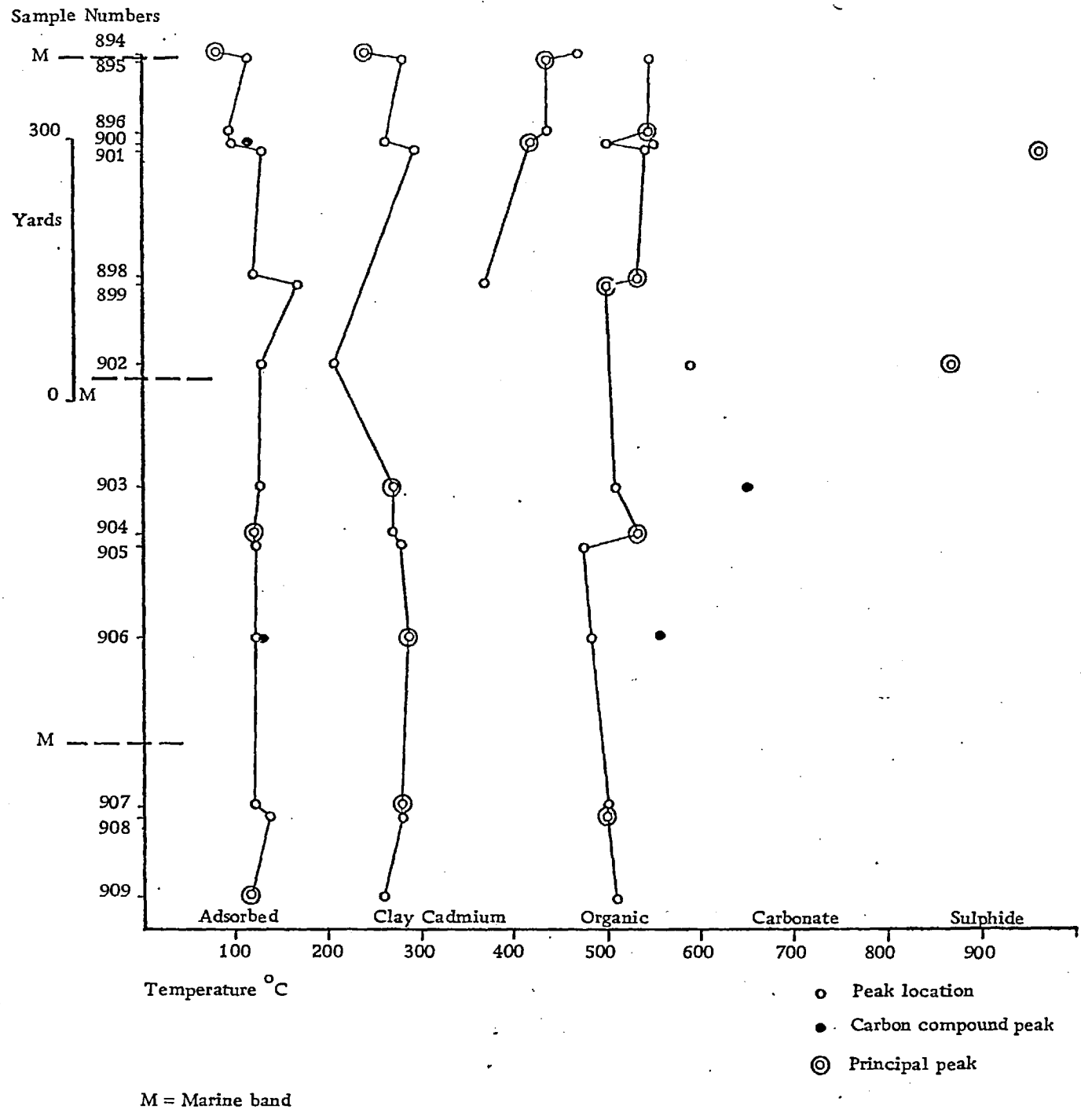


FIG. 9.20 EDALE SHALE GROUP
Temperature location of cadmium species peaks for consecutive samples from the Upper Booth traverse

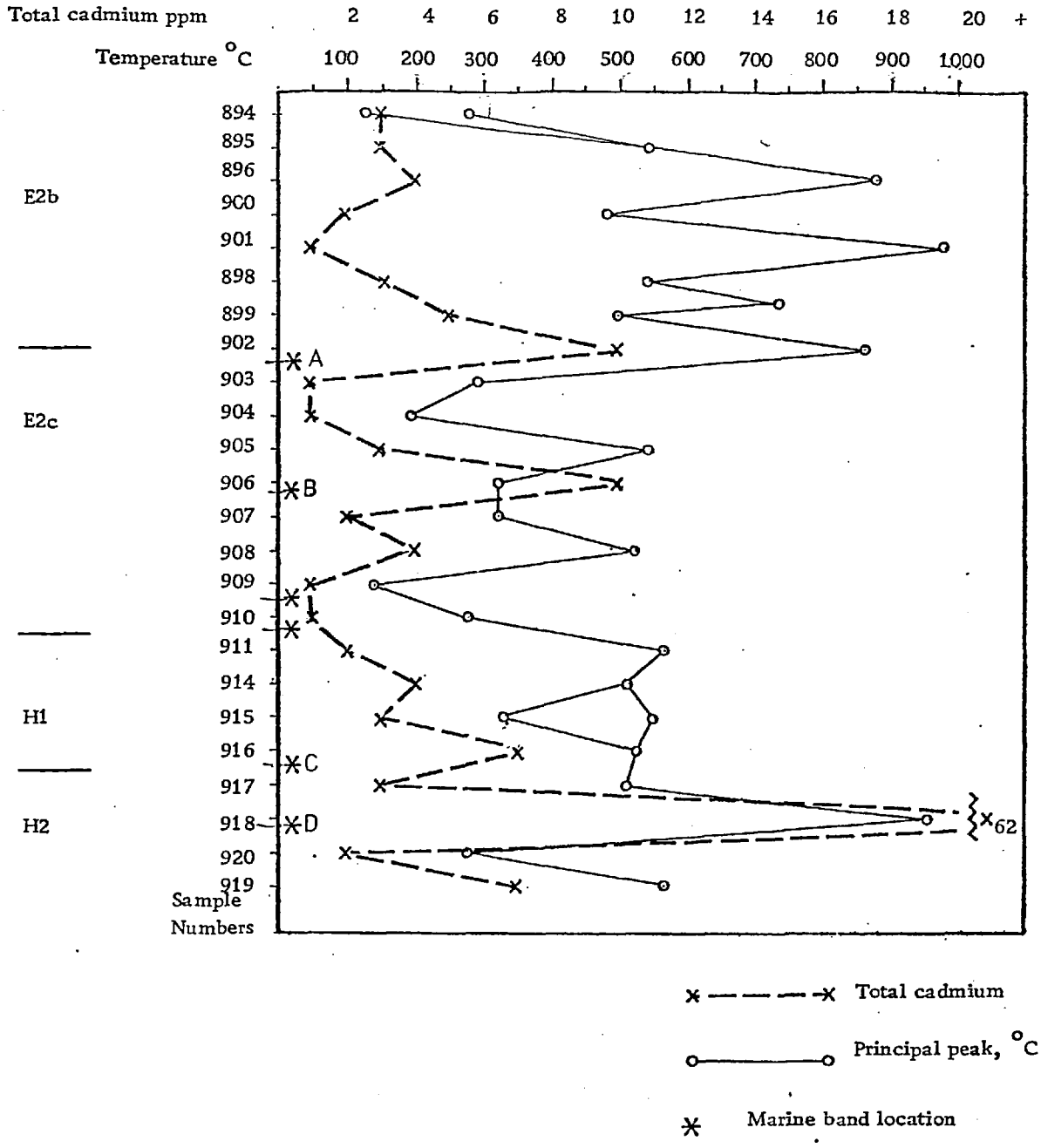


FIG. 9.21 SIMPLIFIED REPRESENTATION OF PRINCIPAL PEAKS OF UPPER BOOTH TRAVERSE SAMPLES, EDALE

The presence of Marine Bands does not affect the temperature of the dominant cadmium peak in samples adjacent in the succession, but the total extractable cadmium content of the rocks noticeably increases following most of the marine bands, falling off in succeeding samples until the next marine band is reached. (Figure 9.21). This is especially true of those bands headed A-D in the diagram. It is suggested that at the time of Marine Band deposition increased environmental toxicity caused by the deposition of excessive organic matter and the bacterial production of hydrogen sulphide, initiated density stratifications in the most stagnant part of the basin preventing metal-rich solutions from reaching the zone of sulphide precipitations. Following the Marine Band,increased aeration enabled the enriched upper waters to come into contact with the sediment, which retained the metal and was consequently enriched at that horizon. The rocks of Edale and Bowland are therefore very different, for in Bowland it is primarily the sulphides and secondarily the carbonates which concentrate and stabilise the great bulk of the available cadmium, while in Edale, these forms of cadmium capture are virtually unknown. The Edale traverse represents comparitively small-scale cadmium activity uncomplicated by the presence of carbonate mineral production. In Edale the most common principal peak in Figure 9.21, is that attributed to the strong carbon association at 500^{o} to 600^{o}C whilst the secondmost common principal peak is attributed to the detrital association of cadmium within the lattices of the mixed-layer clay minerals.

The actual formation of sulphides is comparitively rare and this phenomenon may have resulted because of the following reasons:-

1 The rapid rate of sedimentation prevents thorough in situ mineral weathering and resultant release of detrital cadmium for reprecipitation.

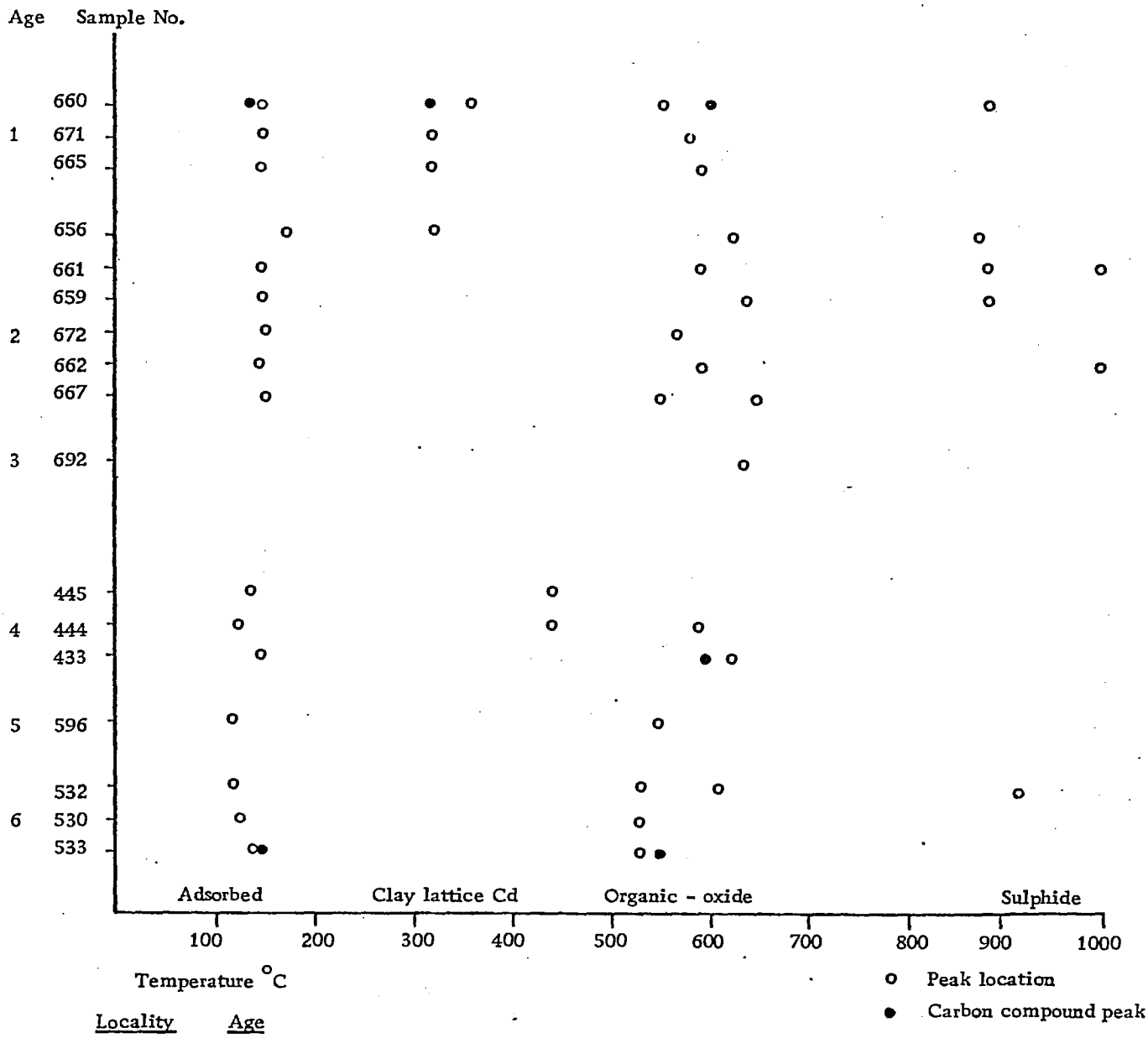
2 The comparitively detrital nature of the incoming cadmium, which has resulted from the formation of cadmium-clay associations in an imobile, non-acidic environment of weathering.

In Bowland, in complete contrast, a good deal of the cadmium enters the basin of deposition in a relatively 'free' form having adsorbed onto clays or formed organic complexes in order to be transported. This 'free' form of cadmium presumably reflects an acidic, mobile environment of weathering in which cadmium is mobilised away from the forming clay minerals before being involved in their growth. Furthermore the excessive reducing conditions which periodically build-up in the basin of deposition, and which may reflect a slower rate of sedimentation, aids the in situ mineral weathering and provides more released cadmium to the precipitating phases.

In Edale, therefore, the most important consideration is the almost continuous presence of the cadmium-mixed layer clay mineral peak at 300^{o}C in Figure 9.21 as this emphasises the already detrital nature of the incoming cadmium.

9.11.3 CULM MEASURES, CORNWALL

In comparison to the rocks of the Central Province, those of the Culm Measures are exceptionally low in total cadmium content; those samples which have 5.0 ppm or more cadmium (for example the rocks of R1 age) contain sulphides, although in such instances, the sulphide peak is insignificant in size in comparison to the dominant 500^{o} to 600^{o}C peak. In general however this 500^{o} to 600^{o}C cadmium-carbon peak dominates all of the Culm rocks analysed on argon-plasma (see Figure 9.22).



	Locality	Age
1	Aureole	R2
2	Aureole	R1
3	Aureole	P2
4	Coast	G1
5	Coast	R1
6	Coast	H1

FIG. 9.22 SOUTH WEST PENINSULA
Temperature location of cadmium species peaks.

The larger temperature range is influenced by the heterogenous desorption evolution-process of cadmium from the organic comples (see Section 9.2). The maximum peak height temperature resultantly shifts to lower temperatures as metal presence in the complex increases.

The rocks of the Culm Measures have all been reconstituted by the thermal metamorphism accompanying the intrusion of the Permian granites, and any contained cadmium would have been removed or redistributed assuming that some 'emmanating front' with sufficient extractant power and capacity affected the rocks. A cadmium-rich 'front', however, coming into contact with fine grained sediments may have utilised these sediments as a 'trap' and caused minor element enrichment. In complete contrast to such a hypothesis a case for the stoichiometric weakening of cadmium bondings in the granite aureole samples could be argued.

The graphs illustrated in Figure 9.23 are the vapour profiles of five rocks chosen to represent the Culm Measure sequence. Three points of note emerge from their study:-

1 All have a dominant cadmium-carbon peak at 500^{o} to $600^{o}C$ and an adsorbed cadmium peak at 100^{o} to $190^{o}C$.

2 The only high temperature peak is shown in sample 1090596. This is formed by the release of cadmium from a dissociating sulphide mineral.

3 The major difference between the granite aureole rocks and the others is the distinctive presence of a peak at around $300^{o}C$. This is formed by cadmium escaping from the lattices of the mixed-layer or vermiculitic minerals. A similar, though less well-developed peak of the same type is also apparent in the trace of sample 1090471.

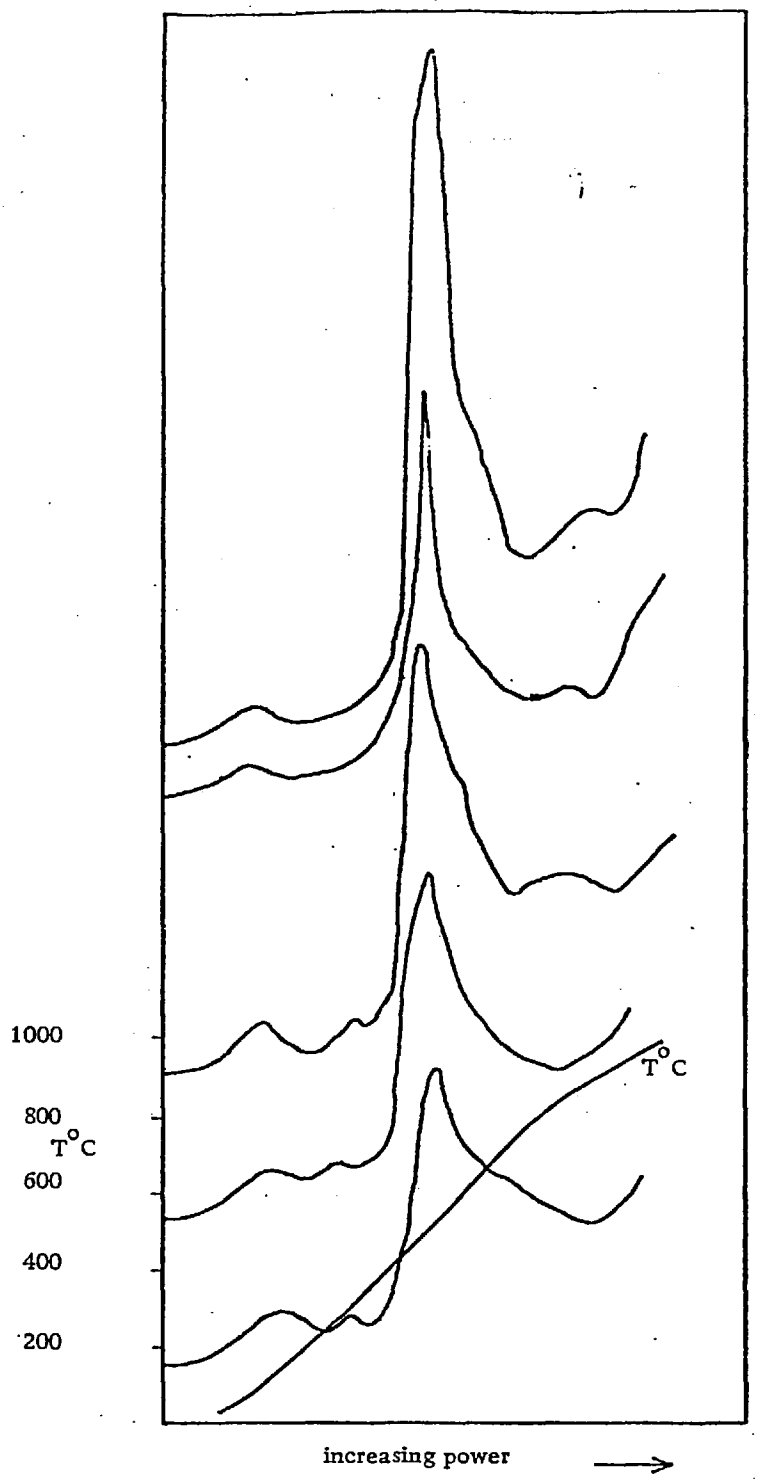


FIG. 9.23 TEMPERATURE LOCATION OF CADMIUM SPECIES PEAKS FROM SAMPLES OF THE CULM MEASURES, CORNWALL

The major difference in the aureole rocks and the coastal Culm rocks can be seen in the schematised Figure 9.22. In this diagram the sporadic nature of many of the peaks reflects basic mineralogical differences within samples collected over a very wide range of geographical and stratigraphical area.

In the sediments which have been deposited near the present-day granite at Okehampton, more cadmium seems to have been available. However, the basic difference in vapour profiles between the Okehampton samples and the coastal samples suggests that a retentive process appears to favour the samples of the Okehampton area and this in itself may explain the anomaly.

One of the two hypotheses may be considered with regard to this anomaly:-

1 The formation of a cadmium-vermiculite association is detrital in nature and such an association would not be produced in a highly reducing basin of deposition where, in fact, processes would tend to erode such associations. The association depends solely on the physicochemistry of the weathering site which, by virtue of immobile, non-acidic formative conditions, permitted cadmium retention and eventual incorporation into the forming clay minerals. In contrast the weathering sites which supplied the coastal sediments did not favour cadmium retention being presumably much more acidic in character. A similar quantity of cadmium can be envisaged as being initially available for these coastal sediments as well as for the Okehampton samples, but here the cadmium was washed into the basin of deposition in a 'free' form, transported as adsorbed and organically complexed cations. Once deposited the cadmium continued to complex in organic forms and form as sulphides where reducing conditions

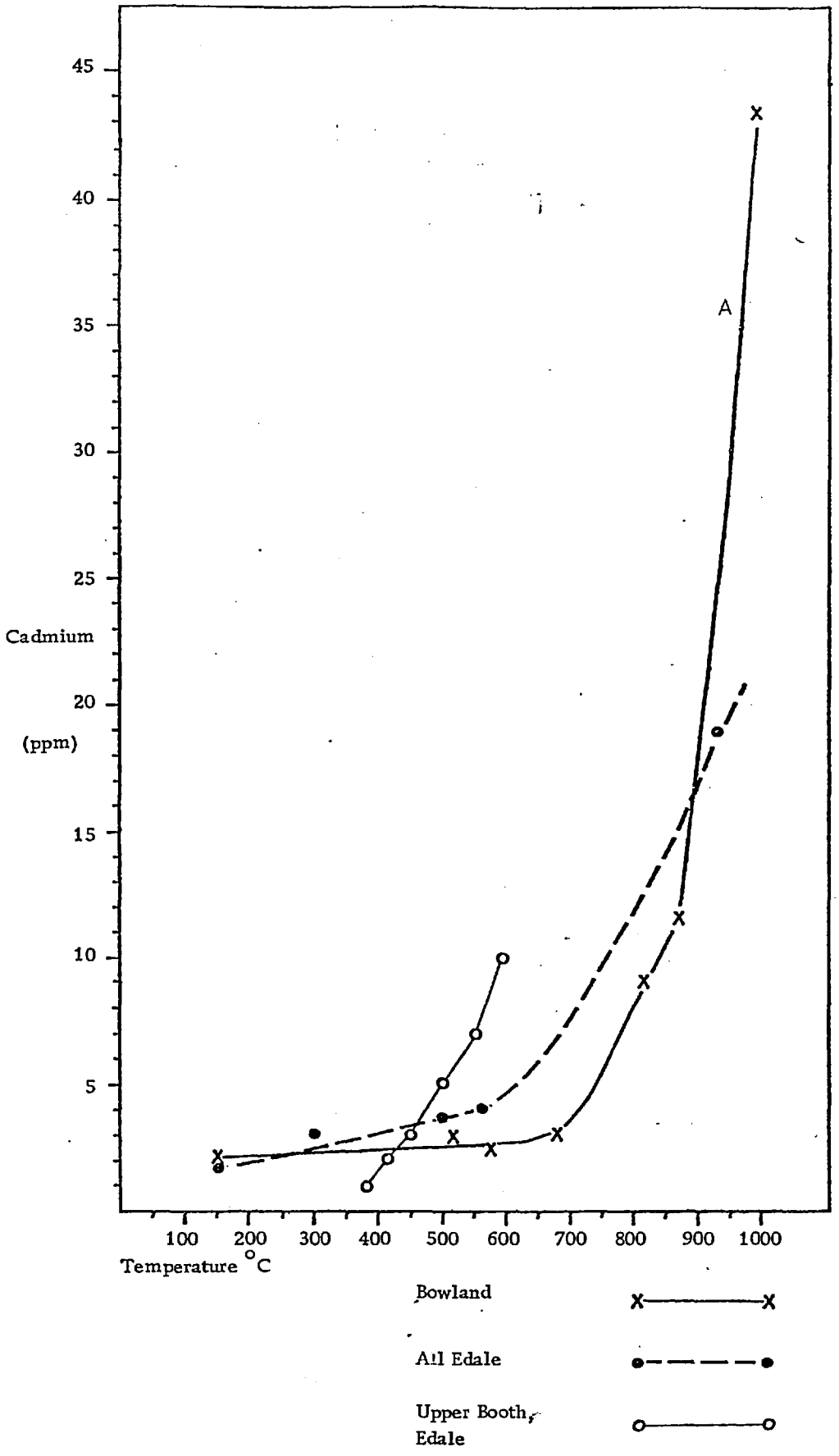


FIG. 9.24 GRAPHS OF AVERAGED DOMINANT PEAK TEMPERATURES AGAINST CORRESPONDING AVERAGED TOTAL CADMIUM

were extreme and secondarily mobilised cadmium sufficiently available. Cadmium which has not been retained in this basin of deposition is presumably dispersed over a large area eventually to be precipitated in a location where conditions are more physicochemically conducive.

2 As mentioned in Sections 9.6. (page 203), 9.7. (page 207) and earlier in this section it is envisaged that a cadmium-rich 'front' did in fact emanate outwards from the granitic intrusions of Cornwall. Aguilar (1974) showed conclusively that arsenic enrichment in granite aureole rocks was caused by emanations from the granites. Minor-element rich solutions encountering 'traps' of highly adsorptive sediments, such as black shales, would readily yield their trace element content to them resulting in selective enrichments.

9.12 STUDIES ON PRINCIPAL PEAKS FROM THE BOWLAND AND EDALE AREAS

The importance of TEVP peak identification for the understanding of the geochemical behaviour of an element throughout a series of rocks has been shown in Section 9.11. In this present section the principal peaks are utilised in a way which conveniently summarizes the fundamental differences in the ways which cadmium behaved during its erosion-deposition cycle, in Bowland and Edale.

Believing that, in Bowland certainly, sulphides (which dissociate at high temperatures) form when sufficient 'excess' cadmium is available in the correct circumstances, then it is reasonable to assume that a sample with a large total contenf of cadmium should have a large or even a dominant, high temperature peak and vice versa, a sample with a dominant high temperature peak would be expected to contain high levels

of cadmium. For each area in turn the cadmium values for principal peaks with temperatures between 0-150°, 150-300°, 300-450°C and so on, are all totalled and averaged. These average cadmium values are then plotted against the averaged principal peak temperature of each of the forementioned categories.

In Bowland, sulphide and carbonate precipitation controlled the high cadmium presence, whilst rocks with low total cadmium may be dominated by any of the low to medium temperature forms (see Figure 9.24.). This is illustrated in curve A where samples with up to 2.0 ppm cadmium have prinicpal peak temperatures ranging through a vast 550°C range. Above this level several specific forms, which dissociate over a relatively narrow range of temperature (250°C) retain much larger quantities of cadmium. This confirms the assumption that in this area the cadmium entering the basin was predominantly in a 'free' form, rather than a specific, or detrital form. The free cations were simply scavenged by whatever process was dominant in a certain part of the basin. Thus some cadmium may adsorb on clays, some may form organic complexes and some may substitute into the lattice of pyrite or even oxides or iron. If conditions were excessively reducing, then cadmium would tend to remain mobile and even re-mobilise in the acidic conditions and in this state it would be precipitated as sulphide if hydrogen sulphide evolution occurred.

In complete contrast, carbonate and sulphide phases in Edale do not predominate and compete for metal which has already taken up specific forms. Thus, the slopes of the graphs (Figure 9.24.) are initially steep with small rises in total cadmium reflecting in large rises in temperature, each rise representing a new cadmium species (see Figure 9.24.). In the low to medium temperature range cadmium-associates

occur on average in specific forms which are determined by the total cadmium content of the rocks. As a result the steep inflection of the curve representing the formation of sulphide species occurs when the cadmium content in the Edale rocks is at least two times that of the Bowland rocks, i.e. at levels greater than 2.0 ppm in Bowland, carbonate and sulphide species start to dominate, whereas the formation of sulphide in Edale happens when the total cadmium content is around 5.0 ppm. This larger total content in Edale indicates that a smaller proportion of the Edale cadmium can actually partake in sulphide precipitations because the greater proportion of it enters the basin in a secure, detrital form.

9.13 CADMIUM SPECIES PRESENCE IN TOPSOILS AND SUBSOILS FROM SOUTH WALES

9.13.1 WATERLOGGED SOILS

The TEVP study of polluted soils in South Wales has been undertaken in order to investigate the behaviour of cadmium in soils upon conditions of burial and increased humification. Most of the anomalous cadmium soils have been taken from hollows at the head of the Tawe Valley which experience intermittent waterlogging. The soils - a topsoil sampled to 15 cms and two subsoils from 15-30 and 30-45 cms- were taken from the centre of one of these hollows and their TEVP graphs are shown in Figure 9.25. While no change in cadmium species type occurs with burial, progressive loss of cadmium occurs and this is reflected in much reduced peak heights (compare graphs 1, 2 and 3, Figure 9.25). The total cadmium content of the soils varies enormously from 58.5 ppm in the topsoil down to 10.0 ppm and 3.0 ppm in the two subsoils. The following identification of cadmium associations in this section has been made with careful reference to DTA graphs of the dissociation patterns of likely mineral groupings and to field observations.

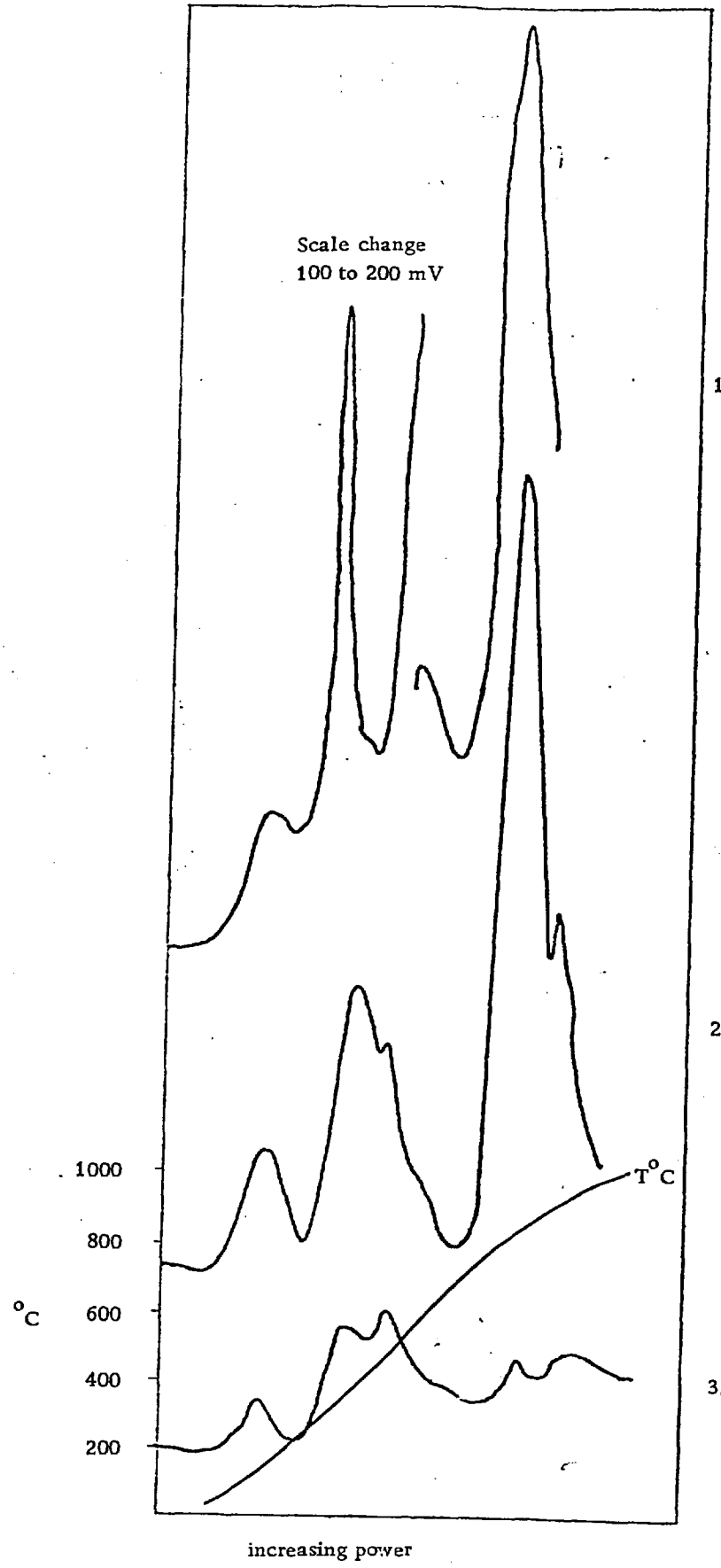


FIGURE 9.25 TEVP GRAPHS OF SOILS COLLECTED FROM THREE DEPTHS IN THE TAWE VALLEY, SOUTH WALES

The low temperature cadmium peak in graph 1 has been most likely caused by the release of the metal from the cation-sorbed region of interstratified montmorillonites and micas. The peak at 335°C is probably due to cadmium expulsion from dissociating iron-oxide gels which visibly form in the marshy surface environment. The 550°C peak has been formed by cadmium loss from the structure of carbon complexes as they undergo active molecular decomposition whilst finally, the high temperature peak at 805°C represents the breakdown of clay mineral structures with the resultant loss of included cations.

Two minor differences are noted in burial (graphs 2 and 3). The first is that the iron oxide gel, which releases cadmium at 335°C in the surface sample, changes to a more ordered goethite-type structure and releases cadmium at the higher temperature of 410°C in the 30 cm soil. A revertion of the iron hydroxide in the 30 cm subsoil to a crystallographically complex iron hydroxide (such as lepidocrocite) can occur at the greater depth. The second difference is the addition in both the subsoil graphs of a peak at 930°C. This may be the sulphide-cadmium association formed in anaerobic conditions as a result of reaction of cadmium with hydrogen sulphide which is produced following the bacterial breakdown of organic matter.

9.13.2 MODERATELY-DRAINED SOILS

The soils illustrated as vapour profiles in graphs 1 to 3 of Figure 9.26 have been collected from the moderately-drained slopes in the same traverse as the soils of Figure 9.25.

The principal topsoil peak is probably caused by release of cadmium from an association with iron hydroxide gels and goethite mixtures, an

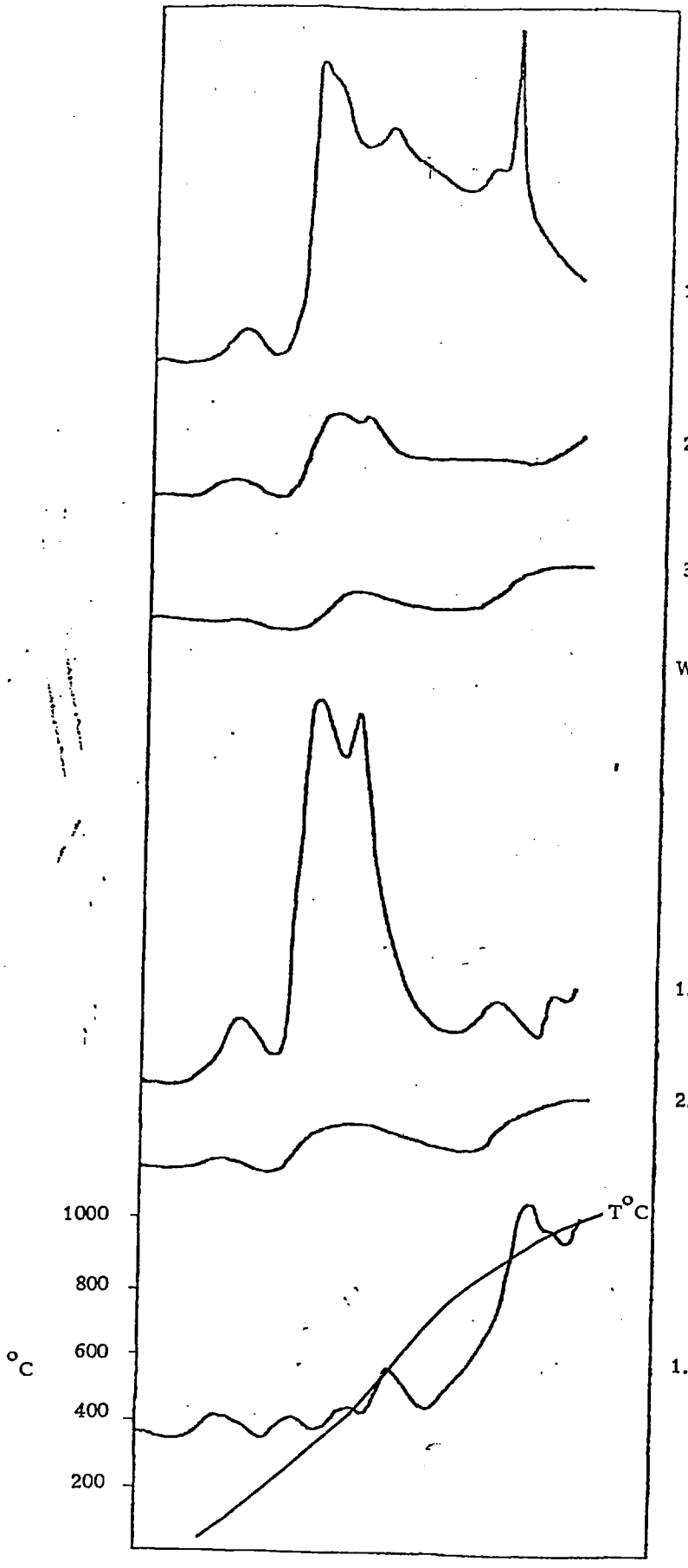


FIGURE 9.26 TEVP GRAPHS OF SOILS FROM MODERATELY DRAINED AND WELL-DRAINED SOILS IN SOUTH WALES

association identified for cadmium by Meyer's study on Keel soils (1973). The peak is still present in the 30 cm subsoil but is absent (probably as a result of eventual leaching-out) in the 45cm subsoil. The carbon-cadmium peak in the topsoil at 520°C, probably representing the principal thermal reactions of the unsaturated materials of high carbon content (such as lignins and humic acids) is the only phase remaining in the 45 cm subsoil from which almost all of the cadmium has been leached out.

The strong cadmium peak at 856°C is, in all likelihood, caused by the release of cadmium from the structural breakdown of montmorillonite clays, which have been fully leached out of the subsoils.

The effect of burial on a moderately drained soil is to cause removal of cadmium (presumably by leaching of the clay and iron-oxide/hydroxide fractions). The production of acidic leaching solutions (formed in the intermittently sodden organic topsoils after vegetative decomposition) will ease the passage of iron oxides, cadmium and fine-grained clay minerals from the subsoils.

9.13.3 WELL-DRAINED SOILS

Collected higher up slope on the same soil traverse as the previous samples, graphs 4 and 5 of Figure 9.26 represent the TEVP's of the topsoil and the 30-45 cm subsoil. Although the iron-manganese oxides again scavenge most of the cadmium in the topsoil, the cadmium-carbon peak is almost as important. As it has been postulated (see Chapter 3 Section 3.2) that the cadmium source for these soils is aerial, then the iron-manganese oxides are probably the 'scavengers' which 'sponge up' the particulate cadmium oxides which deposit from mists and rain onto soil surfaces. Good drainage in soils probably causes the leaching-out of cadmium-included iron-manganese oxides (graph 5). However, some interchange of iron-oxide held cadmium to the organic complexes

may occur especially on occasions when surface waterlogging conditions catalyse the production of mobilising acidic conditions. Cadmium may be then made available for carbon complexation. In the well-drained soils predominance of the organic-cadmium peak at depth is noted. The broad-based, low-peaked nature of the peak is a common feature in DTA graphs caused by soil matter humification.

The peak caused by cadmium release from clay structures which was so dominant in the two more waterlogged soils, is barely present in the well-drained topsoil. As iron-manganese oxides are only common in waterlogged conditions in the environment, and as they can be seen to be the main primary cadmium scavengers in these environments, then the absence of significant cadmium levels in the other well-drained moorland soils of the Black Mountains of South Wales, can be explained by the absence of conditions favourable for iron-manganese oxide precipitation.

9.14 GENERAL CONSIDERATIONS IN CONCLUSION

The rocks which have been considered in this chapter have been deposited as sediments in quiet, predominantly marine waters where the influx of organic materials has been in sufficient excess to initiate reducing conditions and create an environment where available heavy metals can be concentrated.

The most consistent cadmium association with a rock-forming component which can be shown by the vapour profile method, is that with organic matter. The presence of cadmium-carbon peaks in representative samples from the main areas suggests basic differences in the type of organic matter which is present (as already discussed in Chapter 7). In Edale for example, considerable diversity can exist between the temperatures of cadmium-carbon dissociation from different samples of the same period

and this could be explained either in terms of the theories of bitumen distillation from the shales (Pering et al., 1973) or simply in terms of the diversity of incoming organic detritus. In contrast the rocks of Bowland indicate no such diversity and this may indicate a greater maturity amongst the organic debris. Carbonate-carbon precipitation is considered equally as important a phase in the Bowland basin and this may signify a greater depth of deposition, with a resultantly finer and more detrital sediment, and greater destruction of organic materials in a more oxygenated environment. Lastly, in the Culm series the cadmium-organic carbon peak is invariably dominant and it is possible that a good deal of the cadmium arrived in the basin of deposition already in an organic form.

The possibility of the existance of biogenic cadmium presence may prove to be vital in an understanding of the origin of the metal within Visean black shales in comparison to black shales of other ages. The Carboniferous era was a period of unusual and luxuriant vegetation growth which climaxed in the Coal Measures of d5 age. The shales within the Coal Measures differ little mineralogically from the shales of the Visean, but in comparison they are deficient in heavy-metals. It is conceivable that the roots and leaves of the plants growing in Visean times took up and effectively concentrated cadmium contained in the rocks of earlier age before releasing the metal as detrital sediment in the decay stage of the plant cycle. John (1972, 1973) in recently published accounts of the effect of the growth of food crops in a cadmium-enriched acid (pH 5.1) soil, discovered high concentrations of the metal in the plants, especially in the roots and leaves.

The breakdown of organic materials by oxidation in the carbonate-rich basins and by bacterial action in the anoxic sediment basins released

cadmium for involvement in the other processes which have been identified in this chapter and which will be re-iterated below. Only a relatively rapid rate of sedimentation, and hence burial, could prevent total eventual breakdown of the organic detritus, resultant loss to the water and redistribution of biogenic cadmium.

The recognition of four other basic cadmium forms indicates the complexity of each of the basins of deposition and reflects the extent of disequilibria which must have existed in each. Cadmium is known to adsorb onto the surfaces of clay minerals and carbonaceous matter; it can substitute into the clay mineral lattices, substitute for calcium in carbonate structures, form sulphides and enter into the growing pyrite lattice.

Of these, the substitution of cadmium into the clay-mineral structure is the only other predepositional (or detrital) form which can be shown to exist. The possibility of cadmium entering the basin of deposition as free ions or as simple surface-adsorbed forms is also quite likely, but impossible to prove. Once in the basin the cadmium may be mobilised and distributed from its initial hosts and form diagenetic minerals. The process of re-organisation and the formation of diagenetic minerals can be caused by alternationof oxidising (remobilising) and stagnating (sulphide forming) conditions. During the time of remobilisation adsorption forms will dominate with clay minerals and organic complexes as the dominant hosts and in addition cadmium-calcium substitution will take place in carbonate lattices if conditions are conducive for carbonate production. Once buried, migration of the weaker bonded cadmium may help enhance the metal content of sulphides, notably pyrite, which commonly form in reducing conditions below the sediment-water interface.

The most potentially mobile forms of cadmium are those weaker forms which were readily attacked by the less powerful extractants and

thermally dissociated at lowest temperatures; as has been propounded in this chapter, no two areas are in detail very much alike. If cadmium is known to be the cause or accelerator of biological problems in animal husbandry, its readily extractable presence in areas of high black shale incidence may be of considerable importance. The full implications of the results obtained in this and the previous chapter with regard to this consideration, will be fully discussed in the section, 'geographical extent of the cadmium pollution problem' in chapter 13.

CHAPTER 10

THE CORRELATION OF MAJOR ELEMENT GEOCHEMISTRY WITH THE SEDIMENTARY ENVIRONMENT

10.1 THE SIGNIFICANCE OF THE ALUMINIUM\SILICON RATIO

In argillaceous sedimentary rocks silicon occurs both within the lattices of the clay minerals e.g. montmorillonite, illite and as free quartz, SiO_2. The ratio of quartz as SiO_2 to aluminium oxide, Al_2O_3 is accepted as an approximate indication of the proportion of quartz to clay minerals in a sediment, the ratio appearing lowest in the finest grained sediments. Thus, within the sedimentary provinces, the more silica-rich rocks may give some indication of the nearness of the shoreline and hence the detrital source.

In the sets of samples in this study, silicon-aluminium ratios have been calculated for two reasons, firstly to indicate their relative clay-richness and secondly to discover if the inclusion of cadmium into the lattices and onto the surfaces of clay-minerals (deduced from the extraction experiments), can be verified. The percentages of total cadmium associated with the clay minerals can be discerned from Table 8.2 of chapter 8. From this table it will be seen that clays of the Edale and Cornwall region rocks control the distribution of cadmium more noticeably than clays of other areas. Over 75% of the total rock cadmium in both areas can be extracted by the clay-stripping reagents. This clay-richness is reflected in low aluminium\silicon ratios for individual sample sets from both areas (see Table 10.1 and graph, Figure 10.1). The Grand Means for aluminium\silicon ratios from the black shales of the remaining two regions are significantly higher, suggesting that the incoming detritus to the basin is less fine and less clay-rich. In more

TABLE 10.1 A COMPARISON OF THE ALUMINIUM\SILICON RATIO AND ASSOCIATED CADMIUM AND CALCIUM VALUES FOR ALL SETS OF SAMPLES

Sample Location	Geological Age/Name	Number Samples	Ratio Aluminium\ Silicon	Mean Cadmium	Mean Calcium
Bowland, Lancs.	Lower Worston Shale Group	12	3.5	2.3	11.65
	Lower Worston Shale Group + Pendleside Limestone	11	2.5	5.6	5.47
	Bowland Shales, P1	15	8.1	24.5	8.12
	Bowland Shales, P1 + P2	36	2.5	3.1	2.7
	Bowland Shales, E1	18	3.2	4.4	2.54
River Dove	Dove Shales, E2 (excluding Group 223-236)	34	6.8	3.8	0.29
	Dove Shales, E2, Group 223-236	13	2.5	7.6	7.15
Onecote, Mermaid	Onecote Shales, P1-P2	30	4.2	5.1	3.25
Onecote, Hamps	Onecote Shales, P1-P2	22	4.1	5.9	3.7
Onecote, Grange	Onecote Shales, P1-P2	11	2.65	10.6	8.8
Edale Village	Edale Shales, H-R	37	1.44	6.4	0.97
Edale River Noe	Edale Shales, E2	49	2.62	3.7	2.51
Bude Bay, Cornwall	E2C	13	2.5	2.6	0.24
	H1	29	2.7	2.9	0.26
	R1	49	2.3	2.5	0.3
	R2	18	2.7	8.7	3.29
	G1	29	2.1	2.0	0.25
	G2	10	2.3	0.9	0.3
Bideford Bay, Cornwall	Bideford Formation	47	2.7	2.4	0.29
Dartmoor Granite Aureole	P2	19	2.6	3.3	0.18
	R1	19	2.4	1.9	0.24
	R2	33	2.8	4.5	0.16

Cadmium figures in parts per million, calcium figures in percent

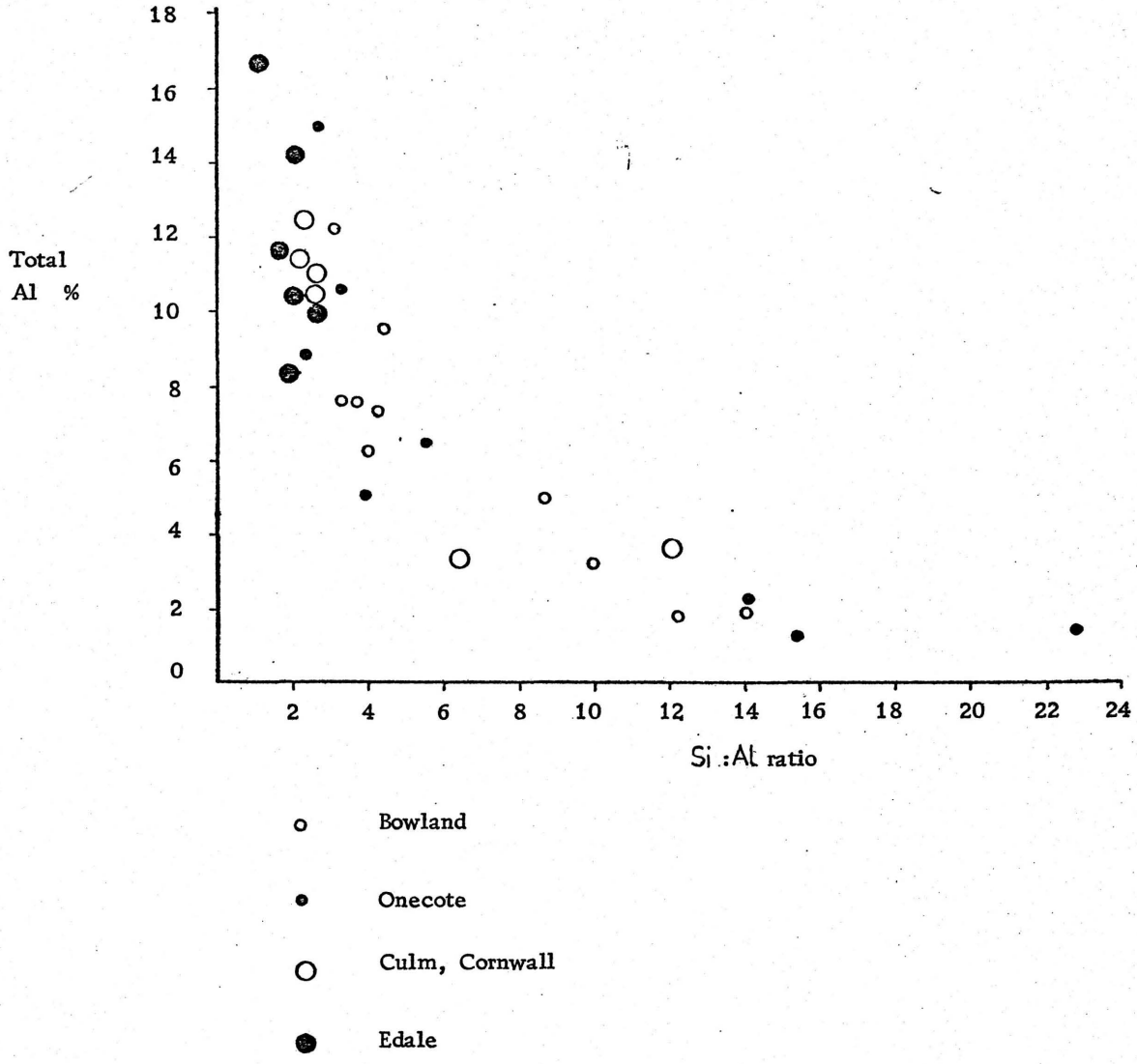


FIG. 10.1 RELATIONSHIP BETWEEN ALUMINIUM AND SILICON IN BLACK SHALES

detail however, the low aluminium\silicon ratio of the shales within the Lower Worston Shale Group - Pendleside Limestone in Bowland is offset by the exceptionally high ratios of the succeeding P1, Lower Upper Mearley Clough shales. The low aluminium and high silicon of the P1 rocks is evidence of a change in the conditions of deposition brought about by the onset of the Pendleside Sandstone by mid P1 times. With respect to that cadmium content which can be shown to be clay dependent, it is expected that as the basin becomes more clay-rich (i. e. as the aluminium\ silicon ratio lessens) then the more cadmium will be present in the clay fractions. Although this is the case in Edale and Onecote, it is not so in the remaining two areas. In Bowland, the highest average total cadmium value occurs where the aluminium\silicon ratio is high and where the calcium presence is high (a point to be discussed later in the chapter), in the P1 set of samples. In Cornwall where cadmium levels are unusually low for Carboniferous rocks, the cadmium value is highest where the aluminium\silicon ratio, although comparitively small, is once again highest. Some other controlling factor (s), such as physiochemical changes, change in the rate of sedimentation and so on, in the retention of cadmium must be identified in these areas.

10.2 ENVIRONMENTAL CONDITIONS DURING THE DEPOSITION OF THE DOVE SHALES, ONECOTE

The behaviour of cadmium within a sediment is subject to any changes in the phys ochemistry of a basin, even on a minor scale. Minor changes within the depositional environment can also lead to fundamental changes in major element geochemistry and this can be suitably demonstrated within a set of samples from the Onecote area in South West Derbyshire. Within this set of samples, from the E1 age Dove Shales, thirteen specimens from the group of 47 are unusual, showing a 59% increase of the aluminium silicon ratio and a doubling of cadmium content. The evidence indicates some

profound alteration in depositive conditions. This set of specimens has been subsequently appraised alongside the remaining samples of the set and the percentage changes in mean element contents are listed in Table 10.2.

In the cadmium-enriched set several changes are immediately apparent which help to clarify reasons for the sudden rise in the aluminium: silicon ratio:

1 A 23-fold increase in the presence of calcium

2 A 22.8% decrease in the presence of aluminium and

3 Practically no change in the presence of silicon.

The large decrease in aluminium in comparison to the small decrease in magnesium (minus 22%) suggests a relative depletion in the aluminium-rich illite mineral group over the magnesium-rich montmorillorite group. The lithophile and detrital minor elements lithium, titanium and gallium all show depletions very much of the same order as that of aluminium. The decrease of a third of the copper content could indicate one of a combination of three things:-

1 An affinity of copper for the depleted illite group of clay minerals.

2 An antipathy of copper for a highly calcic environment, or

3 A decrease in copper supply.

Of the three alternatives 1 seems the most likely although the loss of the illite group is related to the increase in calcium. The environment of deposition at this stage appears to be becoming more oxidising as a result of increasing oxidation potential and increasing pH trends which combine to reflect in the deposition of increased quantities of carbonate.

TABLE 10.2 VARIATION IN MEAN ELEMENT CONCENTRATION BETWEEN A LOW ALUMINIUM SILICON RATIO CADMIUM-RICH SUB-SAMPLE (A) AND A HIGH ALUMINIUM SILICON RATIO CADMIUM-POOR SUB-SAMPLE (B)

ELEMENT	SUB-SAMPLE A Low Aluminium Silicon Ratios N=34	SUB-SAMPLE B High Aluminium Silicon Ratios N=13	Percent Variation A to B
Calcium %	0.29	7.15	+2366
Aluminium %	11.4	8.8	-22.8
Potassium%	2.1	2.5	+ 19
Magnesium %	1.08	0.86	- 22
Iron %	3.09	2.5	- 19
Silicon %	25.7	28.22	+ 10
Strontium (ppm)	39.5	176.5	+ 347
Molybdenum (ppm)	4.4	50.6	+1050
Cadmium (ppm)	3.8	7.6	+ 100
Lithium (ppm)	128.0	14.0	- 89
Titanium (ppm)	3655.0	661.6	- 82
Gallium (ppm)	23.2	5.6	- 76
Copper (ppm)	135.6	91.0	- 33
Aluminium Silicon Ratio	2.2	3.5	+59

Both sub-samples represent Dove Shales of E1, Carboniferous Age from the Onecote Area, S.W. Derbyshire.

Apart from calcium-related strontium, the two elements which exhibit greatest increases in the clay-poor set of specimens are molybdenum and cadmium, the former showing a 10-fold increase, the latter a two-fold increase. The presence of iron compounds may well account for the increased presence of molybdenum in the samples. Within an argillaceous sediment iron can be present:-

1 In the formation of diagenetic concretions and oxides, and

2 By substitution both as Fe^{2+} and Fe^{3+} for aluminium and magnesium in clay minerals.

In the molybdenum-cadmium rich samples similar 20% depletions in iron and magnesium suggest that much of the clay substituted iron has been removed. Change in the nature of an iron mineral from detrital to carbonate can be brought about in two ways:

1 By a change in the oxidation potential towards less reducing conditions, or

2 A change in the pH towards higher values.

Under oxidising conditions iron is initially oxidised to Fe^{3+}, subsequently forming the slightly positively charged Fe_2O_3 or $Fe(OH)_3$ compounds. These have been considered by Hirst (1962) as being possibly instrumental in the attraction of the negatively charged molybdate ions ($MoO_4^{=}$) which mobilise under similar conditions. The problem can hence be resolved by considering major elements in a depositional system which contains both dissolved carbonate and dissolved sulphur. Continuous changes in activity of the two species can be simplified and represented in Eh - pH framework, such as that envisaged by Krumbein and Garrels (see Figure 4.1 page 59).

With increasing Eh calcite may form at pHs of 7 or even less i.e. at a time when free Cd^{++} ions in acid waters are still available to forming non-detrital components. With respect to the formation of carbonate Nicholls (1962) in a study of a Coal Measures succession concluded that in natural aqueous environments the co-existence area of iron sulphide (FeS) and iron carbonate ($FeCO_3$) should be in the region of -0.2 to -0.3V and a pH of 6.0 - 8.5. With an ionic radius of similar size to that of Ca^{++}, Cd^{++} may enter the carbonate phase substituting for calcium (comparitive radii for Ca^{2+}, Cd^{2+} are 0.97A, 0.99 $\mathring{A}$).

The importance, therefore, of recurrent conditions in black shale sequences, such as the precipitation of carbonate in mildly acidic environments, may be vital for the promotion of cadmium retention. Attention will be drawn to the importance of the conditions of weathering at the formative detritus stage, to later cadmium behaviour, in section 10.4.3.

In retrospect therefore, within the sub-set of samples from the River Dove, environmental conditions evolved from those in which low oxidation potentials and acidic, reducing circumstances prevailed, in which sulphides formed and mature clay minerals predominated. The increase in oxidation potential and small increase in pH enabled a carbonate-rich and clay-poor regime to form. Subsequently the precipitation of calcium as the carbonate and iron as the oxide and hydroxide caused firstly, the retention of cadmium as a substitute for calcium in the carbonate and secondly, the retention of molybdenum by processes involving the attraction of released molybdate anion to positively charged iron precipitates.

10.3 MAJOR ELEMENT GEOCHEMISTRY AND EXTRACTION EXPERIMENT DATA

10.3.1 THE NEED FOR CAUTION

The major conclusion emerging from the study of the aluminium: silicon ratio has been that of the four regional areas chosen for study, those of Edale and Cornwall are the richest in the clay minerals. Attention has also been brought to bear upon changes in physicochemistry at one or more sampling localities which have caused radical depletions and enrichments of elements emphasizing the extent of the possible heterogeneity which may exist amongst allied specimens in a set of specimens. With this point in mind the aqueous extraction data with its representative thirty specimens, considered in depth in chapter 9, has been correlated with major element analyses in order to discover if any broad affinities exist. The relative rareness of good correlations which were actually found to exist can be explained in the complex terms of stratigraphical correlatability. As in the classic work on major element geochemistry by Hirst in the surface sediments of the modern Gulf of Paria (1962) any correlation here between samples in a vertical section requires the element or element ratios to remain constant irrespective of facies change, varying rates of sedimentation or physicochemistry. However, expressed as a ratio to a major element (e. g. aluminium) vertical correlations of elements may possess relative constancy despite facies change or they may adjust to a facies dependent ratio such as aluminium:silicon. Likewise the complicated variation of ratios resulting from the distribution of the physicochemically dependent non-detrital elements to the detrital elements at a single horizon may render direct correlations objectively impossible to make. Elemental ratios, even with the major elements, will tend to indicate facies change and those factors responsible for it, such as changing rate of sedimentation etc. In each of the attempts at correlation which follow, regular adjustments in major-minor element ratios from constancy at a horizon or

single locality to a later horizon is interpretated as being synonymous with gradual evolution of detritus from the same source. Irregularities which suggest the interference of a fresh source of detritus are immediately apparent.

10.3.2 PROCEDURE FOR PHASE IDENTIFICATION

Following the work of Hirst and Nicholls (1958), regarding the separation of the detrital and non-detrital fractions of limestones, a 25% acetic acid solution is used to dissolve the carbonate fraction (whilst restricting any attack on the clay minerals). However, knowing that up to 20% of the total cadmium in the rocks of the four regional areas can be removed by a neutral ammonium acetate solution from surface adsorption sites (see chapter 9) this was first subtracted from the acetic acid soluble figure before any correlation with total carbon or calcium is attempted.

The cadmium extracted from clays is taken to be that fraction removed from the total sample by hydrochloric acid, less that fraction extracted by acetic acid (representing adsorbed and carbonate cadmium); correlations with the major elements representing clays can then be made.

The extractive capacity of the EDTA chelating agent as applied to rocks is not known in any great detail but the total carbon of the samples has nevertheless been correlated against EDTA soluble cadmium less the acetic acid soluble cadmium. This is taken to approximate to organic carbon combined cadmium.

Lastly, the cadmium which remains behind in the total sample after the hydrochloric acid extraction has been correlated with that iron which also is insoluble in hydrochloric acid. Positive correlations which can be shown to exist between these two values are taken to be indicative of the participation of the cadmium ion in the growing pyrite lattice.

10.4 CADMIUM CORRELATIONS WITH SELECTED MAJOR ELEMENTS

10.4.1 ADSORBED CADMIUM

The correlation of total aluminium, magnesium and carbon with ammonium acetate soluble cadmium, revealed several associations which may be regarded as meaningful.

For the Onecote group, as the total aluminium in specimens increased, the adsorbed cadmium content increased (see Figure 10.2), suggesting that cadmium is adsorbing onto the surfaces of the aluminium-rich clay mineral groups, illite and kaolinite. The Onecote rocks contained clearly the most kaolinite of the area samples mineralogically analysed (see Table 5.2 page 79).

The plots of the Bowland specimens in Figure 10.3 display a negative relationship between adsorbed cadmium content and total magnesium. Magnesium can be transported in the detrital minerals - principally as clays - and in solution. The ratio of magnesium to aluminium in the Gulf of Paria sediments was found by Hirst (1962) to be almost constant, leading him to the conclusion that magnesium had been structurally included within clays at, or near, the site of weathering and that this constancy argued against any mechanism of magnesium sorption from solution at the site of sediment deposition. Such a process of sorption would effectively destabilise magnesium:aluminium constancy. Thus it has been concluded that magnesium has been included mostly in those clay minerals which contain substantial magnesium. Some regularity in the magnesium: aluminium ratio within the Bowland shales, favours a hypothesis of magnesium inclusion in the clay minerals at an early stage in the weathering processes. Fluctuations in the alumina content of clays entering the deposition basin reflect in sympathetic magnesium

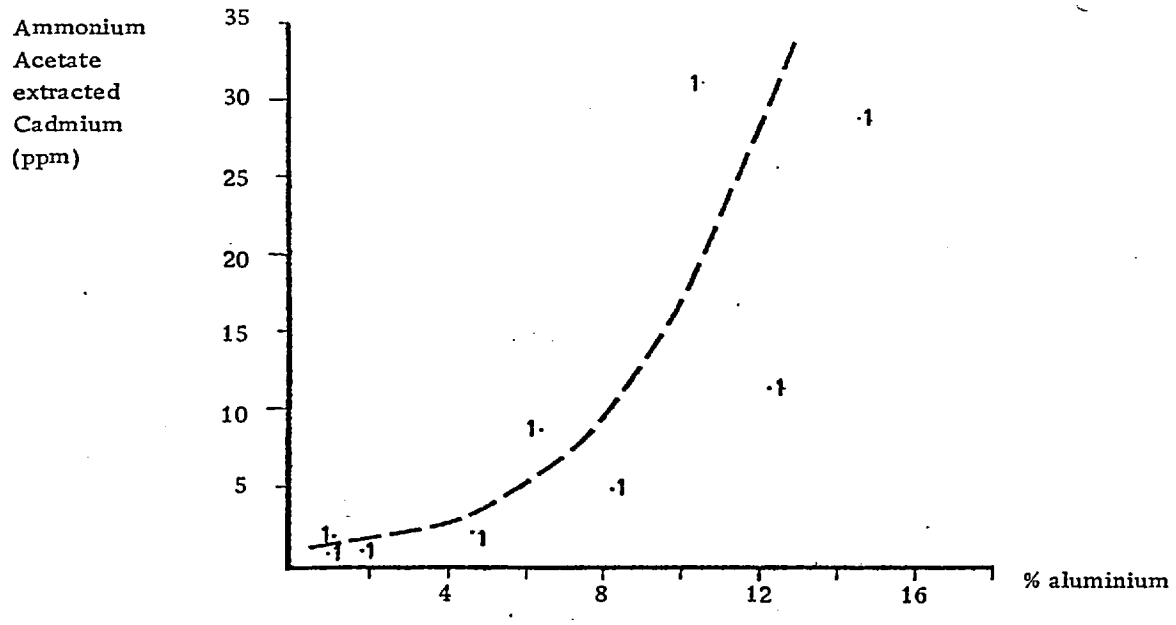


FIG. 10.2 PLOT OF TOTAL ALUMINIUM vs. ADSORBED CADMIUM, ONECOTE REGION

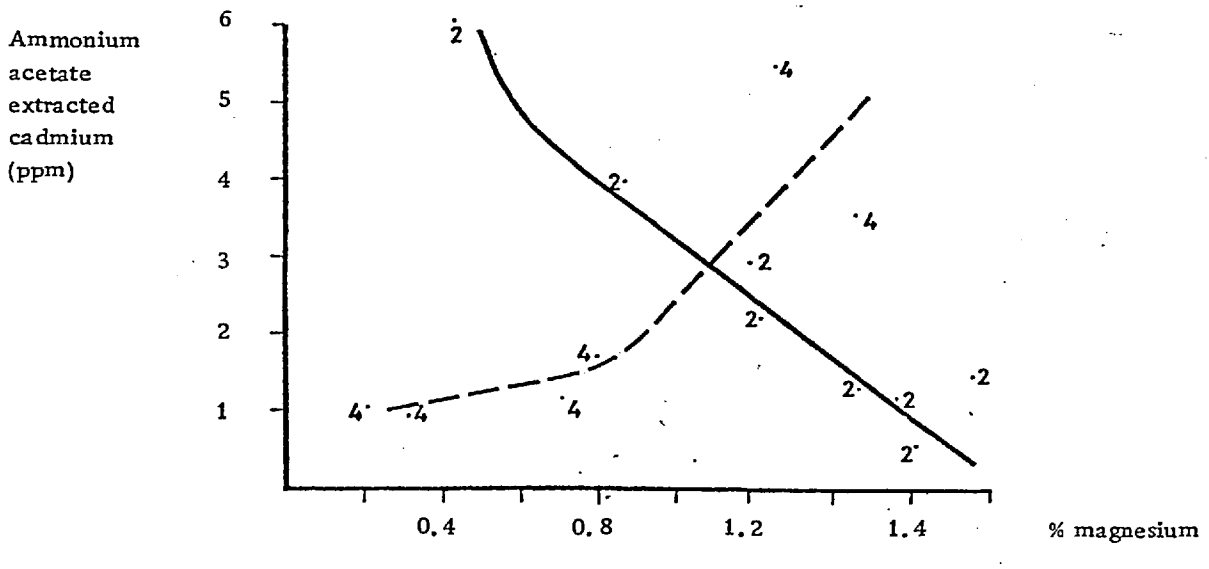


FIG. 10.3 - 10.4 PLOT OF TOTAL MAGNESIUM vs. ADSORBED CADMIUM, 2. BOWLAND, 4. CULM, CORNWALL

fluctuations, suggesting that variations in the pH in the environment of weathering determines the extent to which magnesium-rich clays can develop. Discussion concerning the environmental conditions in the weathering regime follows in section 10.4.3.

The negative relationship therefore indicates that some cadmium may be adsorbing onto the surfaces of magnesium-rich minerals, such as the montmorillonite group, but that such an association is not the only control upon the total adsorbed cadmium content in the rocks of the area.

The other important sorbents in a sedimentary environment of deposition, apart from the clays, are organic materials and colloidal iron, although both will to some extent be destroyed by diagenetic processes and redistribution of adsorbents will occur. Positive relationships exist between small quantities of adsorbed cadmium and total carbon over a large range of carbon concentrations in the areas Cornwall, Bowland and the River Dove section of Onecote. The assumption can be made that the presence of organic matter as an adsorbent during syngenetic and possibly diagenetic times is of some importance.

Lastly, a positive correlation exists between the association of total magnesium and adsorbed cadmium within the Cornwall samples (Figure 10.4). This is without doubt related to the large chlorite (and possibly mica) representation amongst those mineralogicially examined samples from the region.

10.4.2 ORGANIC-CARBON HELD CADMIUM

Like the clay minerals which tend to be transported further than quartz particles from the shore-line, the organic matter behaves in a similar way. Thus an increase in quartz content in an organic sediment

causes a decrease in organic matter and vice versa. The graph of total silicon against total carbon demonstrates this observation clearly for the rocks of the Onecote, Cornwall and Edale areas (Figure 10.5). The rule also broadly holds for the eight carbon analysed samples from the Bowland area.

In chapter 8 few conclusions have been made regarding the EDTA extractable cadmium content of rock samples, the main reason being that little is actually known about the chelating powers of the reagent within carbonaceous rocks which have a relatively matured organic content. The identification of thermally evolved vapour profile peaks in samples resulting from cadmium-carbon associations was made using published data of other work rather than on the basis of the post-extraction TEVP peaks of EDTA treated samples, which commonly showed little change in comparison with the original rock pattern. Nevertheless, EDTA alone removes 19% to 30% of the total cadmium from the rocks of Edale and Cornwall respectively, and, perhaps significantly the samples of the latter set of samples display a good positive relationship with total carbon (Figure 10.6). Positive relations can also be broadly realised for the samples of Edale and, to an even lesser extent, Bowland. The goodness of fit for the rocks of Cornwall region is an agreement with the extraction data for the region given in chapter 8 since, firstly, comparitively little cadmium is in a carbonate form (suggesting that little carbonate carbon confuses the total carbon figures in the correlation) and secondly, the large cadmium content which is EDTA soluble would suggest, if EDTA was actually shown to be an organic specific chelating agent, that some positive relationship should be displayed between it and total carbon.

The moderately good Edale correlation reflects the low content of cadmium which is extracted by EDTA and the exceptionally low content of cadmium extracted from carbonates from the same rocks (refer to chapter 8).

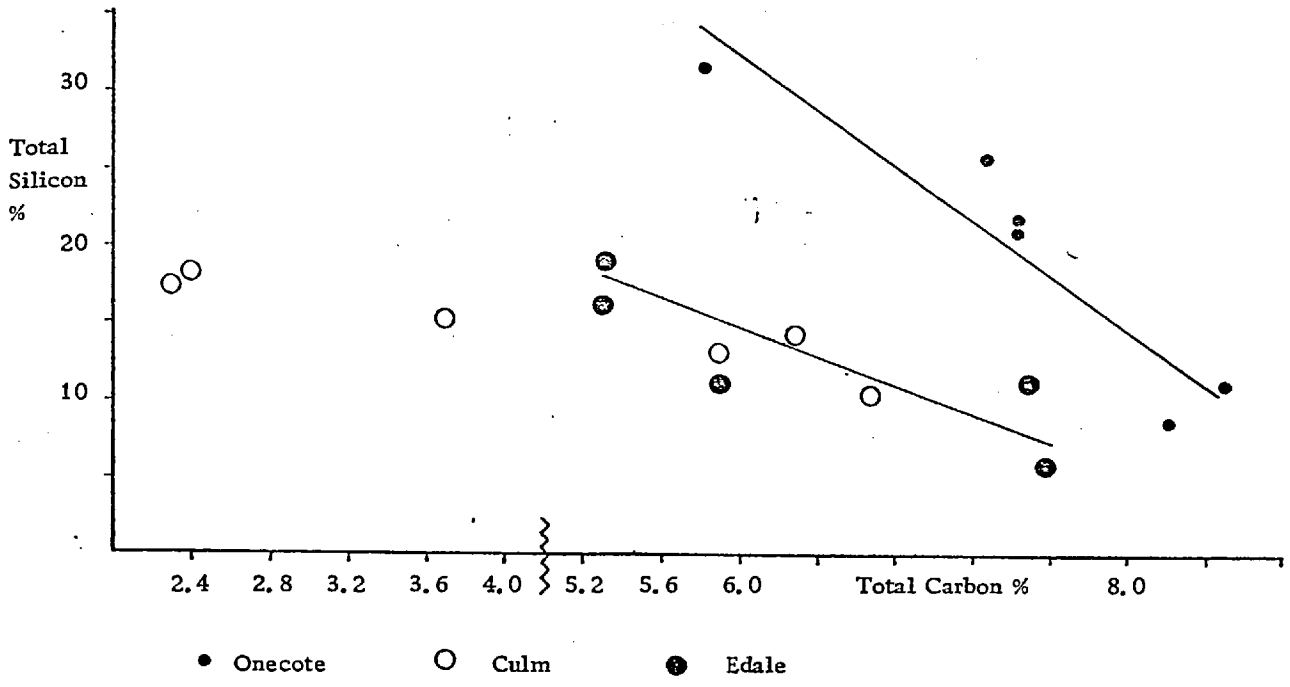


FIGURE 10.5 TOTAL SILICON AGAINST TOTAL CARBON FOR VISEAN BLACK SHALES

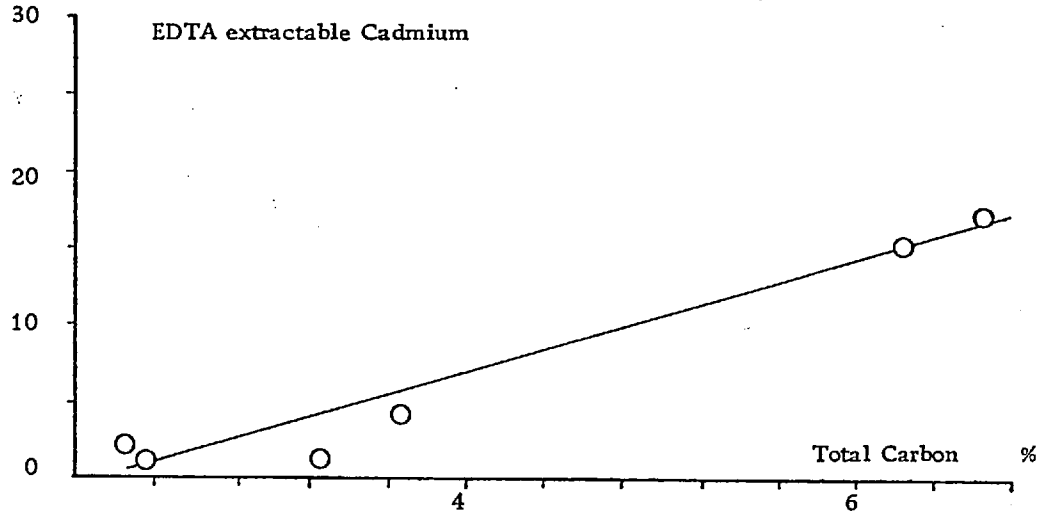


FIGURE 10.6 EDTA EXTRACTABLE CADMIUM AGAINST TOTAL CARBON FOR THE CULM

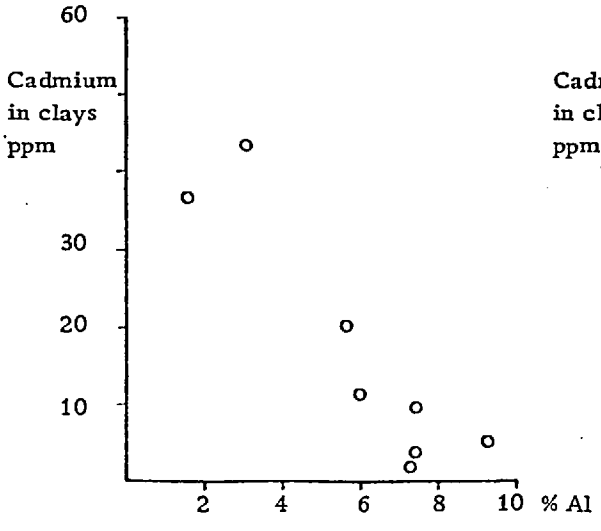


FIGURE 10.7 CLAY CADMIUM AGAINST TOTAL Al. BOWLAND

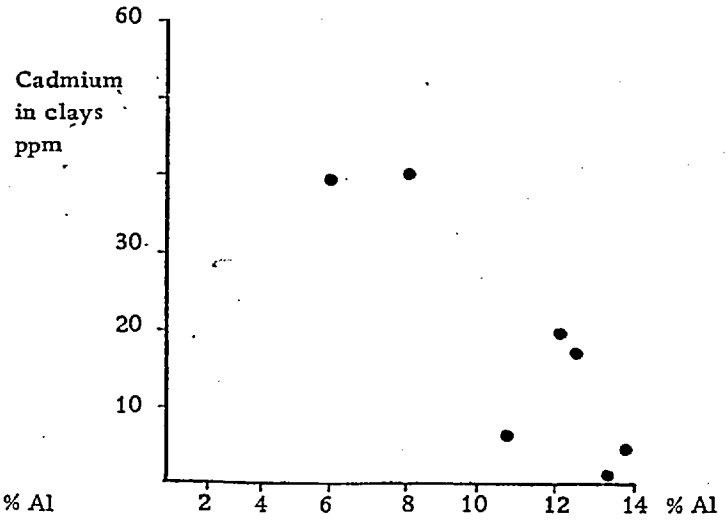


FIGURE 10.8 CLAY CADMIUM AGAINST TOTAL Al. ONECOTE

High carbonate-carbon contents in Bowland and Onecote mask any correlation which may exist between EDTA soluble cadmium and organic carbon.

10.4.3 CLAY-BOUND CADMIUM

The extraction experiments showed that a significantly large proportion of the total cadmium in carbonaceous shales (i.e. between 39% and 44%) is included in clays and is present in hydrochloric acid soluble sulphides. Figures 10.7 and 10.8 show the correlations of clay-contained cadmium from the Bowland and Onecote samples against aluminium. In both instances the correlation is negative indicating that as the clays become more dominant less cadmium is included within them. This is in direct relation to the silicon: aluminium vs. aluminium graph of Figure 10.1 where samples with low clay cadmium: aluminium ratios have low aluminium\silicon ratios. It indicates a progressive facies change to a clay-dominated type. This is also so with respect to magnesium-rich clays. The relative constancy of aluminium\silicon vs. clay cadmium:aluminium ratio as aluminium increases can be interpretated as meaning that most of the cadmium was included in the clays at or near the site of weathering, and that little or none has been included at the site of deposition which would destroy any regularity in relationships. Thus some content up to 44% of total cadmium in the samples can be assumed to be detrital in nature. The figure can be defined with no more accuracy owing to the absence of any sulphur determinations in this work. Furthermore, it may be assumed that in Bowland the cadmium was included in aluminium-rich minerals such as illite or kaolinite. Carens (1949) in a paper on the solubility of silicon and aluminium in relation to pH concluded that at pH 4, aluminium is much more soluble than silicon, wheras at pHs of 5 to 9 silicon increases in solution whilst

aluminium remains the same. So at pH 4 clay minerals have more contained aluminium and thus kaolinite would be expected to form in low pH environments and montmorillonite in high pH environments. The cadmium inclusion in magnesium-rich minerals, such as montmorillonite in Onecote suggests, using Carens' findings, that the pH of the environment of weathering was nearer to neutral than that of Bowland. This may help to explain why a smaller amount of cadmium eventually formed in carbonates in Onecote compared with at Bowland (15% compared with 26%). The acidic environment of weathering in the Bowland region would have resulted in increased cadmium mobilisation either in the form of free Cd^{2+} ions or as an adsorbed form upon clays, organic particles, iron colloids etc. The latter would enter the basin of deposition and release during a later physicochemical change, such as increase in oxidation potential and rise in pH. In Onecote, however, cadmium may be expected to be more detrital in nature or form more detrital associations at the weathering site before entering the basin of deposition. The large compliment of surface adsorbed cadmium in the Onecote specimens (refer to Table 8.2 chapter 8) which can be shown to have a good correlation with aluminium, may indicate that the cadmium detrital function was at one stage even stronger than is apparent in the mature rocks today. It can be envisaged that the decay of clay minerals caused by some inherent degree of environmental disequilibrium, released lattice-held cadmium and made it immediately available for the new mineral form into which the clay is reverting e. g. from montmorillonite to kaolinite.

If this model represents two fairly extreme weathering environments, it may be possible to place the remaining sets of samples somewhere between. The Edale samples contain considerable quantities of cadmium in clay lattices (up to 44%) and adsorbed upon clay minerals (18%). A neutral environment of weathering, supplying detritally-bound cadmium to a basin

with depositive conditions in strong disequilibrium (caused possibly by a fast rate of sedimentation) may lead to the formation of highly adsorbative aluminium-rich clay minerals. It was tentatively suggested in chapter 6 section 6.6.3 that a link may exist in Edale Shales between the minor elements and the detrital elements.

The ammonium acetate soluble cadmium in the Cornwall samples is correlatable with total magnesium. This cadmium has however, been completely redistributed as a result of thermal metamorphism into micas and chlorites which comprise about 30% of the rock minerals. The cadmium associated in the clay minerals and in sulphides is considerably less than those levels contained in the same category in the three remaining sets of samples (32% compared with 41% to 44%) confirming the extent of redistribution. The influence of the environment of weathering to samples from the coastal Culm Measures and the Granite Aureole Culm Measures have been summarized in section 9.8.3.

10.4.4 CARBONATE HELD CADMIUM

The determination of a relationship between carbonate cadmium and carbon is made difficult by the lack of separate carbonate carbon and organic carbon analyses (as in Section 10.4.2). In the previous section, it was concluded that in the case for Bowland, high carbonate carbon content masks any good correlation which may exist between EDTA soluble cadmium and organic carbon.

The only positive correlation which exists between carbonate cadmium and total carbon is with the Bowland samples (Figure 10.9). This confirms the earlier conclusion that a good proportion of the total carbon analyses of the Bowland specimens is, in fact, carbonate carbon. This cadmium is non-detrital in nature having been precipitated in the basin of deposition.

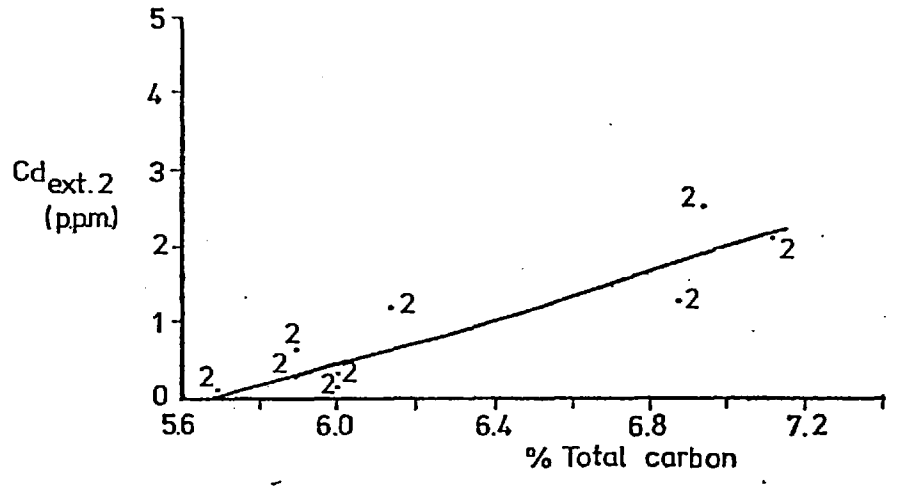


Fig. 10.9 Plot of carbonate cadmium vs total carbon, Bowland samples.

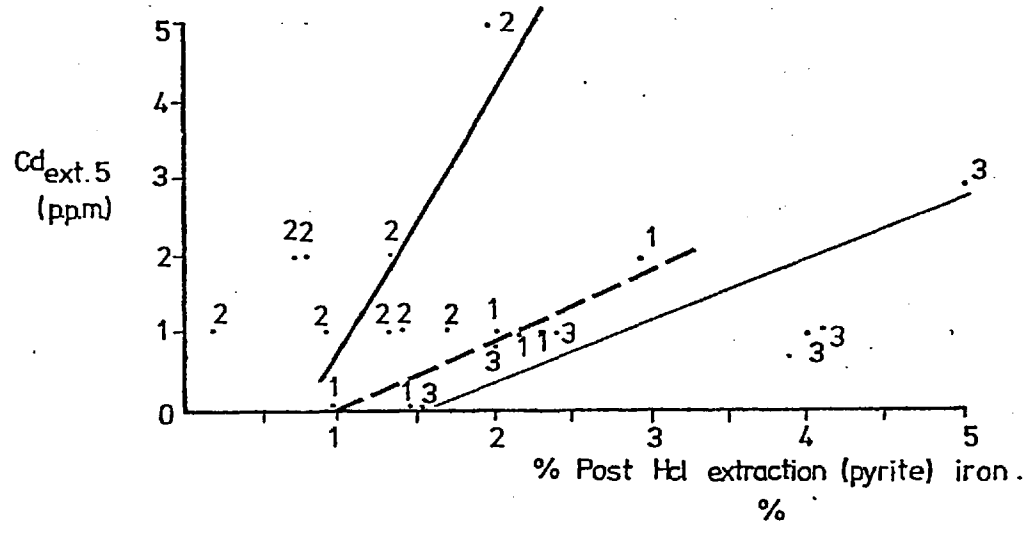


Fig. 10.10 Plot of Hcl insoluble cadmium vs acid insoluble iron in samples from Onecote., 1, Bowland, 2 and Edale, 3.

Although no other good correlations can be shown to exist a study of Table 10.3 indicates the importance of calcium presence to the retention of cadmium. It also re-emphasizes the nature of the incoming detritus (as was argued in section 10.4.3) where as a result of the highly acidic environment of weathering in the Bowland area, less cadmium effectively partook in clay-lattice production and was instead mobilised as adsorbants on clays, organics, iron colloids etc. Thus more cadmium was more readily available for carbonate substitutions. In the Table 10.3, it can be seen that despite the fact that the mean calcium level for the Onecote samples is very close to the mean calcium level for the Bowland samples, the latter has about eight times as much cadmium in the carbonate-extracted phases. The remaining two areas have such low calcium levels in their specimens that carbonate production does not attain such a position of prominence. However, there do seem to be indications that during those exceptionally rare times of carbonate precipitation, the cadmium-calcium interaction was well developed.

10.4.5 PYRITE HELD CADMIUM

Although mention has already been made in Section 10.2 concerning the behaviour of iron in a depositing sediment, no reference has yet been made regarding the formation of iron sulphide.

No correlation was noted to exist when, either total iron and total aluminium or hydrochloric acid soluble iron and aluminium were compared. Irregularities in the first instance suggest the presence of non detrital sulphide and carbonate and carbonate alone in the second instance. Spears (1963) concluded that in Coal Measures shales growth of pyrite causes an enrichment in iron - as the sulphur increases - with the metal coming from both inside as well as outside the sediment. Dunham (1960)

TABLE 10.3 MEAN AND MEDIAN CADMIUM VALUES COMPARED WITH CALCIUM VALUES

Sample Location	Number Samples	Average Calcium	Median Calcium	Average Cadmium	Median Cadmium
Bowland	10	5.3	3.86	11.0	8.3
Onecote	8	4.7	5.78	1.6	1.5
Edale	6	1.2	0.28	2.6	0
Cornwall	6	1.6	0.22	7.4	1.0

has suggested that in Carboniferous Coal Measure times, conditions were such that transport of iron in solution was not impossible and that this source contributed alongside that provided by adsorbed iron in the growth of pyrite. Conditions in the black shales of d4 age may be broadly comparable.

Some attempt has been made to discover if cadmium actually enters the pyrite lattice. Fleischer (1955) reports one instance of 10 ppm cadmium being found in one of three pyrites. Figure 10.10 plots hydrochloric acid insoluble cadmium against iron and this suggests that the amount of cadmium, in what is effectively pyrite, increases as the iron content increases. The cadmium:iron ratio is considerably higher within the Bowland samples than in the Onecote or Edale samples, which could suggest that less sulphur had been present in the Bowland area than the others. The richness of the Bowland samples in carbonate phases could agree with this. Under conditions of a possible slower growth, owing to the basic lack of ingredients, the lattice may have permitted more cadmium to enter. Thus up to 5.0 ppm cadmium may be entering the pyrite structure in the Bowland area, whilst up to 2.0 or 3.0 ppm may enter the pyrite structure in the Onecote and Edale areas.

CHAPTER 11

11 PRESENCE AND BEHAVIOUR OF METALS IN SOILS DEVELOPED ON BLACK SHALE-RICH BEDROCK

11.1 PRINCIPLES OF SOIL SCIENCE

Soils are composed of organic and inorganic materials and are formed by a series of geochemical processes from the weathered products of parent rocks and transported materials. In temperate latitudes most soil profiles comprise three main horizons: the topmost or 'A' horizon where the downward percolation of water through accumulated humic and organic complexes formed amongst the plant debris of the surface causes a mobilisation and transport of colloids and chemical elements to lower horizons. This leaching removes notably iron and aluminium and colloidal clay minerals leaving a relatively silica-rich lower top-soil layer. Under certain conditions, such as areas with cool, humid climates under heath vegetation, the second or 'B' horizon is a zone of accumulation of some of the leached materials. This is the case with the development of podsols where lower horizons are resultantly clay and iron-rich, commonly red-brown in colour and sometimes display iron pans. The clays, colloids and oxides which are retained in the 'B' horizon do not however retain and concentrate all the leached material carried downwards by rain water. Loss of calcium, magnesium, sodium and some fine silica leaves the area comparitively aluminium and potassium-rich, thus favouring the formation of kaolinite. The lowermost or 'C' horizon commonly consists of weathering bedrock but it may also be a geologically transported overburden or a fossil soil.

Many of the processes of soil formation are dependent on the presence of microorganisms which interact with chemical constituents sometimes causing redistribution of the trace elements vital for plant

growth within the profile. The presence of organic matter in the surface soil will affect the soil fertility by complexing plant nutrients, for example as humates, a number of elements such as iron, magnesium and aluminium and increasing the reducing capacity of the soil. Such processes affect weathering and transportation of the inorganic constituents of soil. Humus, by its affect on the hydrogen-ion concentration and oxidation-reduction regime of the soil and by its capacity to adsorb certain toxic compounds, influences the growth of plants (Rankama and Sahama, 1969).

The inorganic constituents comprise remains of parent rocks and their decomposition products, the most important of which are clays and iron oxides. The most active part of soil is the colloidal fraction which consists mostly of clay minerals but also of organic matter. The presence of these clays with high cation exchange capacity are very important, especially with regard to their capacity to retain soluble metallic trace elements and contaminants which may affect soil fertility.

The pH of soil ranges from 2 to 12. In peaty soils the pH usually varies between 4.4 and 7.3 and in mineral soils between 4.8 and 8.2 (Donahue et al 1971). The pH of soils regulates metal uptake by plants by affecting the solubility of salts in soils.

As a result of a growing realisation of the importance of trace elements in the nutrition of plants and animals many authors (e.g. Thornton, 1968) have attempted, with some success, to correlate geographic distribution of diseases with soil geochemistry. The following elements are known to become concentrated in humic soils (Rankama and Sahama 1969): silver, gold, beryllium, zinc, cadmium, scandium, tellurium, germanium, tin, lead, arsenic, manganese, cobalt and nickel. Donahue et al (1971) list sixteen elements at a minimum which are known to be essential for the growth of crop plants: carbon, hydrogen and oxygen from air

and water, phosphorus, potassium, sulphur, calcium, iron, magnesium, boron, manganese, copper, zinc, molybdenum and chlorine from the soil and nitrogen from both air and soil. The deficiency of certain of the essential elements in soil or the excessive presence of antagonistic elements may cause deficiency diseases in plants, grazing animals and even man. The accumulation of non-essential and toxic elements in the soil may be due to the abundance of such metals in the parent rock or pollution from mining and other industrial sources. On the other hand certain plants may accumulate specific metals and lend to their enrichment in the decaying plant debris in the surface horizons.

11.2 METHODS OF SOIL SAMPLING

Soils are part of a complex and dynamic system which changes in character both laterally and horizontally through the course of time. Such changes in space and time pose a number of theoretical and practical problems for the sampler; superimposed on major changes of soil types determined by the physical and chemical nature of their parent material are local variations which represent changes due to, for example, topography, secondary environments and the influence of man. Sampling should be based on some system of randomization but the choice is invariably made subjectively. Samples should be chosen at places to represent areas of apparent uniformity as well as attempt to determine the rate and type of change throughout a series. Principles of soil sampling were ably described by Cline (1944) but few systematic studies have been made on the subject and therefore it must be concluded that any samples collected may or may not represent a target population. In contrast to topsoil heterogeneities, subsoil characteristics show less variation and can be sampled in less detail and with greater reliability. As a general rule the number of topsoil sample points examined is increased as the rate of change in soil type increases.

Soil sampling which was carried out for this study in the Bowland Forest area of Lancashire has been supplemented by reanalysing samples collected by Thomson (1971) which have been described in his unpublished PhD. thesis. Thomson's samples have been collected along regional traverse lines at intervals of 50-150m and at depths of 30-45 cms. The traverse lines were orientated so as to cross the strike of bedrock and the approximate direction of ice-flow, thus enabling studies to be made of the role of both bedrock and drift in controlling the distribution of anomalous soils (see Figure 11.1). Sampling traverses carried out by the author during the present study also included topsoils. Sampling took the form of bulking six topsoils collected to a depth of 15 cms from 25 meter square grids estimated at 100 meter intervals and two subsoils collected to a depth of 30-45 cms. at random within the same grid. In addition, in the Onecote area of South West Derbyshire and in the Edale area of Northern Derbyshire the soils of Fletcher (1968) supplemented the author's soil sampling programme. Samples were collected at 150 and 250m intervals along traverse lines and grids, at depths of 30-45 cms. The author obtained composite soils in the manner described from the Bowland Forest. In all instances details of the site and sample were noted as fully as possible with particular attention being given to any obvious evidence of secondary accumulations or mottling and the general drainage conditions.

11.3 A REVIEW OF SOIL CHARACTERISTICS

11.3.1 BOWLAND FOREST, LANCASHIRE

In his work on the Bowland Shales Thomson (1971) concluded that the main control of distribution of metals in Bowland is the parent material. The highest mean contents of the elements vanadium, chromium and gallium are found in residual soils developed upon the Bowland Shales, whilst high means of the elements molybdenum, vanadium, chromium, gallium and titanium are revealed on transported soils rich with black shale debris.

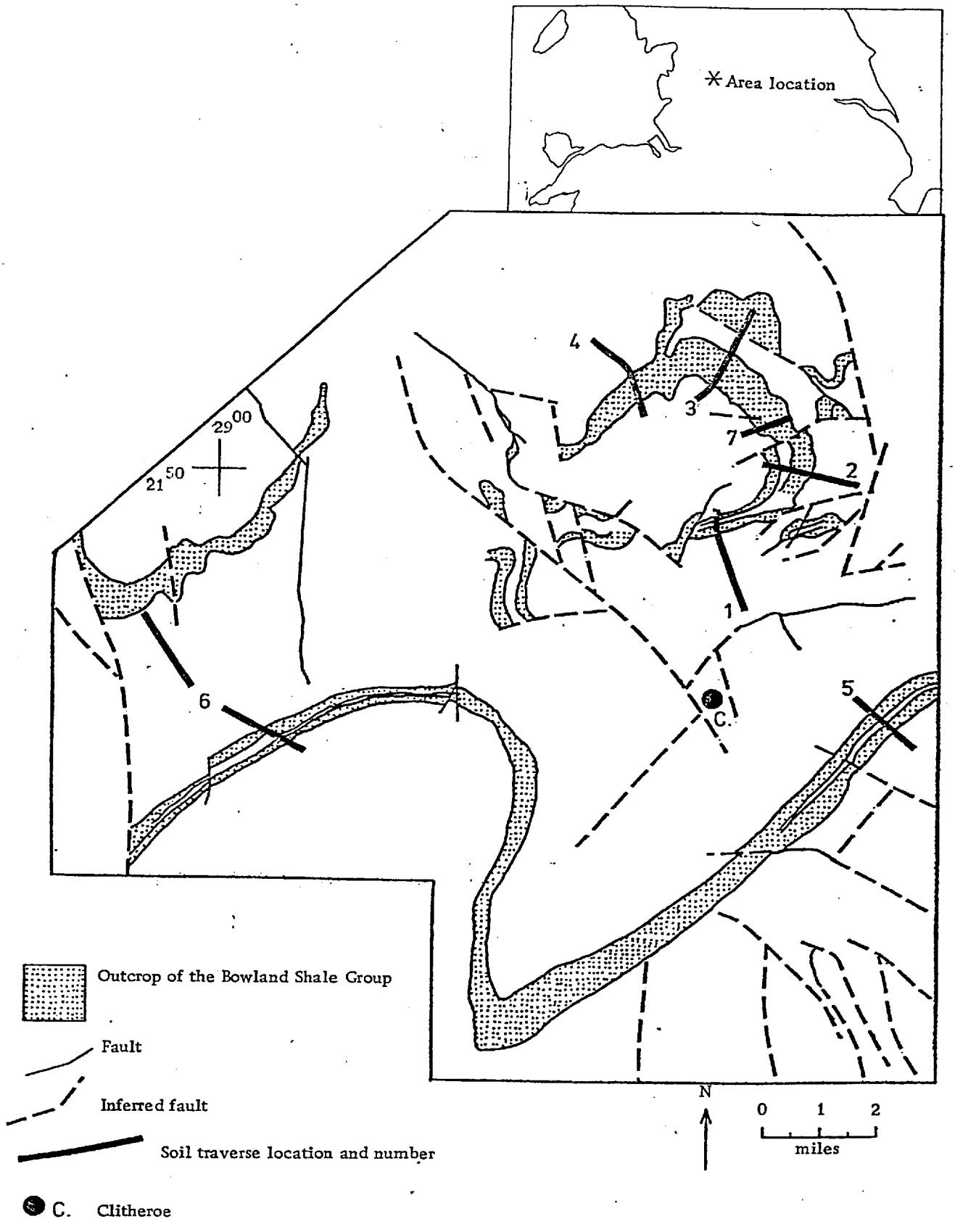


FIG. 11.1 LOCATION OF BOWLAND STUDY AREA WITH SOIL TRAVERSE LOCATIONS AND OUTCROP OF BOWLAND SHALE GROUP

Pepper (1963) divided soils in the Bowland Forest area into residual and transported soils, the latter comprising soils derived from glacial drift, colluvial head and alluvium. The residual soils are typically well-developed below the grit scarp of the upper fells on the long moderate to free-draining lower slopes. Gleying, with poor drainage in the lower horizons is caused by lateral movement downslope of water draining through the moderately well-drained sandy soils of the Pendle Grit. This downslope movement also promotes residual soil contamination with sandy soils creeping down from the fell tops to the sites of the in situ Bowland Shale soils. Similarly, where no break of slope occurs below the Bowland Shale slopes, colluvial downwash of residual soil spreads over the Lower Worston Shale Group in the valleys and mixes freely with barren drift material. Gleying is frequently noticed in soils developed on the poorly-drained drift materials in the lowlands around Clitheroe.

Earp et al (1961) wrote that black shale debris had been collected from drifts which had been smeared downdrift in a Northeast to Southwest direction for up to 2.4 kms. from the residual soil sites. Thomson (1971) recorded that an increase in the black shale content of drift increases the anomaly of molybdenum, vanadium, copper etc., suggesting that the main process of metal dispersion is the result of clastic physical transport of weathered black shale material. Conversely expected anomalies of molybdenum in soils overlying Bowland Shale bedrock have been nullified by the introduction from the North of barren drift. The fact is especially noticeable in the North end of traverses taken to the North of the sampling area off Newton Fells.

Where soils are gleyed, elements such as manganese, iron, nickel and zinc are mobilised and leached into the drainage by circulating ground waters. This is particularly so at the break of slope soil sites

below the Bowland Shale on the fell slopes which receive the excess run-off. In the better-drained soils of the slopes above the break of slope, the slightly acidic pH of the topsoils favours leaching of for example, molybdenum whilst the more alkaline nature of the lower subsoils causes immobilisation by, for example adsorption, with clays and, or secondary oxides (see location map, Figure 11.1).

11.3.2 ONECOTE, SOUTHWEST DERBYSHIRE

The soils of the West Midlands have been fully described by Mackney and Burnham (1964). Dominantly residual soils rest on Namurian shales and sandstones beyond the limits of the Newer Drift. These soils are not strictly residual as they generally have been mixed by colluvation which has added a minor quantity of Older Drift. They are poor and very poorly drained heavy textured clays and clay loams which may, if sufficiently impeded, develop a peat and initiate a reduced zone. These gleys and surface-water gleys alternate with brown earths and imperfect brown earths with gleying on the shales and sandstones of the Upper Carboniferous. Fletcher (1968) concluded that the soils of the Lower Namurian and Visean shales are characteristically molybdeniferous and enriched in copper, arsenic and vanadium. Zinc, copper and lead are strongly enhanced in the soils developed on the limestones and shales of the Mixon anticline, just South of the Mixon copper mine (see location map, Figure 11.3). Highest levels of base metal presence had been realised at Mixon and at the end of the long traverse at Warslow. These are probably due to contamination from the mine dumps. Fletcher explained deficiencies in the presence of the elements copper, cobalt, manganese, nickel and vanadium in the soils in terms of the mobilisation and dispersion of these elements by leaching from within sorption sites and weathering sulphides of the underlying shales. The soils from the

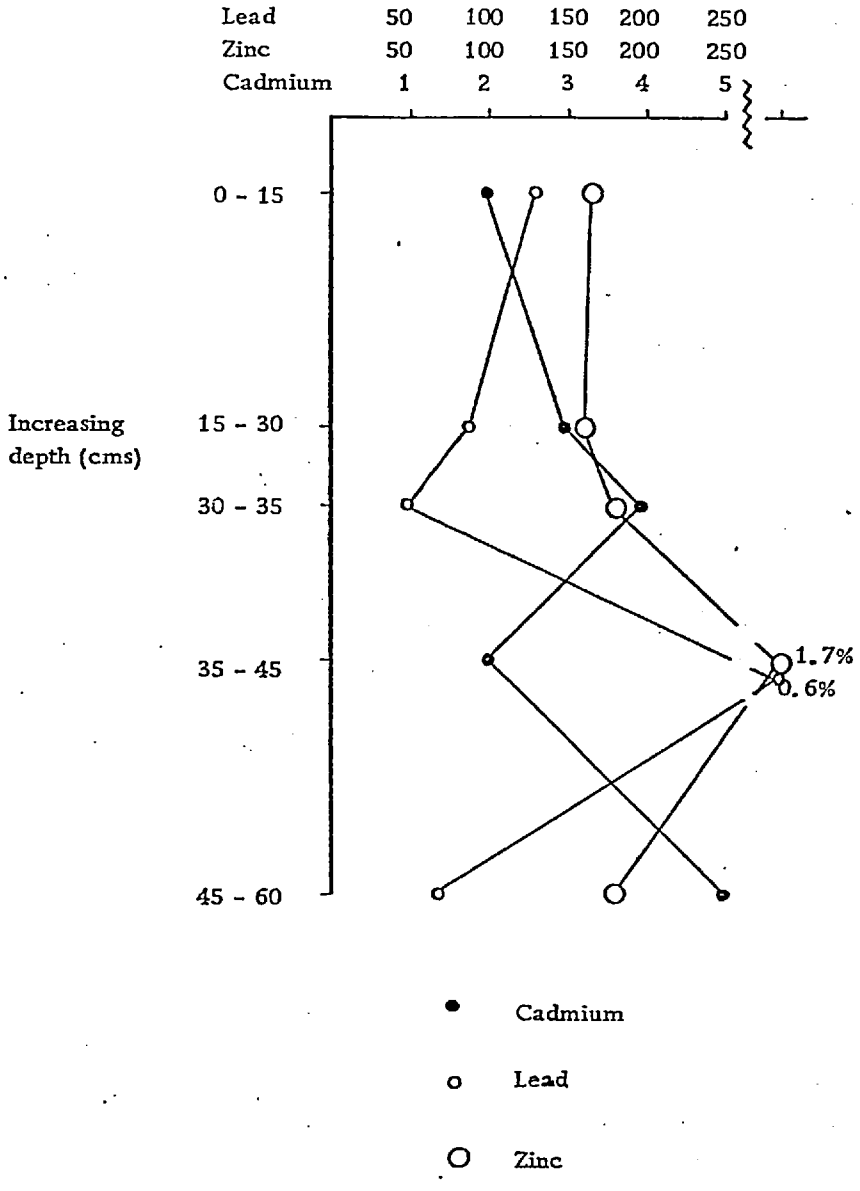


FIG. 11.2 PRESENCE OF CADMIUM, LEAD AND ZINC IN A SOIL SECTION DEVELOPED OVER LOWER WORSTON SHALES

Namurian Shales are naturally acid (pH 5.5) approaching neutrality only by liming (to pH 6.5). The dispersion of elements in the soils results in an increase with depth in the profile of the elements chromium, copper, manganese, molybdenum and nickel. At many localities the mobility of some of the elements is limited by retention on secondary oxides. Copper and lead are the only metals which do not increase with depth of soil as these metals are in all probability, fixed by the organic matter of peaty covers.

11.3.3 EDALE, NORTH DERBYSHIRE

The soils of Edale, like those in the Onecote area, describe a series of freely-poorly-very poorly drained profiles on the same traverse. The variation in soil types reflects the combination of parent material and pedological redistribution by the processes of solifluction and colluviation. The dilution of molybdenum-rich parent material by barren colluvium from sandstone outcrops is shown by the sandstone fragments which are persistently present in the sandy-brown loams developed at the bottom of the Shale Grit topped Edale Valley (see location map, Figure 11.4).

In the Edale section the low molybdenum of the lower zones (E1 + E2) relative to the upper zones (H + R1) reflects low molybdenum values of less than 2.0 ppm in shale horizons in the lower sequence (Fletcher, 1968). Fletcher concluded that there is no obvious relationship between molybdenum content in soils and lithology. Levels of vanadium are similar in both lower and upper sequences whilst in contrast, copper and molybdenum values are greatest in the upper parts of the succession.

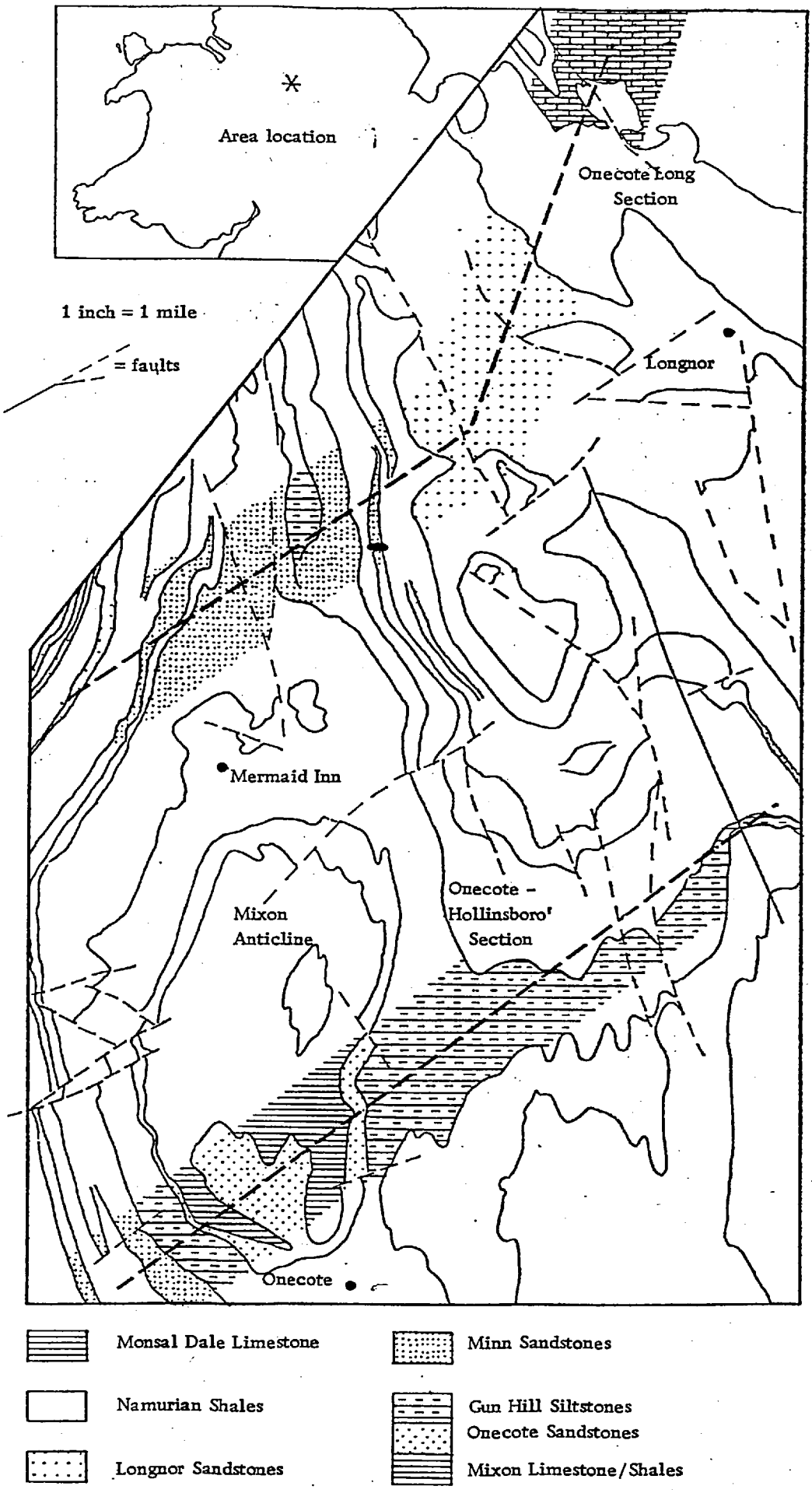


FIG. 11.3 LOCATION OF ONECOTE/DOVE STUDY AREA, GEOLOGY AND SOIL TRAVERSES

11.4 BOWLAND FOREST TRAVERSES

11.4.1 INTRODUCTION

In an attempt to ascertain if the parent rocks were the main control of the distribution of metals in the overburden, several deep augerings were made in soil overlying rocks which had been previously identified as being metal enriched. These results are meant to supplement the results of the six major traverses in the region where 30-45 cm soils alone have been analysed. The discussion dealing with these traverses occupies the remainder of this section.

The soils overlying the Lower Worston Shale Group at a point about 500 m. north of Ashnott reef were sampled first (map reference, hereafter referred to as M.R., 36940, 44875). The soils (collected from a permanent pasture) were well-drained brown earths with signs of slight mottling at depth. The general trend is for cadmium, zinc and lead content to increase with depth although lead is also slightly enhanced in the topsoil (see figure 11.2). The presence of mineral fragments in the regolith originating from inferred mineral veining in the underlying shale is presumably the reason for the sudden rise in zinc presence to 1.7% and lead to 0.58% at a depth of 35-45 cms. No mechanical or chemical process can be reasonably seen to cause such an enhancement. With regard to the slight fall in cadmium content at the same horizon it is possible either that the sphalerite of the area contained little cadmium or that cadmium had been preferentially removed from the soil.

Soils were also sampled from five depths at a site overlying the Upper Bowland Shales near Harrop Fold (M.R. 37510, 44915). These samples proved to be barren drift material with cadmium normally not detectable (less than 0.5 ppm) and zinc and lead slightly enhanced in the

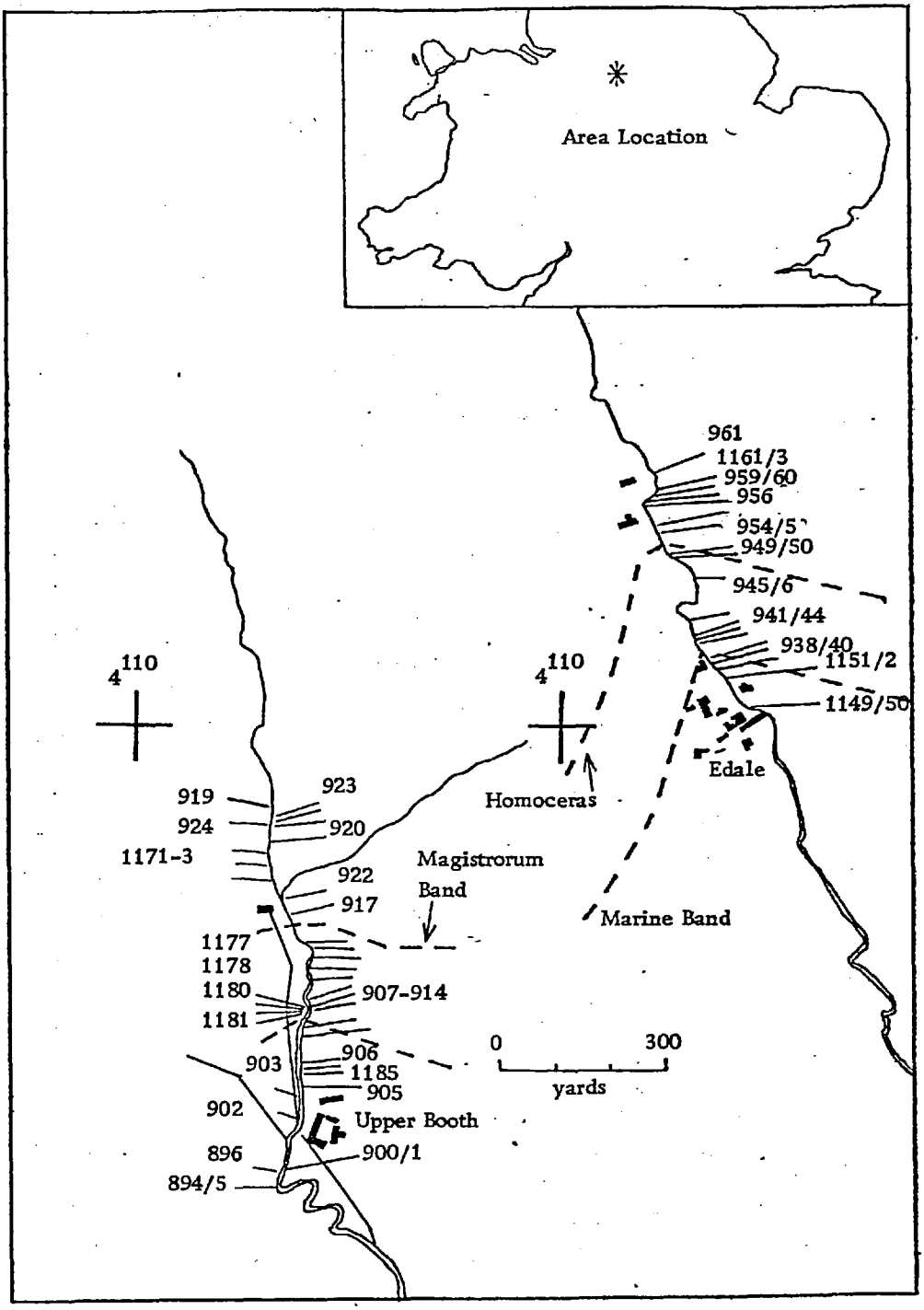


FIG. 11.4 LOCATION OF EDALE STUDY AREA ROCK SAMPLING SITES AND MARINE BANDS

organic rich topsoil. From a soil traverse across the Harrop Fold area (M.R. 37480. 44870 for 1.2 kms at 150 m. intervals in a Northeast direction to M.R. 37595. 44940) soils at the 30-45 cm depth proved to be always more rich in zinc and iron, less rich in lead and manganese and have unchanging cadmium content in comparison to the topsoils. The lead is accumulated by fixation with organic matter whilst it is probable that leaching by slightly acid waters results in a relative surface impoverishment of zinc and iron. The poorer levels of cadmium overlying the Upper Bowland Shales at this locality compared with content in soils from the following traverses suggests that extensive mobilisation and dispersion of the metal has taken place.

11.4.2 TRAVERSE 1

Location: from M.R. 37425, 44680 for 2.8 kms in a southeasterly direction to M.R. 37655, 44450.

The traverse follows constantly falling ground with a gradient of about 1 in 18.5 commencing at about 225m. above sea level and terminating at the River Ribble at a height of 75m. (see Figure 11.5.2). Cadmium levels in the soils reach 4.0 ppm on the low, lower gradient ground next to the river; throughout the rest of the traverse the soil cadmium content rarely rises above 1.0 ppm. When the levels do rise they do so at a time when zinc levels are at a peak or are also rising. Soil zinc content peaks momentarily over and slightly below the outcrop of the Upper Bowland Shales but attains twice these levels (at 230 ppm) to the south of the traverse at the foot of the Newton Fells (see Figure 11.5.2). Iron and manganese levels also significantly increase to the south of the traverse (see Figure 11.6.1). This may be caused by one or both of two factors:-

1 As suggested by Thomson (1971) the upper slopes are 'shedding' sites where circulating ground waters in gleying conditions mobilise and transport metals towards the more poorly drained 'receiving' sites.

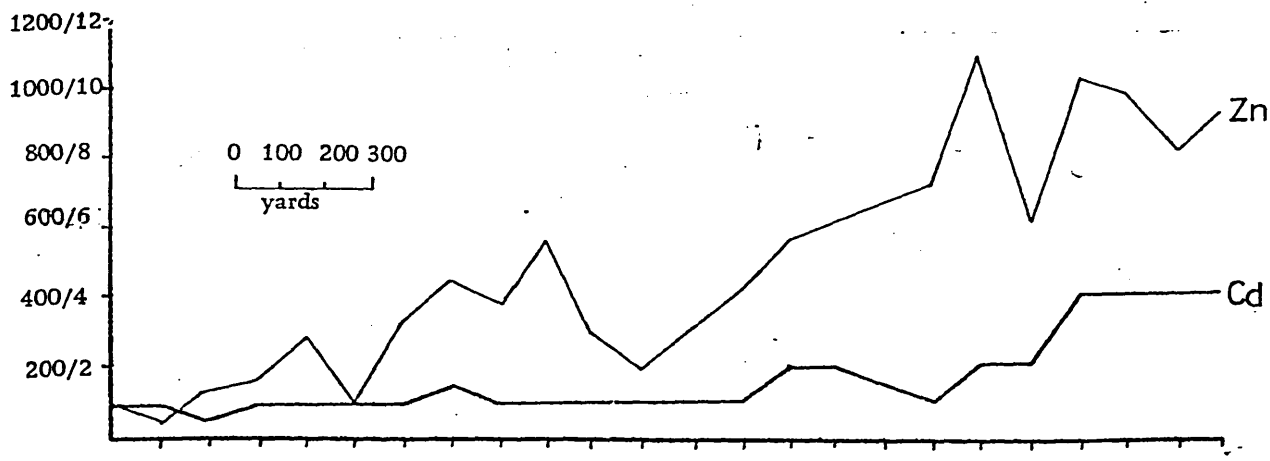


FIG. 11.5.1. TRAVERSE 1

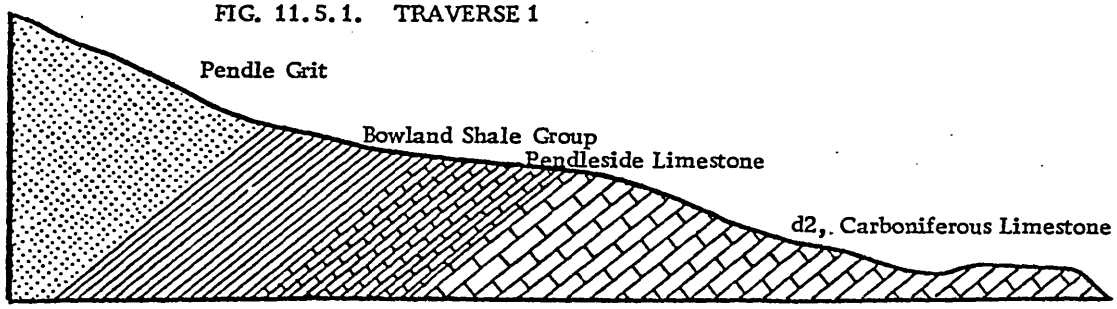


FIG. 11.5.2. GEOLOGY, TRAVERSE 1

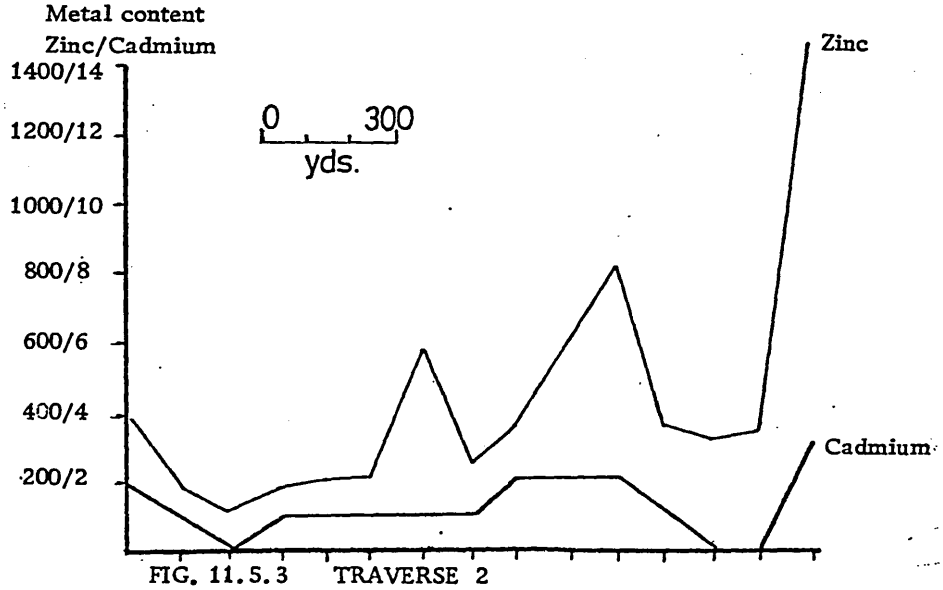


FIG. 11.5.3 TRAVERSE 2

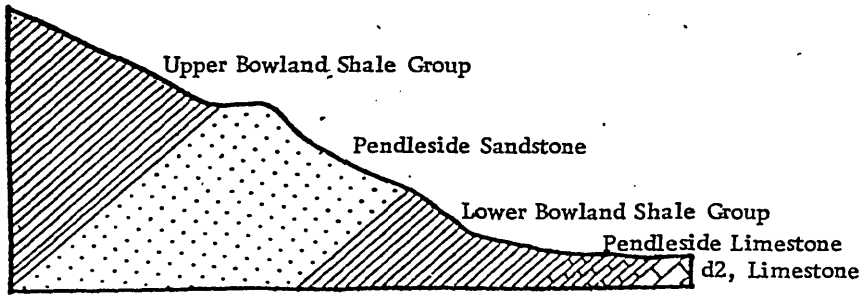


FIG. 11.5.4 GEOLOGY, TRAVERSE 2

All figures in parts per million

FIG. 11.5 CADMIUM, ZINC VARIATION IN BOWLAND TRAVERSES 1 AND 2 WITH RELEVANT GEOLOGICAL CROSS SECTIONS

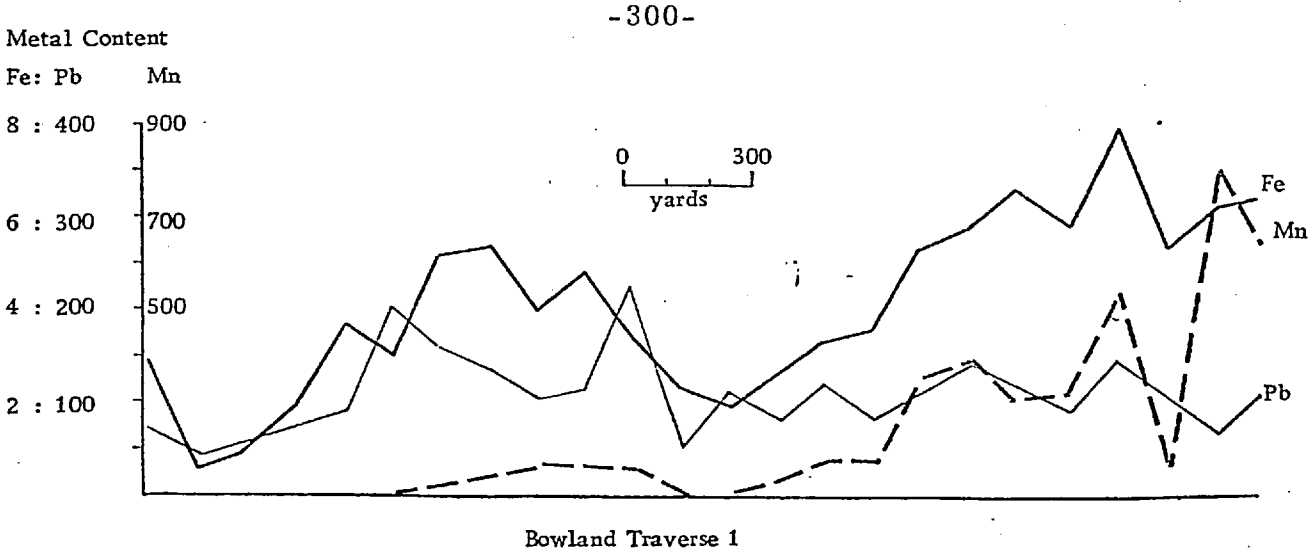
2 The pre-Ice Age residual soils had been transported by ice movement, a matter of a kilometer and a half to the South.

Closer to the river improved drainage conditions cause the precipitation of iron oxides and to a lesser extent manganese oxides and these precipitates scavenge zinc and cadmium from migrating groundwaters, by sorption. Most of the manganese however remains in the groundwaters to subsequently precipitate in the stream channels.

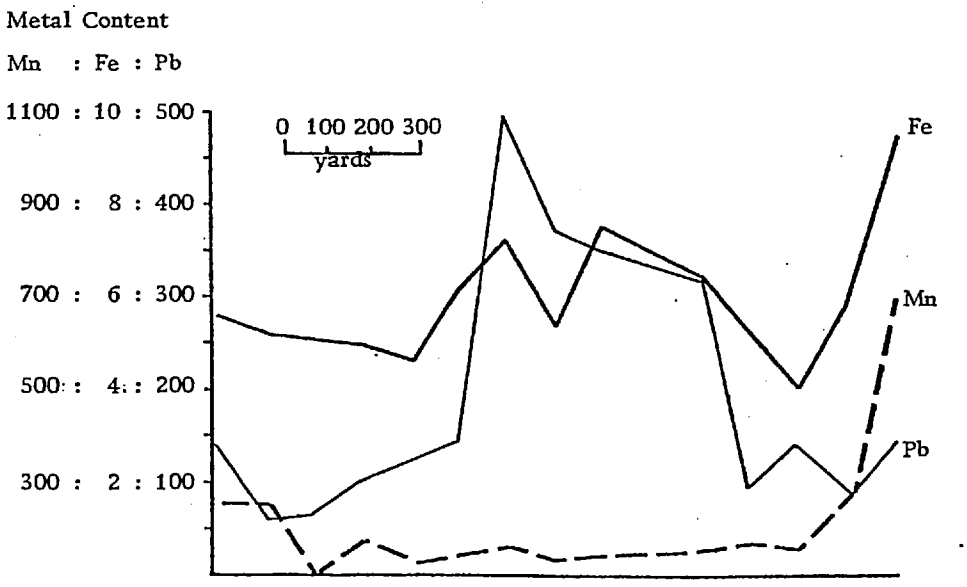
The behaviour of lead in soils differs from that of elements already considered as the lead is characteristically immobile. There is no increasing enrichment of lead in the slope-foot soils, instead some enhancement takes place at and slightly below the outcrop of Bowland Shales. The movement of bedrock material slightly downslope from the trace element enriched Bowland Shales either under the influence of solifluction, gravity or glacial transport, may explain this displacement (see Figure 11.6.1).

The groundwaters percolating from the peaty topsoils seems to have been sufficiently acidic to remove most of the cadmium from the soils overlying the Bowland Shale Group and although the presence of iron and manganese oxides does appear to scavenge some of the mobilised cadmium most of it is removed from the area to be concentrated in stream sediments and eventually transported to the sea, probably in a soluble form. Fletcher (1968) suggested that soils from Namurian black shales and sandstones are naturally acid (pH 5.5).

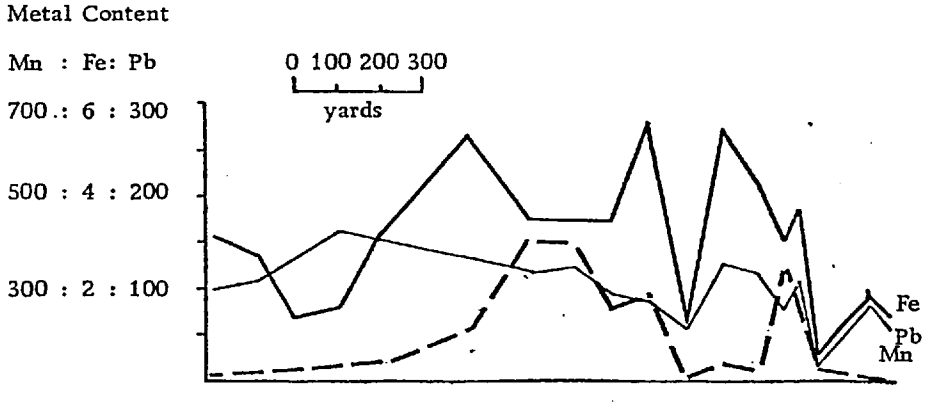
Cadmium in stream sediments is not enhanced in the region of traverse 1 which suggests that the scavenging action of hydrous oxides in the streams with respect to cadmium is a temporary and not a permanent feature.



Bowland Traverse 1



Bowland Traverse 2



Bowland Traverse 3

Manganese, Mn and lead, Pb figures in ppm, iron figures in percent.

FIG. 11.6 PRESENCE OF IRON, MANGANESE AND LEAD IN THE SOILS OF BOWLAND TRAVERSES 1, 2 AND 3

11.4.3 TRAVERSE 2

Location: from M.R. 37540, 44810 for 2.5 kms. in an Easterly direction to M.R. 37770, 44755.

This traverse follows steeply falling ground averaging a 1 in 11 gradient but with a marked bench of Pendleside Sandstone formed to the West, one-third from the top of Beacon Hill (see Figure 11.5.4).

Over the sandstone outcrop iron levels in soils increase along with those of zinc and lead. Lead increases in content to almost 700 ppm and falls off slowly in subsequent samples along the traverse through levels of 336, 288 and 220 ppm to a background level of about 70 ppm (see Figure 11.6). The source of this anomaly is likely to be from the bedrock as lead has been shown previously to be immobile, although such unusually high levels do indicate a possible undiscovered epigenetic source of lead in the underlying sandstone or shale.

Zinc levels increase again above the Lower Bowland Shale Group and in the low-lying land close to the River Ribble. Iron and manganese levels increase also in the soils nearer the river in the freer drained soils. A cadmium level of 3 ppm is reached near to the river in conjunction with increased levels of all other analysed elements although in the sample point underlain by Pendleside Limestone immediately above the river the soil contained no detectable cadmium. Levels of metal around the detection limit (0.5 ppm) are present in samples underlain by Lower Bowland Shales.

Despite the increased slope gradient in this traverse the pattern of metal enhancement is not as dominated by migrating leaching of elements to poorer drained soils as was the case in traverse 1 (Figure 11.5.1).

Colluviation probably aided by glacial transport may in addition assist in the explanation of the minor eastward displacement of metal peaks which presently overlie the barren (trace metal poor) Pendleside Sandstone and not the Upper Bowland Shale source rocks.

Slight enhancements of zinc, cadmium and lead over the barren Warley Wise Grit may indicate the presence of fragments of black shale within overburden transported from the Northeast.

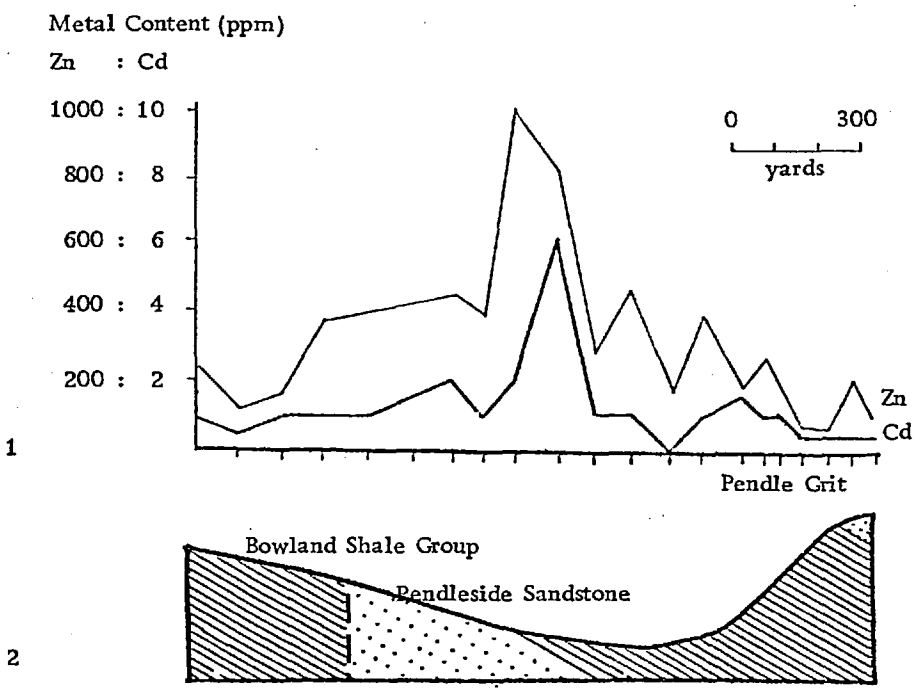
11.4.4 TRAVERSE 3

Location: from M.R. 37036, 44965 for 2.6 kms. in a North-North-east direction to M.R. 37047, 44519.

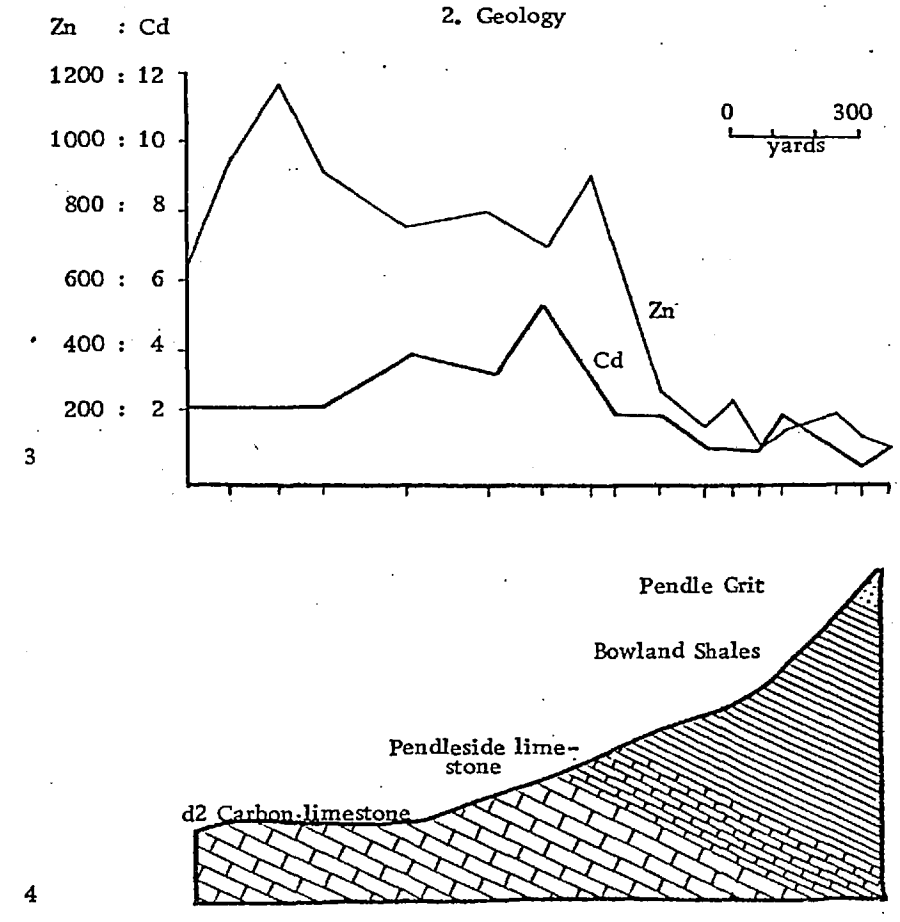
The traverse follows a hollow in the topography, the land first dropping steeply to the Northeast at a gradient of less than 1 in 4 from the Pendle Grit and Upper Bowland Shales and then gradually rising up again at a gradient of 1 in 20 over the Carboniferous Limestone (see Figure 11.7.2).

In the area of the hollow, which is not drained by a stream, cadmium and zinc are strongly enhanced. Manganese contents, although highest for the traverse at this point, are low (always less than 200 ppm). Lead increases in content away from the Grit at the south end of the traverse to peak some distance beyond the hollow but still overlying the Bowland Shale Group. The behaviour of iron is erratic, especially when located away from the freely-drained Grit soils and within those soils developed on generally poorly drained shales (see Figures 11.7.1 and 11.6.3).

The soil cadmium content of 6.0 ppm is unusually high for the region. It is noteworthy that no surface drainage system is intercepted by the traverse, thus preventing the total dispersion of cadmium associated



Bowland Traverse 3, 1. Cadmium, zinc presence
2. Geology



Bowland Traverse 4, 3. Cadmium, zinc presence
4. Geology

FIG. 11.7 PRESENCE OF CADMIUM AND ZINC AND GEOLOGICAL CROSS SECTIONS: BOWLAND SOIL TRAVERSES 3 AND 4

with fine-grained transported material. The good correlation of cadmium with manganese in the soils may be a significant factor in the process of cadmium capture although the gathering and concentration of colloids and clays at the break of slope may be an equally important factor in this process.

11.4.5 TRAVERSE 4

Location: from M.R. 37075, 45120 for 2.3 kms in a southeast direction to M.R. 37220, 44940.

The traverse follows a concave-section path from the flat banks of the River Hodder up to over 225m. at the crest of Easington Fell (see Figure 11.7.4).

Cadmium levels in the soils increase from nearly zero over the Pendle Grit in the North to 5 ppm beyond the Pendleside Limestone. To the East of the limestone the cadmium levels in the soil fall to 2 ppm. Lead and manganese also peak at the same position on the traverse (see Figure 11.8.1) although both achieve greater levels nearer the path of a small tributary of the River Hodder further along the traverse. The precipitation of iron oxides occurs in the region of this tributary. The zinc level in the soils steadily increases to a maximum beyond this tributary region in the flat bank of the River Hodder at a sample point where iron and manganese soil levels are not especially high. The metal content in this 'receiving' site, below the metal source, may have been enhanced by colluvial drift of material rich in black shale. Upon reaching the freer drained areas cadmium is likely to be dispersed in the drainage system. If manganese oxides are being actively precipitated as they are earlier in the traverse, cadmium which is transported not only in solution but also as a sorbent on clays and colloidal matter can be retained and enhanced. The sediments collected in stream beds parallel to the soil

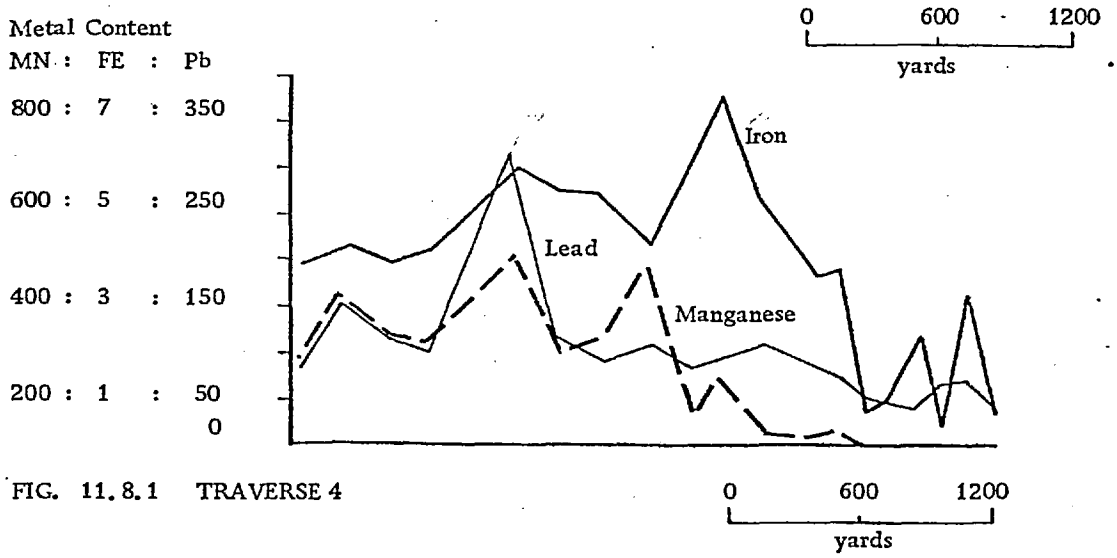


FIG. 11.8.1 TRAVERSE 4

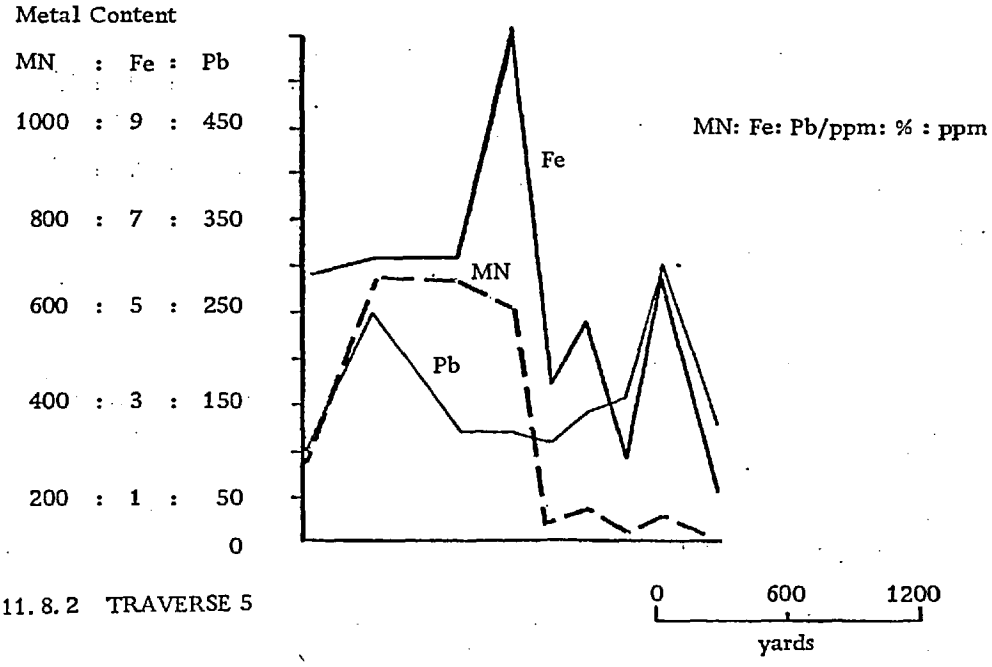


FIG. 11.8.2 TRAVERSE 5

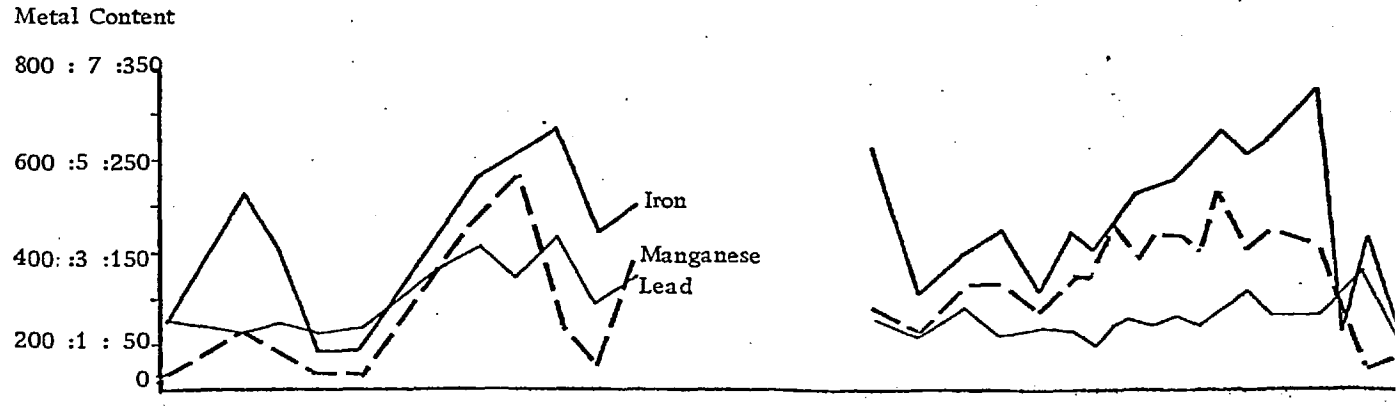


FIG. 11.8.3. TRAVERSE 6

FIG. 11.8 PRESENCE OF IRON, MANGANESE AND LEAD IN BOWLAND SOIL TRAVERSES 4, 5 AND 6

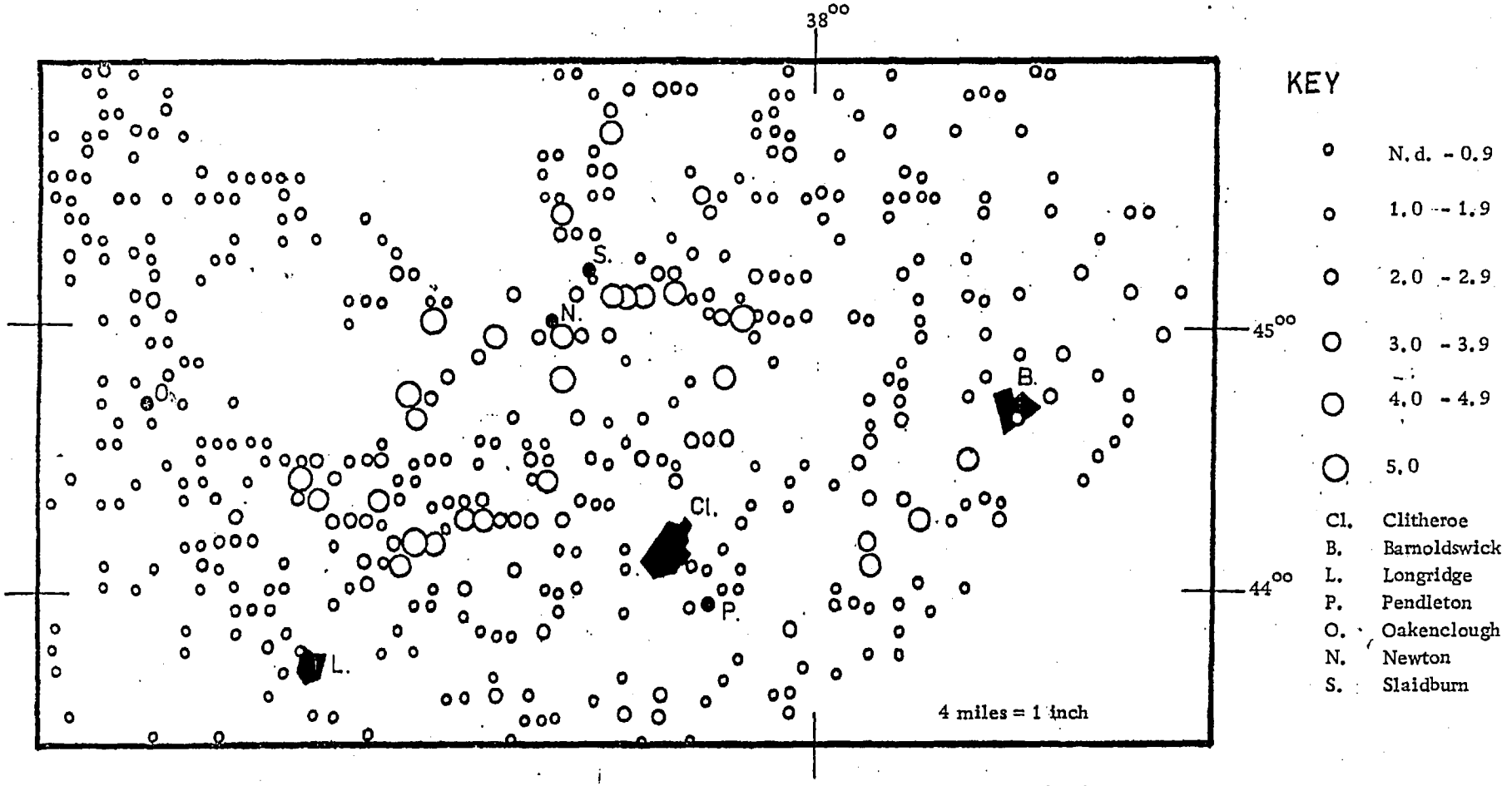


FIG. 11.9 CADMIUM PRESENCE IN STREAM SEDIMENTS OF THE BOWLAND FOREST DISTRICT OF YORKSHIRE

traverse contain anomalously high cadmium contents and this can be readily explained in terms of manganese oxide precipitation (see Figure 11.7).

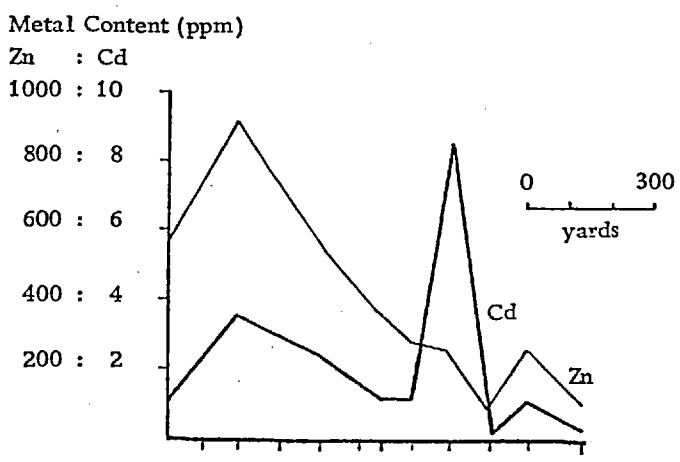
11.4.6 TRAVERSE 5

Location: from M.R. 36700, 44285 for 1.7 kms. in a southerly direction to M.R. 36770, 44130.

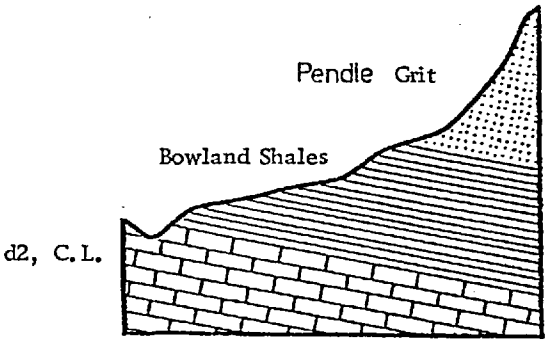
The traverse is made from the high ground formed by the Pendle Grit atop Longridge Fell and follows a fine concave section over a wide outcrop of the Bowland Shale Group to the flatter land of the banks of the River Hodder. The traverse negotiates the youthful notch of a small stream at Wallbanks (see Figure 11.10.2).

Cadmium levels reach a high of .0 ppm in the soil collected immediately beyond to the West of the Pendle Grit/Bowland Shale contact. Further West the cadmium levels firstly fall (and this is accompanied by considerable increases in the iron and manganese presence) before rising again alongside increased contents of zinc, iron and manganese at the base of the Bowland Shale Group and near the small transected stream.

The soils of the Pendle Grit are well-drained and rich in the precipitated oxides of iron and manganese. In contrast the soils formed over the topmost shales are waterlogged from the Grit. These conditions cause deep weathering of the shales and the subsequent extraction of unusually high levels of cadmium from them. The cadmium is retained by processes of sorption and is eventually mechanically transported away from the area as drainage conditions fluctuate.

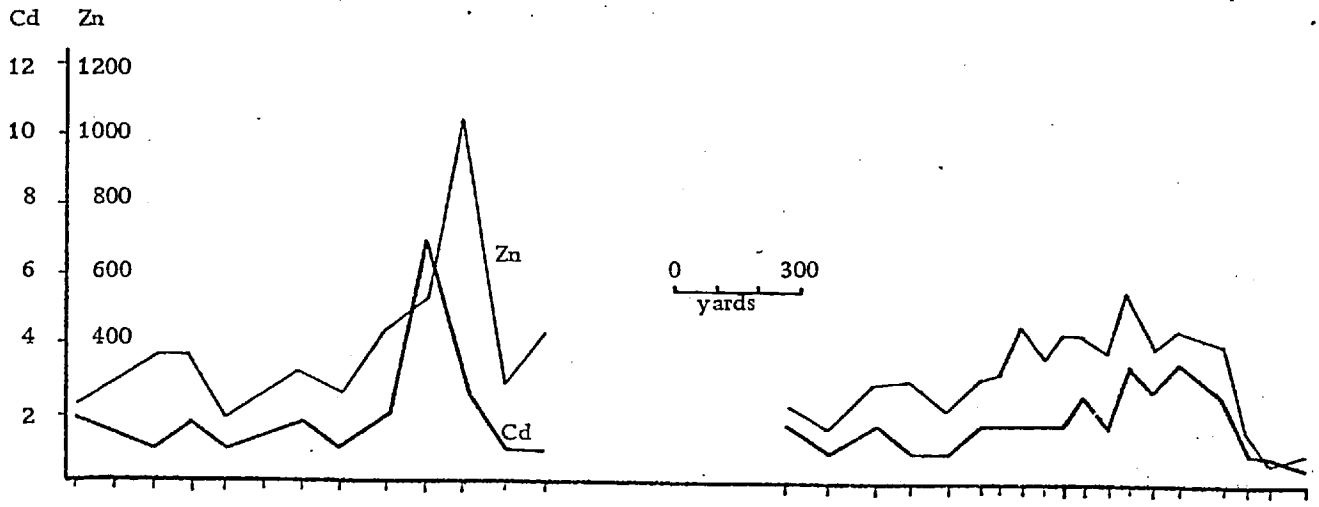


1

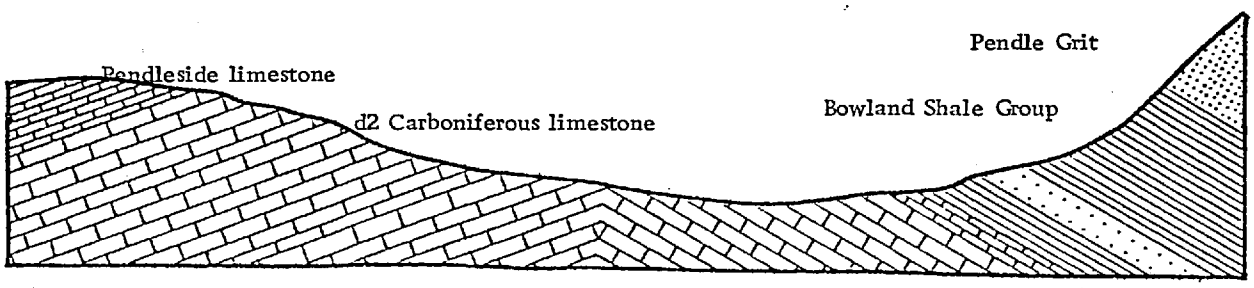


2

Bowland Traverse 5,
1. Cadmium, zinc presence
2. Geology



3



4

Bowland traverse 6, 3. Cadmium and zinc presence
4. Geology

FIG. 11.10 PRESENCE OF CADMIUM AND ZINC AND GEOLOGICAL CROSS SECTIONS: BOWLAND SOIL TRAVERSES 5 AND 6

Zinc is more readily mobile and only attains significant levels in soils downslope where the oxidising realm surrounding the small transected stream enables 'scavenging' oxides to be precipitated. Cadmium and lead which are more noticeably retained in the poorly-drained soils of the upper Bowland Shale Group are also retained at this juncture.

11.4.7 TRAVERSE 6

Location: from M.R. 3600, 44380 for 5.6 kms in a Northwest to Southeast direction to M.R. 36425, 44030.

The traverse is taken across the valley of the River Loud. To the South, the slope off Longridge Fell is steep (about 1 in 4) whereas the rise up to Wolf Fell to the North is much more protracted and gentle (gradient about 1 in 22, see Figure11.10.4).

To the North the soils contain increasingly higher levels of metal towards the base of Wolf Fell with cadmium reaching 8.0 ppm and zinc 240 ppm (see Figure11.10.3). Cadmium may be correlating with the presence of over 3,000 ppm manganese whilst the zinc is most enriched in a soil with about 4% iron. The peaks overlie the junction between Lower Worston Shale and Carboniferous Limestone. The shales of the Bowland Shale Group are more than four times enriched in cadmium and almost twice enriched in zinc compared with the rocks of the Lower Worston Shale Group, which are nevertheless fairly enriched in the minor elements. It would therefore seem reasonable to assign the metal source for the soils to black shale bedrock of the Bowland Group. Some process of physical transport of shale rich soil material, for example, during glacial times could only explain a move of such an anomalous overburden 2000 m. from its source.

To the South, soils with high cadmium, zinc, iron and manganese exist directly over the outcrop of the Upper Bowland Shale Group indicating that no downslope migration of sorbed metal or colluvation has taken place. However, if glacial action can be seen to have caused a 2 km south easterly move of overburden in the other section of this traverse, then presumably the ice could have literally pushed metal-rich colluvium from the Easington Fell slopes back up the slope or else diluted very enriched, low-ground soils at the foot of the Fell with barren drift material. In this section also, some correlation does seem to exist between the presences of zinc and cadmium and manganese and iron.

Lead content in soils of the Southern transect is notably lower than that of the northern transect. The better-drained soils of the steeper slopes to the South may be in part responsible for aiding in the mobilisation of lead-rich detritus which nevertheless is present in greatest amount directly over the Upper Bowland Shale Group.

11.5 BOWLAND FOREST SOILS SUMMARY

The study of six traverses has suggested, with respect to cadmium presence, that three main pedological and redistributive processes operate:

1 The mobilisation of metals by slightly acidic percolating ground waters on the long, generally steep 'shedding sites' to the flat, poorly-drained 'receiving sites' where physical movement of colloids and clays is restricted.

2 The colluvial movement of soils from long, steep slopes resulting in the survival of few true in situ residual soils.

3 The dilution and smearing processes resulting from the transport of residual overburden and drift by glacial action.

It has been seen that the enrichment of cadmium in soils is a comparitively uncommon event, the normal behaviour of cadmium being decided by the acidity regime of the circulating ground and surface waters. As the waters draining slightly acid soils over black shales are themselves mildly acidic, the expected behaviour of the element, once mobilised through weathering, is to adsorb onto fine grained and colloidal materials, form soluble compounds and disperse out of the source area into the drainage systems. However, exceptions to this rule were seen to exist and in each case a unique set of secondary environmental circumstances combined to cause retention. In one case (Traverse 5) unusually deep and protracted weathering had caused excess cadmium to be mobilised from the rock and in the absence of free drainage circulation to physically remove this material from the locality, the metal had been retained. It is conceivable that during long periods in the soil the metal may enter more stable complexes and resultantly be not affected by processes of solution and easy dispersion. In a second traverse (number 3) inadequate drainage from a receiving site again resulted in the retention of cadmium. Judging from cadmium's ability to adsorb onto clays and organic materials as shown in chapters 8 to 10, it is assumed that the presence of high cation exchange capacity materials were instrumental in cadmium retention. In a final case (traverse 6) the correlation with freshly precipitated oxides in active drainage areas has been noted.

There seems little doubt that the main control of metals in the overburden in the Bowland area is the parent material. The contrast of zinc, manganese and iron levels in the soils of the traverses studied is due to erratic mobilisation caused by fluctuating conditions in the secondary environment. The immobility of lead in soils is caused by fixation onto organic matter in the topsoils, a phenomenon which readily indicates the locality of the source rock.

The Grand Mean of cadmium analysed in several hundred rock samples from the black shales of the Bowland area is 12.3 ppm. In comparison the Grand Mean of soils sampled from the whole Bowland region is 1.8 ppm and that of soils overlying the Bowland Shale Group alone is 1.7 ppm. A very considerable mobilisation of cadmium has therefore occurred from the area. The stream sediment map of the area (see Figure 11.9) displays a pattern of anomalous cadmium samples and this suggests that a retentive process such as scavenging by manganese oxides may prevent large levels of cadmium dispersing in the waterways in a soluble or adsorbed form at a single instant. The process of cadmium dispersion may be seen to be one of step-by-step migration controlled by the presence of manganese oxides as they 'scavenge' and then release cadmium through precipitation and dissolution. The possibility of unusually large amounts of cadmium being released from one of the streambed-sediment rich rivers in the country, as a result of natural or man-made changes in river physiochemistry, and the possible repercussions of such an event may be sufficient to give rise to some concern amongst environmentalists.

Finally the lack of enhancement of cadmium in the soils immediately overlying the rocks of the area suggests that the element has been extensively leached, mobilised and dispersed away from the area.

11.6 ONECOTE TRAVERSES, SOUTHWEST DERBYSHIRE

The long Onecote traverse has been made from Longshaw, near Bradnop, (M.R. 35430, 40130) for 10 kms. in a northeasterly direction to just Northwest of Warston (M.R. 36000, 40920). The traversed topography is hilly rising to over 390m in the core of the Mixon anticline and falling to a low of 225m. at the base of the wide-angled, v-shaped valley of the River Manifold. The traverse is made predominantly over the Namurian Gunn Hill Siltstones but in addition cuts across the Mixon Limestone with Shales and the Onecote Sandstones with Shales exposed in the core of the Mixon anticline (see Figure 11.11.2).

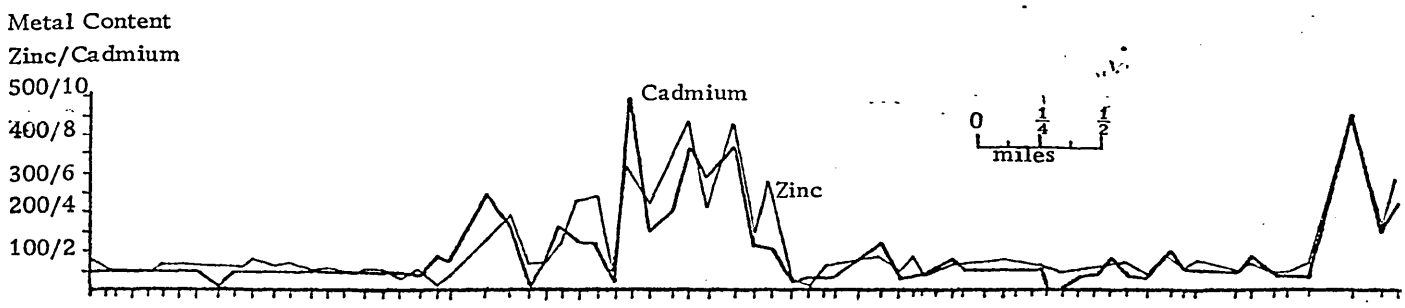


FIG. 11.11.1 CADMIUM, ZINC PRESENCE IN THE ONECOTE LONG SECTION

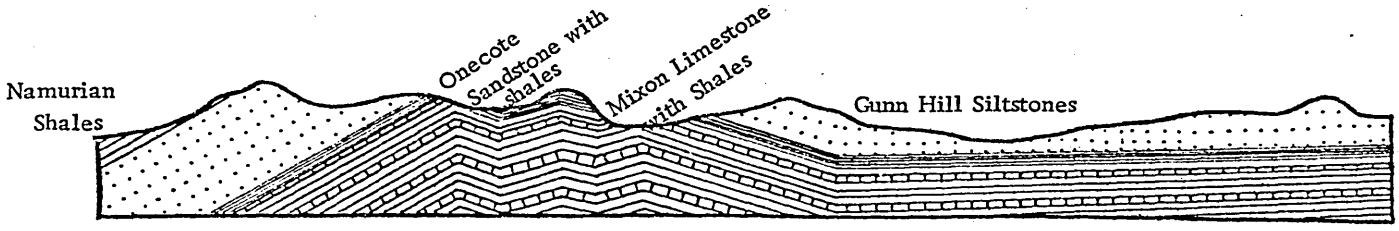


FIG. 11.11.2 GEOLOGY, ONECOTE LONG SECTION

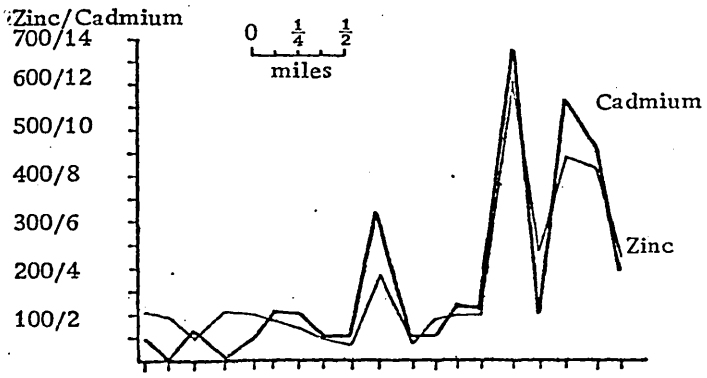


FIG. 11.11.3 CADMIUM, ZINC PRESENCE IN THE ONECOTE-HOLLINSBOROUGH SECTION

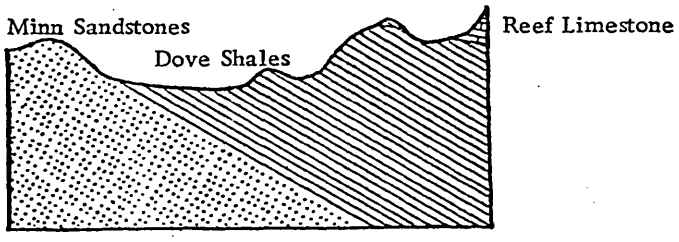


FIG. 11.11.4 GEOLOGY, ONECOTE-HOLLINSBOROUGH SECTION

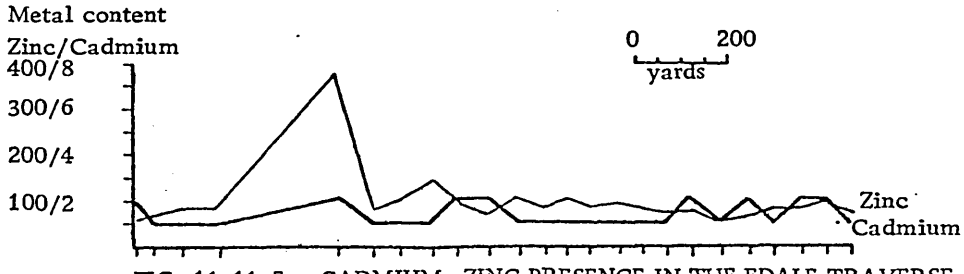


FIG. 11.11.5 CADMIUM, ZINC PRESENCE IN THE EDALE TRAVERSE

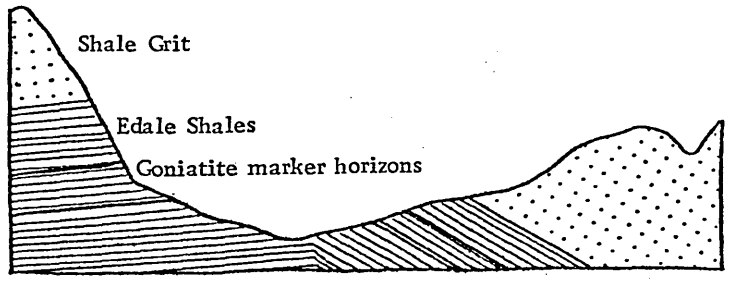


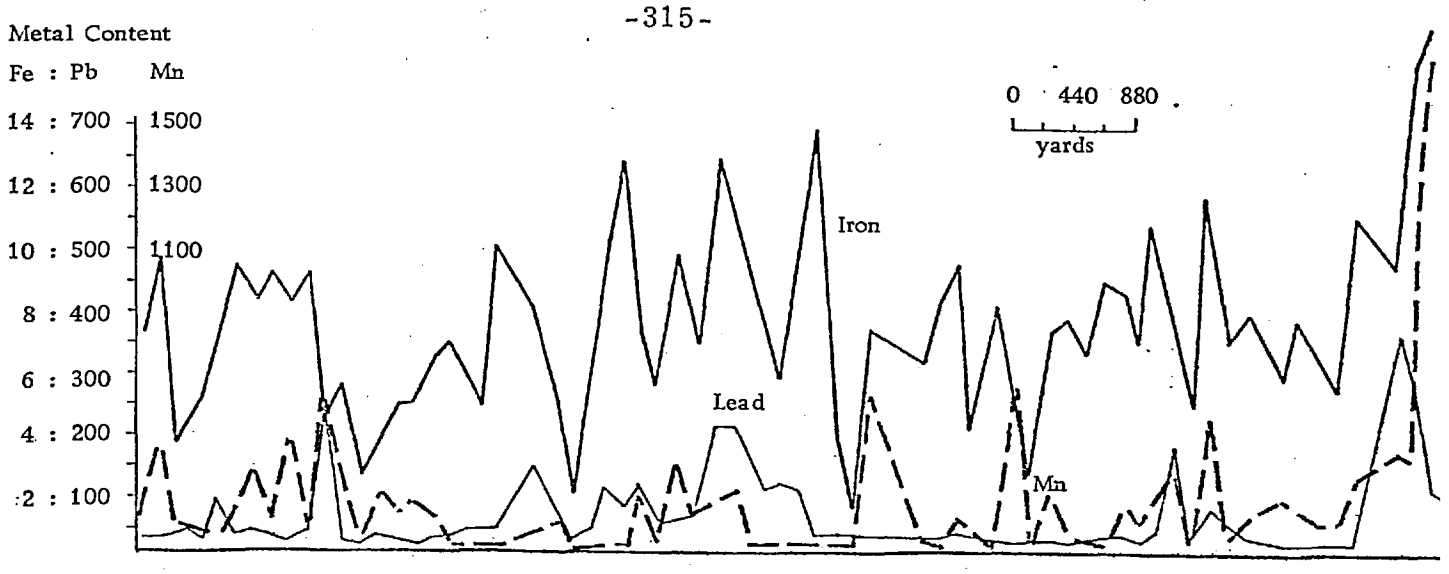
FIG. 11.11.6 GEOLOGY, EDALE SECTION

All figures in parts per million

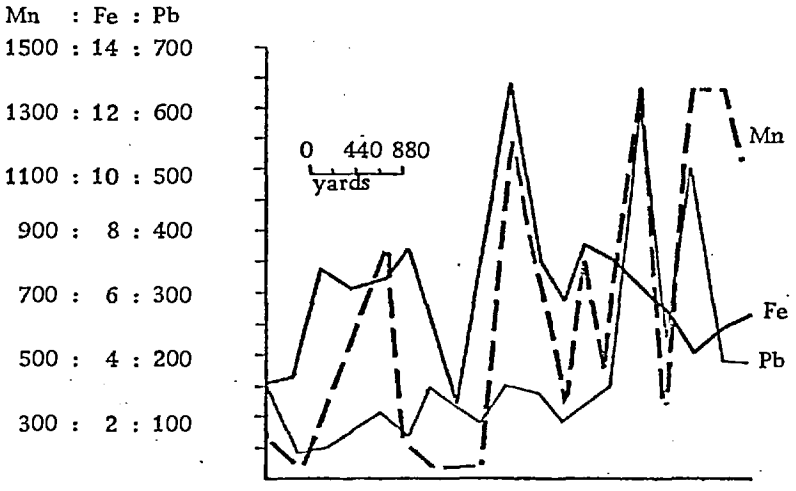
The graph of trace metal content for the soils is shown in Figure 11.11.1 and this clearly denotes two areas of interest separated by a long series of soils where cadmium levels are 2 ppm and less and zinc levels are 100 ppm and less. Within the anomalous zone cadmium averages 4.6 ppm, zinc 265 ppm and lead 184 ppm. At all times within the anomalous zone the relationship between the three elements cadmium, zinc and lead is good. The relationship of each of the three trace metals to manganese and iron presence is confusing. Both manganese and iron fluctuate quite predictably in presence reflecting local variations in topography and so on, but there does appear to be an overall increase in iron content near Mixon, in the anomalous trace metal zone and in the trace element enriched zone on the Northeast tip of the traverse at Warston (see Figure 11.12.1). Some relationship may well exist between the presence of iron either as sulphide or oxide, and base metals.

The traverse has been made some 500 m. South of the old Mixon copper mine workings mentioned by Fletcher (1968) within the Mixon limestones with Shales and finishes in the East within an area of disused mine shafts. The anomaly reflects this mineralisation with cadmium and zinc apparently associated with it. Dispersion of lead is less marked. It seems likely that the intense enrichments of the trace metals (notably lead, which is present at levels of 1.3% at Warston) is due to contamination either from mine tips or from underlying rock veining.

The Grand Mean of cadmium levels in the rocks of the Onecote area is 8.9 ppm which, if compared to the Grand Mean of 2.4 ppm cadmium in the soils of the area, suggests that the element has been extensively leached mobilised and dispersed out of the area. Significantly the degree of leaching of metals from rocks into soils and out of soils in Onecote,

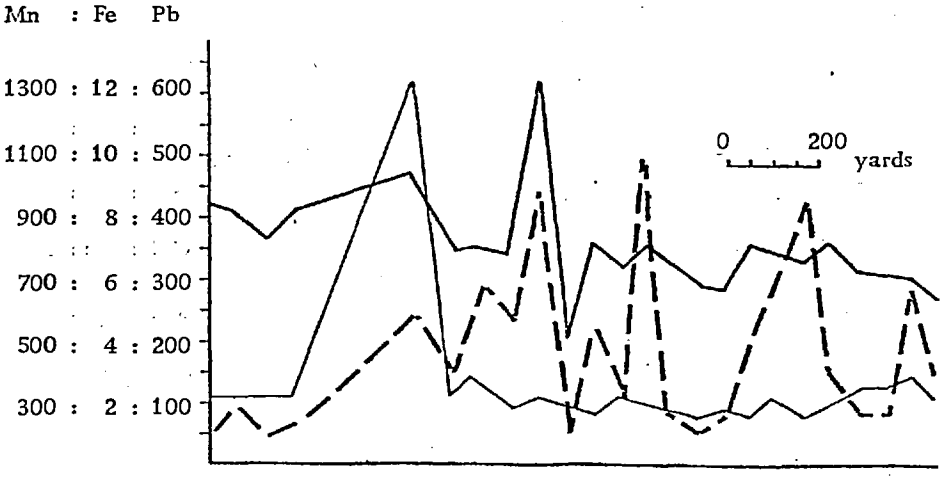


1. Onecote Long Section



Manganese, Mn and Lead, Pb figures are in parts per million. Iron, Fe, are in percent

2. Onecote-Hollinsborough Section



3. Edale traverse

FIG. 11.12 PRESENCE OF IRON, MANGANESE AND LEAD IN SOILS OF 1. THE ONECOTE LONG SECTION, 2. THE ONECOTE-HOLLINSBOROUGH SECTION AND, 3. THE EDALE TRAVERSE

where the form of the base metals is probably as the moderately resistant sulphide, is rather less than that at Bowland where metal enrichment is more likely syngenetic in origin. The ratio of mean soil \ rock cadmium in Onecote is 3.7 whilst that for Bowland is 7.0.

The second section studied in the Onecote area concerns soils overlying the younger Dove Shales around the Hollinsclough area and traversed from M.R. 36540, 40675. The traverse was made in a North easterly direction for three kilometers to M.R. 36845, 40800. The area is high-lying hardly falling below 300 m. and the traverse disects steep ridges either side of the kilometer wide, flat River Dove valley (see Figure 11.11.4). The three main trace-element peaks, rising at one point to 13 ppm cadmium, 590 ppm zinc and 408 ppm lead, are all remarkably coincident with peaks of high manganese content (see Figures 11.11.3 and 11.12.2). Once again, these anomalous samples are probably related either to contamination from mines and mine-tips in the area or directly to base metal mineralisation. The identification of cadmium form by the method of aqueous chemical extractions (see chapter 8) in rock sample 483345 collected from the banks of the River Dove (750m. West of anomalous soil sample-point 1530 and along the direct line of strike of the Dove Shales) confirmed this conclusion. No less than 50 percent of total cadmium in the sample was insoluble in hydrochloric acid; the relevant percentages of lead, zinc and iron insoluble in the acid were 49, 24 and 41 respectively. Galena and pyrite are known not to be decomposed by hydrochloric acid and it has been resultantly concluded that the dominant cadmium partitioning in the rocks of the Hollinsborough area is controlled by the presence of epigenetic base minerals.

Beyond the area of anomalous soils, cadmium levels in soil are low and fluctuate between undetectable and 2.0 ppm (the realms of analytical imprecision). The mean cadmium content in the Dove shales is 6.4 ppm whilst the mean cadmium content of all soils in the area is 3.3 ppm. The ratio of soil \ rock cadmium is 1.9. Even accounting for the anomalous presence of cadmium contamination from mine tips in soils, most of the cadmium from the rocks of the Dove Shales, like that from the Onecote Shales and Bowland Shales has been mobilised and dispersed.

Stream-sediments from the area are predominantly anomalous with levels of cadmium commonly between 4.0 - 5.0 ppm. In the Southwest Derbyshire region the scavenging power of the colloidal hydrates is greater and more consistent than it is in the Bowland Forest region.

11.7 EDALE TRAVERSE NORTH DERBYSHIRE

Only one soil traverse has been taken in Derbyshire. This from M.R. 38340, 41175 for 3.7 kms. in a Northerly direction to M.R. 38725, 41175. The traverse follows the steep slope off the Scarp Grit down into the wide-angled, v-shaped valley of the River Noe before climbing back up towards the Scarp Grit on the other side of the valley (see Figure 11.11.6).

In two thirds of the samples cadmium is barely detectable (at 1.0 ppm) and in the remainder the element is never present at a level greater than 2.4 ppm (see Figure 11.11.5).

The analysis of one sample from immediately below the Shale Grit/Edale contact in the South of the traverse disclosed 364 ppm of zinc

and 1,300 ppm of lead, increases above background which are of the magnitude of four and eighteen times respectively (see Figure 11.12.3). This local anomaly would appear to reflect either contamination from nearby lead mines or minor veining around the area of the contact between the shales and the overlying grit.

Considering that the average cadmium content in the H1 shales just below the Shale Grit is over 16 ppm, the soil traverse has not indicated that such levels are present. However, massive rock slumps, considerable colluviation of head material and a thick covering of boulder-clay are apparent in the Edale Valley and it must be concluded that addition of trace element poor, barren material has successfully prevented a soil anomaly from being displayed.

The Grand Mean of cadmium content in the soils of the Edale area is 1.6 ppm whilst that of the shales is 7.6 ppm. The resultant rock:soil cadmium ratio is 4.7. Levels of cadmium in stream sediments are not unusually high although anomalous samples, with cadmium contents greater than 4.0 ppm have been analysed. In comparison to the other areas already considered large amounts of cadmium have been removed from the soils and in comparison to Bowland this metal has been largely dispersed in the surface drainage system out of the area.

11.8 SOIL TRAVERSE SUMMARY

Of the three areas, that of the Bowland Forest is the only one in which the presence of cadmium in soils can be without doubt related to syngenetic trace element enrichment in the bedrock. The bedrock presence of cadmium in Onecote is completely masked by eipigenetic base metal mineralisation although, in addition Fletcher (1968) indicated large areas of black shale removal from the area. Environmental factors combine in Edale to prevent the evolution of a soil profile related to bedrock.

The comparitive ratios of rock to soil cadmium are: Bowland 7.0, Edale 4.7, Onecote 3.7 and Dove 1.9. These ratios indicate the degree of mobilisation to which cadmium has been subjected in each area. Where environmental factors favouring retention are rarely developed, as in Bowland, resultant loss of cadmium during soil profile development is high, whereas where conditions are more favourable for retention, as in the heavy, waterlogged clays of Edale, the resultant cadmium loss to the surface drainage system is not nearly as marked. Hence the lower ratio figure. In the remaining areas cadmium is present in the regolith predominantly in the form of moderately resistant, epigenetic sulphides and these have not weathered to the same extent as the predominantly organically and clay-bound cadmium which is present in the syngenetic black shales of the Bowland and Edale areas. More cadmium is therefore present in a residual form and thus the rock:soil cadmium ratio is consequently lower.

11.9 THE USE OF AQUEOUS CHEMICAL EXTRACTIONS TO DETERMINE CADMIUM PARTITIONING IN SOILS

11.9.1 PARTITIONING SITES IDENTIFIED IN SOILS

The use of the aqueous extraction technique for the identification of cadmium form in the rock media, extractants used, estimation of error etc. has been described and applied in chapter eight. In the reinterpretation of the technique for soils attention has been paid to the type of weathering products which have formed from shale parent-materials and the extent to which the weathering processes have evolved. The soils are composed of three main components: clay minerals, which are primary and secondary in origin: humus, which is colloidally-sized organic matter which has formed as a temporary end-product of the decomposition of plants and animals: and quartz, which is the residual end-product of the weathering of primary minerals.

Partitioning sites in soils can be broadly divided into six groups on the basis of strength and effectiveness of the extractants used. Cations or cation complexes may therefore:

1 Adsorb on readily exchangeable manganese-iron oxides.

2 Chemically adsorb onto the surface of essentially the montmorillonite clay group and associate with 'free' colloidal iron precipitates which transform by ageing to more stable goethite.

3 Cations may substitute into the structure of non-exchangeable iron-manganese oxides.

4 Cations may be attracted inside the expanding-lattice type clay minerals upon wetting, substituting in within-layer sites.

5 Cations may be present in part-weathered primary minerals such as the sulphides galena and pyrite, the silicates and residual kerogenous matter.

6 Cations may be present in the more readily soluble sulphides, such as sphalerite (which dissolves in hydrochloric acid).

Two soil groups have been studied by this method of aqueous extraction. The first set of samples comprises two soils from the Onecote area, which were underlain by metal-rich shales, whilst the second set comprises six topsoils from the area surrounding an old lead mine at Harrop Fold in the Bowland Forest from which one representative sample has been compiled. The underlying bedrock in this case, although obviously not the dominant source of metal to the soil is black shale of the Upper Bowland Shales.

All conclusions made in the following two sections are based on the study of chapter 8, details of extractants used etc. are deliberately omitted in order to avoid tedious repetition. Extractant combinations used to determine cadmium partitioning sites are shown in Tables 11.1 and 11.2.

11.9.2 SOILS OF THE ONECOTE AREA

The Onecote soilwas taken from a depth of 30-45 cms. within an area of pronounced seepage. Enhancement of metal takes place at depth indicating that the source of metal to the organic-rich peaty soil is the underlying bedrock.

The behaviour of cadmium and zinc are broadly similar. Neither of the elements is present in the rocks in an adsorbed form and about 75% of total exchangeable cadmium and zinc is contained in inter-layer clay substitution sites and within manganese oxides (see Table 11.1). Cadmium is accepted into the manganese oxides in greater amounts than is zinc, presumably because of its larger ionic radius and greater attractability. Both elements are incorporated into inter-layer clay absorbtion sites in more or less equal amount. Comparitively little cadmium is present in the stronger adsorbed positions in the clay lattice or in the soluble sulphides such as sphalerite. Conversely zinc is well represented in this category and this may be due either to the presence of zinc as a primary sulphide mineral or to for example, part or total replacement of aluminium by zinc to form a smectite mineral such as sauconite. Both elements are perceptibly present, aside high iron after extraction with hot hydrochloric acid. This suggests that cadmium and zinc may well be still present within primary pyritous minerals.

TABLE 11.1 THE BEHAVIOUR OF TRACE ELEMENTS (INCLUDING CADMIUM) BASED ON AQUEOUS CHEMICAL EXTRACTIONS IN SOILS OF THE ONECOTE AREA

Simplified Metal Associations	Cadmium	Zinc	Lead	Manganese	Iron
1. Adsorbed	N. d	N. d	80	61	61
2. Carbonates/iron oxides/ within clays	38	43	1	N. d	N. d
3. Stable iron-manganese oxides	47	27	11	14	N. d
4. Clay lattices/(Sulphides)	7	22	N. d.	20	9
5. Pyrite/(Galena, residual organics)	8	8	11	5	30
6. Broad-based organics (EDTA extractable)	62	43	92	42	25
Average total extractable metal	13	420	565	565	4.55%

NOTES

Number of samples = 2. Values are means of 'percent of total available metal extracted'

For error estimation see Table 8.1

For explanation of extractants used in determining associations 1 to 6, see Table 8.2

N. d. = not detected

61% of both iron and manganese are in a readily exchangeable form having been removed with neutral ammonium acetate solution. It is noticeable that neither zinc nor cadmium are associated with them. The existence of almost all the lead (81% of total) in an adsorbed form and the fact that 92% of total lead can be removed by the EDTA chelating agent can be taken to indicate that although lead is fixed onto the surfaces of organic material it is not strongly complexed but is in an adsorbed state.

It is noticeable that no iron is extracted from the manganese-rich oxides dissolved by the combined acid-reducing agent. Altogether 75% of the total manganese is present as readily exchangeable or fixed oxides. In non-acid waters higher manganese oxides commonly precipitate first as colloids and may be transported long distances as sols. In this state the negatively charged particles commonly adsorb soluble cations. With sufficient exposure to oxygen a more stable form of the oxide such as pyrolusite (MnO_2) would ultimately form.

The effect of EDTA upon the total exchangeable cadmium present in the soils is to remove 62%. This cadmium is presumably related to the presence of humic or other organic materials at depth. Humus in particular is able to form distinct compounds with iron and other metals (Goldschmidt, 1958) and its cationic exchange capacity is many times greater than that of the clay minerals. Mutual attractions of cadmium-containing clay minerals and manganese-iron oxides to humic and other organic materials, presumably also containing metallorganic cadmium complexes, increases the sphere of influence of the chelating agent on use. The extent of the actual formation of cadmium-carbon complexes is thus masked, although it does appear to be considerable.

11.9.3 SOILS OF THE BOWLAND AREA

The soils used for the second set of extraction experiments have been contaminated by the workings of a lead mine. Nevertheless, the comparison of the behaviour of cadmium in an epigenetic setting with that of cadmium in a syngenetic setting is of some interest.

Within the topsoil small unweathered chips of rock contained common pyrite minerals, sphalerite and rare ghost-galena. It was apparent therefore that much of the cadmium in the soil would be associated within the sphalerite and possibly pyrite lattices.

98 percent of total extractable cadmium is in fact present in the two partition categories which represent these phases (see Table 11.2). It is possible that some of this cadmium is contained in addition, within lattices of clay minerals and that some is associated with residual kerogenous organic matter.

The three remaining chalcophile elements zinc, lead and iron are also very strongly represented in the sulphide category (category 4, Table 11.2). Cadmium is one of the more important trace element substituents in the sphalerite structure, but the principal substituent for zinc is iron. The identification of the presence of 85% of the total extractable lead in this category is explained by the presence of partly soluble lead sulphide identified as ghost galena in hand specimens possibly occurring in addition as a contaminant mineral within the sphalerite structure. The actual averaged presence of the four chalcophile elements in the phases of this category are: cadmium 89 ppm, zinc 12,719 ppm, lead 1,360 ppm and iron 4.5%. This results in a zinc to cadmium ratio (making the assumption that both elements are solely in the sphalerite of 1:143. El Shazly

TABLE 11.2 THE BEHAVIOUR OF TRACE ELEMENTS (INCLUDING CADMIUM) BASED ON AQUEOUS CHEMICAL EXTRACTIONS IN SOILS OF THE BOWLAND AREA

Simplified Metal Associations	Cadmium	Zinc	Lead	Manganese	Iron
1. Adsorbed	1	3	N. d	83	9
2. Carbonates/iron oxides/ within clays	N. d	1	N. d.	N. d.	N. d.
3. Stable iron-manganese oxides	2	N. d.	9	N. d.	N. d.
4. Clay lattices/(sulphides)	48	46	85	2	69
5. Pyrite/(Galena, residual organics)	50	51	6	15	22
6. Broad-based organics (EDTA extractable)	3	2	9	10	1
Average total extractable metal	185	2.76%	1600	50	5.55%

NOTES

Number of samples = 2. Values are means of 'percent of total available metal extracted'.

For error estimation see Table 8.1

For explanation of extractants used in determining associations 1 to 6 see Table 8.2

N. d. = not detected.

et al (1956) recorded that the average cadmium content of zinc blendes from the South Pennines was about 4,000 ppm and that its presence ranged from 300 ppm to 1%. He also suggested that the lack of detectable cadmium in the oxidised zinc minerals hydrozincite and hemimorphite is due to the total leaching of cadmium out of cadmium-rich sphalerites during oxidation. The probability of much of the cadmium having been leached from this soil during the oxidation process is great. With regard to this point it is worth noting that of a total exchangeable cadmium content of close on 200 ppm, less than 2.0 ppm (or 1%) is in an adsorbed form although, in contrast almost all the manganese (83% of total) is present in this condition.

Up to 93 ppm of the total extractable cadmium is present as a substituent in the pyrite lattice, along with 14,100 ppm zinc, 96 ppm lead. The iron present in this phase amounts to 1.44%. The commonest trace elements described in pyrite by El Shazly et al (1956) were, amongst others, zinc and lead. Deer et al (1969) suggested that reported minor element contents in pyrite are often present in impurities, for example, lead in galena and zinc-cadmium in sphalerite.

The soils of the area were sparsely vegetated and this may have reflected in the low content of organic matter and in the very low proportions of total available metals contained in it. A mere 6 ppm cadmium is associated with organic matter. However, the actual formation of organic compounds containing cadmium, although not important, is a more common event than that of simple adsorption onto the surfaces of organic complexes (compare categories 1 and 6 from cadmium in Table 11.2).

11.9.4 SUMMARY COMPARISON OF SOILS EXAMINED

In soils developed above rocks with contained metal of syngenetic origin, cadmium is not present in significant amount within the lattices of

clay minerals or in sulphides. The metal almost totally relates to inter-layer clay mineral exchange sites and to the presence of the more stable forms of manganese oxides. In addition the presence of organic matter exerts a profound influence on the behaviour of cadmium. Significantly almost no cadmium is adsorbed in the soil or is associated with the presence of readily exchangeable manganese oxides.

In contrast the soils developed upon rocks with contained metal of epigenetic origin contains cadmium which is almost totally contained within the sulphide phases. When weathering of the rocks zinc and iron minerals does take place, acid soluble trace elements are leached out thus preventing substitution into inter-layer clay mineral exchange sites and the initiation of a strongly adsorbed content. The sparsity of organic matter in the soils assures the relative unimportance of organic matter in the processes of cadmium retention.

11.10 THE IDENTIFICATION OF CADMIUM SPECIES FROM CONTAMINATED SOILS BY THE USE OF THERMALLY EVOLVED VAPOUR PROFILES

11.10.1 INTRODUCTION

The theory and practice of the use of the thermally evolved vapour profile method (hereafter referred to as TEVP) is fully detailed in chapter nine where the identification of cadmium species in black shales has been demonstrated.

The TEVP study of polluted soils from South Wales, the localities of which are accurately listed in the following chapter, has been undertaken

in order to investigate the partitioning behaviour of cadmium in topsoils and the metamorphoses of these identified forms which take place at depth and in conditions of increased humification. Most of the anomalous cadmium soils from South Wales have been collected from hollows at the head of the River Tawe valley which experience intermittent and occasionally heavy waterlogging. Anomalous cadmium in soils is restricted to the waterlogged, uplands area in the Black Mountains, well-drained soils are relatively cadmium deficient.

11.10.2 Cd IN WATERLOGGED SOILS

The soils whose TEVP graphs are shown in Figure 11.13, have been collected from the centre of a heavily waterlogged hollow. A topsoil was sampled to 15 cms. and two subsoils were sampled at 15-30 cms. and 30-45 cms.

No fundamental change in cadmium species occurs at all at depth there only being a progressive decrease in total cadmium content in the samples downprofile, reflected in much reduced peak heights and areas. The total extractable cadmium content of the soils varies enormously from 58.5 ppm in the topsoils to 10.0 ppm and 3.0 ppm in the two subsoils.

In Section 11.9.1 the identification of broad species categories of cadmium partitioning in soils has already been made with reference to the aqueous chemical extraction method. This primary identification is of assistance to the processes of TEVP interpretation which relies upon the study of relevant pyrolysis reference curves from comparitive evolved gas analyses. The process of species identification in clay shales made in chapter nine should be consulted.

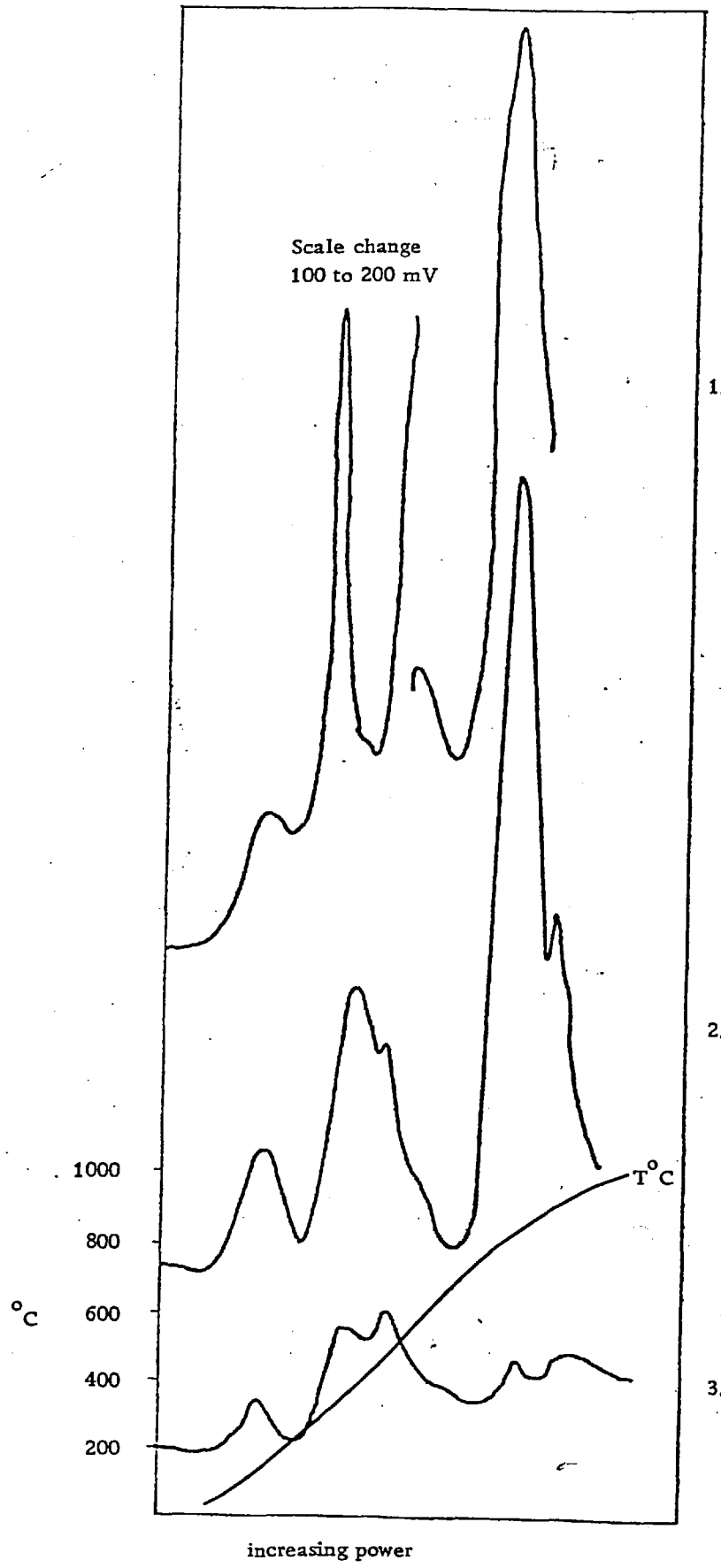


FIGURE 11.13 TEVP GRAPHS OF SOILS COLLECTED FROM THREE DEPTHS IN THE TAWE VALLEY, SOUTH WALES

Four definite peaks can be recognised in Figure 10.13 and represent temperatures of dissociation of cadmium from different species at 140°-150°C, 335°-410°C, 485°-555°C and 805°C-845°C. In addition, attention is drawn to the appearance of a minor peak in the two subsoil graphs between 930-940°C.

The low temperature peak in graph 1 is thought to be caused by cadmium release from sites of adsorption on clays and organic humates. The relative area of this peak to the others in the graph indicates its comparitive importance. The peak at 335°C is formed in all probability because of cadmium expulsion from colloidally-sized agglomerations of iron-manganese oxides, plainly visible in the wet surface soils, and clay minerals (see Section 9.6 pages 203 - 7). The relationship of cadmium to the clay minerals is likened to that suggested in section 11.9.1, the cadmium occupying mainly inter-layer sites. The 550°C cadmium peak is formed by release of the metal from the structures of organic complexes as they undergo active molecular decomposition (see Section 9.5 page 201). Finally the high temperature peak at 805°C represents the breakdown of clay mineral structures and the resultant loss of within-lattice cadmium (see Section 9.7 page 207). The incorporation of cadmium within expanding lattice type clay minerals is the principal form of cadmium in the topsoil and the upper subsoil. The conditions of poor drainage and paucity of potassium derived from sandstone bedrock are optimal for the formation of montmorillonite-type clays with high cation exchange capacities. The virtual non existence of this cadmium species at depth (45 cms. see graph 3) is due either to leaching during times when drainage conditions improve or non leaching down profile when the soils are persistently waterlogged.

Adsorbed forms of cadmium exist at depth, although the organic-cadmium peak dominates. Downwards percolation of humic

materials which have scavenged cadmium may have taken place. The effect of surface flushing of cadmium-rich colloidal material during floods could effectively be to remove most of the cadmium from the surface soils and into the more active drainage systems. The presence of large amounts of cadmium in local stream sediments does suggest that mobilisation and dispersion into the river system does take place.

Three minor differences are noted at depth (Figure 11.13 graphs 2 and 3) and interpreted by the author as follows: the first concerns cadmium associated with the iron oxide gel which released cadmium at 335^{o}C in the graph 1. The reconstitution of oxide gels at depth into a more stable form, such as a goethite structure, whilst retaining some proportion of its trace element content will result in a material which, by virtue of its ordering process, will decompose at a higher energy level. The loss of peak height in this species in the 30-45 cm. soil (graph 3) is caused either by cation exclusion on further crystal ordering or by a scarcity of cadmium supply at depth.

The second minor difference accounts for minor discrepancies in peak temperatures of species which have been considered similar. This results from a phenomenon whereby, according to the type of pyrolysis process taking place (summarized in Section 9.2, pages 193-5) the curve shape resulting takes the form of one of three broad types: a gradual rise to a peak followed by a steep tail-off, a steep rise to a peak followed by a gradual tail-off or a symetrically shaped peak. The effect of increased peak amplitude resulting from release of larger concentrations of trace element will cause an effective shift of peak temperatures either in a positive or a negative direction. A process of zero order desorption or decomposition can be envisaged in Figure 11.13. where a positive temperature shift with increased peak amplitudes are associated (in graph 1, compared with 2 and 3).

The final difference in cadmium species at depth is the addition of a peak at 930°C in graphs 2 and 3. This may be caused by dissociation of the sulphide form of cadmium which may form in anerobic, waterlogged conditions at depth as a result of the bacterial destruction of organic matter and production of hydrogen sulphide. The tiny amplitude of the peak indicates its relative unimportance.

11.10.3 MODERATELY-DRAINED SOILS

The soils illustrated as TEVPs in graphs 1 to 3 of Figure 11.14 have been collected from the same soil traverse as the rocks just considered in section 11.10.2, although in this case the soils are from the moderately or intermittently well-drained slopes above the hollow.

Five peaks are dominant in the topsoils; at 140°C, 325°C, 530°C, 815°C and 865°C. The principal topsoil peak occurs at 325°C and represents release of cadmium associated with iron oxide colloids. Little cadmium is present in an adsorbed form as shown by the smallness of the peak at 140°C. The peaks which dominated the waterlogged soils examined in section 11.10.2, representing cadmium release from organic matter and from within the lattices of clays, are still present although neither achieve the importance which they attain in waterlogged soils. The needle peak at 865°C is also related to the release of cadmium from the lattices of clay minerals and represents the rapid decomposition of a specific clay mineral.

The effect of depth on cadmium forms in a moderately drained environment is for clays and iron-manganese oxides to be removed by leaching. Thus at a depth of 30 cms. the only cadmium species which exist are related to the presence of iron oxides and organic matter and the presence of a barely detectable, low temperature adsorbed cadmium peak. At 45 cms. only a broad, low peak representing cadmium release from organic substances is present.

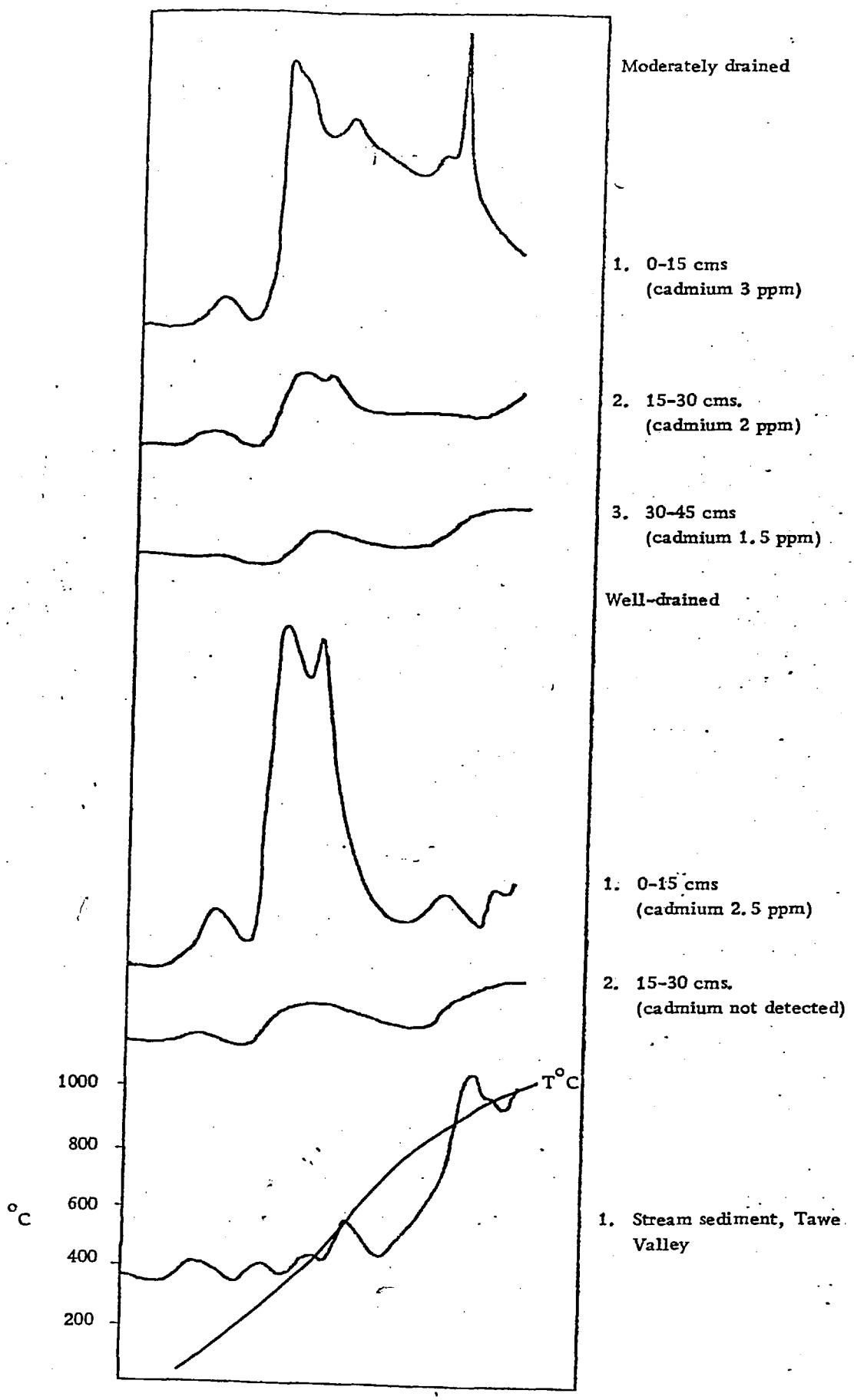


FIGURE 11.14 TEVP GRAPHS OF SOILS FROM MODERATELY DRAINED AND WELL-DRAINED SOILS IN SOUTH WALES

The behaviour of cadmium in a moderately drained soil is therefore, to associate primarily with the presence of iron oxide colloids but also to be attracted into humic substances and incorporate into growing lattice structures of clays. At depth clays and organic substances containing cadmium are leached out of the soil to varying degrees and cadmium is expelled from the re-ordered oxide gels. At a depth of 45 cms. cadmium is barely detectable in the soil, its host components having been reconstructed and mobilised. No source metal is available from the barren bedrock.

11.10.4 WELL DRAINED SOILS

The samples representing well drained soils have been collected on the dry, higher slopes from the same traverse as the previous two sets of samples. Graphs 4 and 5 of figure 11.14 are the TEVPs of the topsoil and the 30-45 cm. subsoil respectively.

Although iron-manganese oxides scavenge most of the cadmium available in the topsoil, the cadmium-carbon association is almost as important (peaks respectively at 355^{o} and 465^{o}C). The cadmium source for these soils is from airborne particulates and not from bedrock so the presence of iron-manganese oxides in the topsoils as scavengers to 'sponge-up' airborne cadmium which deposits in mists and rain onto the soil surfaces, is of fundamental importance. The good drainage capabilities of these soils enables leaching to remove those colloids which have retained trace metals. It is possible that some interchange between cadmium in iron-manganese oxides and cadmium on organic complexes may occur. In time organo-metallic complexes may form and it appears that these are less mobile than the colloidal materials which are totally removed from the subsoils (graph 5). The broad-based, low-peaked

nature of the cadmium-carbon peak in the TEVP of the subsoil is a common feature of a pyrolysis curve representing a well humified soil (see Figure 9.7). The peak resulting from cadmium release from clay-lattices, which was such a common feature of the more waterlogged soils is barely detectable in the well-drained soil.

11.10.5. CONCLUSION AND SUMMARY

The presence in heavily waterlogged soils of colloidal material with high cation exchange capacities is seen to be a vital factor in the retention of cadmium. In better drained soils cadmium is usually readily mobilised and dispersed into the surface drainage system and this trend will be emphasized in acidic soils. The absence of significant cadmium contents in the majority of soils in the South Wales study area can be explained firstly by the rarity of conditions which are suitable for iron-manganese precipitation in the soils and secondly by the ease of mobilisation of cadmium in what are in the main, sandy textured and freely-drained soils. The only cadmium species which does appear to be moderately immobile in soils is that in which cadmium has entered into metallorganic form during the processes of humification and is thereby retained in the humic top layers of the soil.

CHAPTER 12

12 A STUDY OF CADMIUM IN AERIALLY CONTAMINATED AND NATURALLY ENRICHED STREAM SEDIMENTS AND SOILS IN WALES

12.1 INTRODUCTION

The area in South Wales was chosen in order to investigate a prominent cadmium stream sediment anomaly present along the foothills of the Black Mountains and Brecon Beacons at the head of the Swansea and Neath Valleys (see Figures 3.6, page 48 and 12.1). Upon studying the stream sediment map of England and Wales it was noted that the continuity of the anomalous stream sediments between Swansea and the Brecon Beacons was broken about seven kilometers Northeast of Swansea. In addition, beyond the East-West trending watershed divide of the Beacons, the anomalous contents of cadmium in the stream sediments, so typical of samples collected to the South, were absent. It appeared, therefore, that two centres of metal build-up in stream sediments existed, firstly immediately around Swansea and secondly an area of the Southward facing uplands of the Black Mountains.

A second area in the Denbighshire Moorland region in North Wales, was chosen again because of the presence of inexplicable anomalous levels of cadmium in stream sediments. On this occasion the site was well beyond the influence of large urban centres of population and was also considered to be a sufficient distance beyond areas of known mineralisation to be contaminated.

12.2 LOCATION, GEOLOGY AND SOILS OF THE SOUTH WALES AREA

The area is located 35 kms. Northeast of Swansea in the lower slopes of the Black Mountains, lies at an average altitude of 1,200 ft. and encompasses the headwater region of the River Tawe. The characteristic

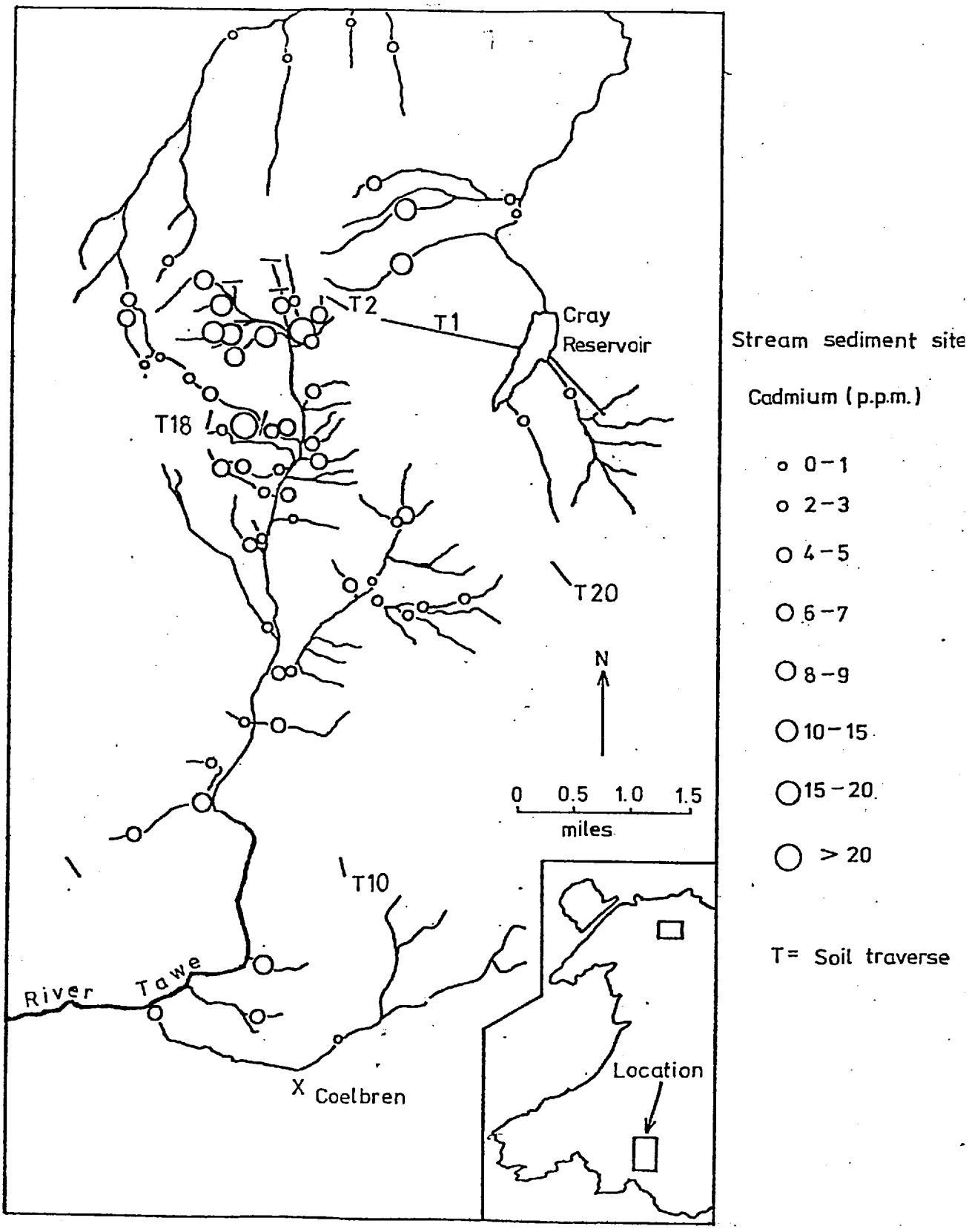


Figure 12.1 Geographical location of South Wales area with stream sediment and soil traverse sites.

soils of the area are developed on glaciated land-forms and amongst them a certain topographic zoning can be distinguished. The crests of the ridges are commonly blanketed by peaty-gley soils with characteristic paling and greying of colours and mottling developed on occasions below covers of gulleyed peat. The less steep slopes of the valleys are mantled by shallow, acid, red, silty loams topped usually by a thin mor humus or peaty layer. The less steep valley sides and the basin head are characterized by silty-loam textured podzolised soils with characteristic reddish-brown 'B' horizons and sporadically developed A2 iron-pans. South of the upper river reaches the soils developed on the Carboniferous Limestone are drift derived of Old Red Sandstone origin. Here up to 15 to 30 cms. of topsoil peat have developed above a light-grey second horizon, with occasional iron-pan presence, and a deeper, mottled, yellow-red horizon (details modified from Soil Survey of Great Britain No. 13, 1960: Glamorgan).

The mean annual rainfall in the area ranges from 50.5" at the coast (Briton Ferry) to 82.7" just West of the source of the River Tawe. The upper reaches of the Tawe river cut into dull-red and green mudstones and micaceous sandstones of the Old Red Sandstone Group. At Glyn Tawe the river flows in quick succession over outcrops of the Carboniferous Limestone and Millstone Grit before completing its journey to the Bristol Channel over bedrock of dirty-blue and dark grey shales of the Rhondda Coal Measure Group.

12.3 METAL CONTENT OF THE ROCKS OF SOUTH WALES

Rock specimens were collected from all of the geological formations exposed in the Upper Swansea Valley area. These ranged from Old Red Sandstone to the Coal Measures of the Upper Carboniferous. Only three specimens out of 20 contained 1.0 ppm or more cadmium and none exceeded 1.5 ppm (see Table 12.3). The overall average cadmium

TABLE 12.3 TRACE METAL CONTENT OF ROCKS FROM SOUTH WALES

Geological Age		Rock Type	No. of Samples	Cadmium		Zinc		Lead		Manganese		Iron	
				Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Ordivician	b7	Shale	5	N. d.	-	104.0	86.0-140.0	36.0	5.0-77.0	402.0	270.0-530.0	3.6	1.3-4.1
Old Red Sandstone	C	Sandstone-Conglomerate	3	0.6	N. d-1.5	44.0	24.0- 65.0	27.0	10.0-48.0	1090.0	260.0-1810.0	1.17	0.05-1.8
Old Red Sandstone	C	Shale Mudstone	5	0.5	N. d-1.0	77.0	36.0-142.0	18.0	10.0-29.0	844.0	360.0-170.0	2.1	1.1-2.7
Carboniferous Limestone	d2	Limestone	3	N. d.	-	20.0	16.0- 28.0	59.0	58.0-62.0	57.0	40.0- 90.0	0.006	0.003-0.01
Millstone Grit	d4	Sandstone	1	N. d.	-	8.0	-	5.0	-	10.0	-	0.01	-
Coal Measures	d5	Shale Mudstone	4	0.25	N. d. -0.5	119.0	19.0-360.0	30.0	10.0-62.0	2766.0	260.0-9400.0	7.9	0.79-28.8
Coal Measures	d5	Black Shale	2	0.75	N. d. -1.5	103.0	78.0-128.0	75.0	53.0-96.0	310.0	190.0-430.0	3.8	1.73-4.8
Coal Measures	d5	Limestone	2	N. d.	-	104.0	86.0-140.0	36.0	5.0-77.0	402.0	270.0-530.0	3.6	1.3-4.1

Iron figures are in percent, all others are in parts per million

from all the samples is 0.3 ppm which is the figure used by Wedepohl (1961) as the average cadmium value in shales. In the context of the following report, therefore, the possibility that the sedimentary bedrock is a source for soil and sediment cadmium is considered highly unlikely.

Zinc content was highest in the Coal Measures rocks of d5 age and within two samples of black shales from the same Formation. Lead content averages 75 ppm (see Table 12.3). Iron and manganese also attained their highest average contents within the rocks of the Coal Measures although they did so in the group of mudstones-shales and not in the black shales. The rocks of Old Red Sandstone age, which underlay the source area of the River Tawe contained low but noteworthy zinc contents, moderately high manganese contents and low, insignificant contents of cadmium, lead and iron.

12.4 CADMIUM PRESENCE IN STREAM SEDIMENTS

One of the areas of outstanding interest which was identified on the stream sediment cadmium map in the geochemical atlas of England and Wales (Figure 3.2 page 40) was located in the South Wales area 35 kms. from the centre of Swansea. In their paper 'Plants as indicators of heavy metals in the air', Goodman and Roberts in 1972, identified heavy metal pollution caused by airborne particulate matter around the Lower Swansea Valley and predicted that the distribution of heavy metals may be as far as 32 kms. from Swansea. Wakeley (1973) during a symposium entitled 'Cadmium in the environment' reported that monitoring of cadmium had been undertaken by Rio Tinto Zinc around their zinc smelter establishments in the Swansea Valley and at Avonmouth and indicated that the tiny amounts of cadmium particulate matter which were emitted by smelting processes were easily washed from the surfaces of

receiving plants. It does now appear however, that the extent of environmenta contamination centred on the zinc smelters encompasses a greater area than was at first realised. It seemed possible, therefore, that a topographical control was responsible for the entrappment of airborne particulates which had been carried in upper air streams away from the fall-out areas surrounding the smelter sites. Rainfall exceeds 80" per annum in the area of cadmium enhancement and clinging mists and smogs were encountered on many occasions during field sampling excursions.

Of the 77 stream sediment sites indicated in Figure 12.1, 50% (39 samples) had cadmium contents which were in excess of 4.0 ppm and which were considered anomalously high. Two sediments from different tributaries near the source of the River Tawe contained cadmium contents of 30.0 and 44.0 ppm.

The correlation matrix of five analysed elements in stream sediments, cadmium, zinc, lead, iron and manganese, is shown in Table 12.1.1. Amongst a total of 115 samples the correlation coefficient between cadmium and zinc was easily the most significantly positive (0.81 at P = 0.001) followed by manganese: iron (0.52 at P = 0.001). The remaining coefficients significant at P = 0.001 were manganese:zinc (0.44) lead:zinc (0.40), manganese:cadmium (0.37) and lead:cadmium (0.36). The isolation of all highly cadmium anomalous samples with greater than 5.0 ppm and recalculation of associate element means showed a 50% increase in mean zinc, a 12% increase in mean lead and no change in the mean presence of iron and manganese. The resultant changes in the correlation coefficients, listed in Table 12.1.2 with respect to cadmium were as follows; the zinc:cadmium correlation, although still significant (to P = 0.001), dropped to 0.66; the manganese:cadmium correlation, significance(P= 0.01) rose to 0.45; the cadmium:iron correlation rose marginally and the cadmium:lead correlation fell considerably. Cadmium

TABLE 12.1.1. CORRELATION MATRIX FOR CADMIUM, ZINC, LEAD, IRON AND MANGANESE IN STREAM SEDIMENTS OF SOUTH WALES

Element	Manganese	Iron	Lead	Cadmium	Zinc
Manganese	-	.52	.30	.37	.44
Iron		-	.24	.13	.16
Lead			-	.36	.40
Cadmium				-	.81
Zinc					-
Mean Metal content (parts per million)	2398	2.8%	81.7	4.1	362.3

Number of samples N = 115

Levels of significance (for N = 100) P 0.001 = .32
P .01 = .25
P .05 = .19

TABLE 12.1.2 CORRELATION MATRIX OF CADMIUM, ZINC, LEAD, IRON AND MANGANESE FOR STREAM SEDIMENT SAMPLES HIGHLY ANOMALOUS IN CADMIUM FROM SOUTH WALES

Element	Manganese	Iron	Lead	Cadmium	Zinc
Manganese	-	.30	.13	.45	.38
Iron		-	-.15	.23	.03
Lead			-	.09	.30
Cadmium				-	.66
Zinc					-
Mean metal content (ppm)	2341	2.49%	91.1	6.66	516.8

Number of samples, N = 38

Levels of significance (for N = 38), P 0.001 = .50
P 0.01 = .40
P .05 = .31

enrichment would appear therefore to be almost equalled by proportional zinc enrichment and to be much in excess of lead enrichment. Cadmium enrichment in stream sediments appeared to be, at least in part, controlled by the presence of manganese oxides.

12.5 IDENTIFICATION OF CADMIUM FORM IN STREAM SEDIMENTS BY THE USE OF AQUEOUS EXTRACTIONS

The theories behind the use of aqueous chemical extractions, and the expected action of each of the five extractants used is given in detail in Chapter 8, pages 167 - 170. Extractant combinations used to determine cadmium partitioning sites are given in Table 12.2.

84% of total available cadmium can be removed by two reagents (see Table 12.2); 39% was removed by acetic acid which accounted for cadmium which was held within the layers of clay minerals (and possibly as carbonate) and the remaining 45% was removed by the reducing-oxidising agent which was known to be manganese specific. Of the remaining 16%, 8% was surface adsorbed, presumably on oxidate, clay and organic colloids, 3% was removed from either within clay lattices or from sulphides and finally 5% was either related to iron sulphide or was in a residual organic form. The organic chelating agent EDTA removed 14% of total extractable cadmium from amongst the three strongest cadmium associations. Some of this organically-bound cadmium may be associated with the manganese oxides.

The dominant habits of cadmium, therefore, in stream sediments are firstly, to be retained by precipitated manganese oxides and secondly, to substitute into the inter-layer cation exchange sites in the clay minerals. In comparison, any remaining cadmium association is subordinate.

TABLE 12.2 THE BEHAVIOUR OF TRACE ELEMENTS (INCLUDING CADMIUM) IN STREAM SEDIMENTS FROM SOUTH WALES BASED ON AQUEOUS CHEMICAL EXTRACTIONS

Simplified Metal Associations	Cadmium	Zinc	Lead	Manganese	Iron
1. Adsorbed	8	16	2	14	9
2. Inter layer clay/carbonates	39	25	11	9	N. d.
3. Manganese - iron oxides	45	17	42	67	N. d.
4. Clay lattices/sulphides	3	39	27	8	62
5. Pyrite lattice/residual organic	5	3	18	2	29
6. Broad-based organics (EDTA extractable)	14	1	20	8	2
Average total extractable metal	25.2	1568	188	20995	3.48%

NOTES

Number of samples = 5. Values are means of 'percent of total available metal extracted'

For error estimation, see Table 8.1

For explanation of extractants used in determining associations 1 to 6, see table 8.2.

N. d. = not detected.

The significant presence of 39% of total zinc and 27% of total lead in a form soluble only in hot hydrochloric acid can be explained by their presence either in sulphides or within the clay minerals. In addition 29% of total iron, insoluble in the acid, may be in the form of the resistant pyrite but the majority of iron removed (62% of total) was with hydrochloric acid. Iron appeared therefore, to be an integral part of the clay mineral constitution.

12.6 IDENTIFICATION OF CADMIUM FORM IN AN ANOMALOUS STREAM SEDIMENT BY THE USE OF THERMALLY EVOLVED VAPOUR PROFILES (TEVP)

Reference to the background and methodology of pyrolysis studies from which the following interpretation has been made should be made to Chapter 9, pages 190-260.

The original TEVP graph for the cadmium-rich stream sediment displayed no clear cadmium peaks and consequently this indicated that the metal was so diversified in its form that no clear metal associated component existed (see Figure 12.2 graph 1). In graphs 2, 3 and 5 readsorption occurred but the removal of manganese oxides from the sediment system by the manganese-specific reducing-oxidising agent effectively removed almost all the cadmium from the sediment (graph 4). This indicated that cadmium association with manganese oxides dominated over any other possible association. Small peaks do remain however, even after the action of the manganese specific reagent at temperatures of 470^{o}C and 615^{o}C. The former peak was effectively removed by EDTA and was untouched by hot hydrochloric acid, whilst the latter was more or less untouched by all of the remaining reagents. The former peak in all probability was formed by the release of cadmium from dissociating carbon compounds, whilst the latter appeared to be caused by the thermal release of cadmium from the lattices of pyritous minerals.

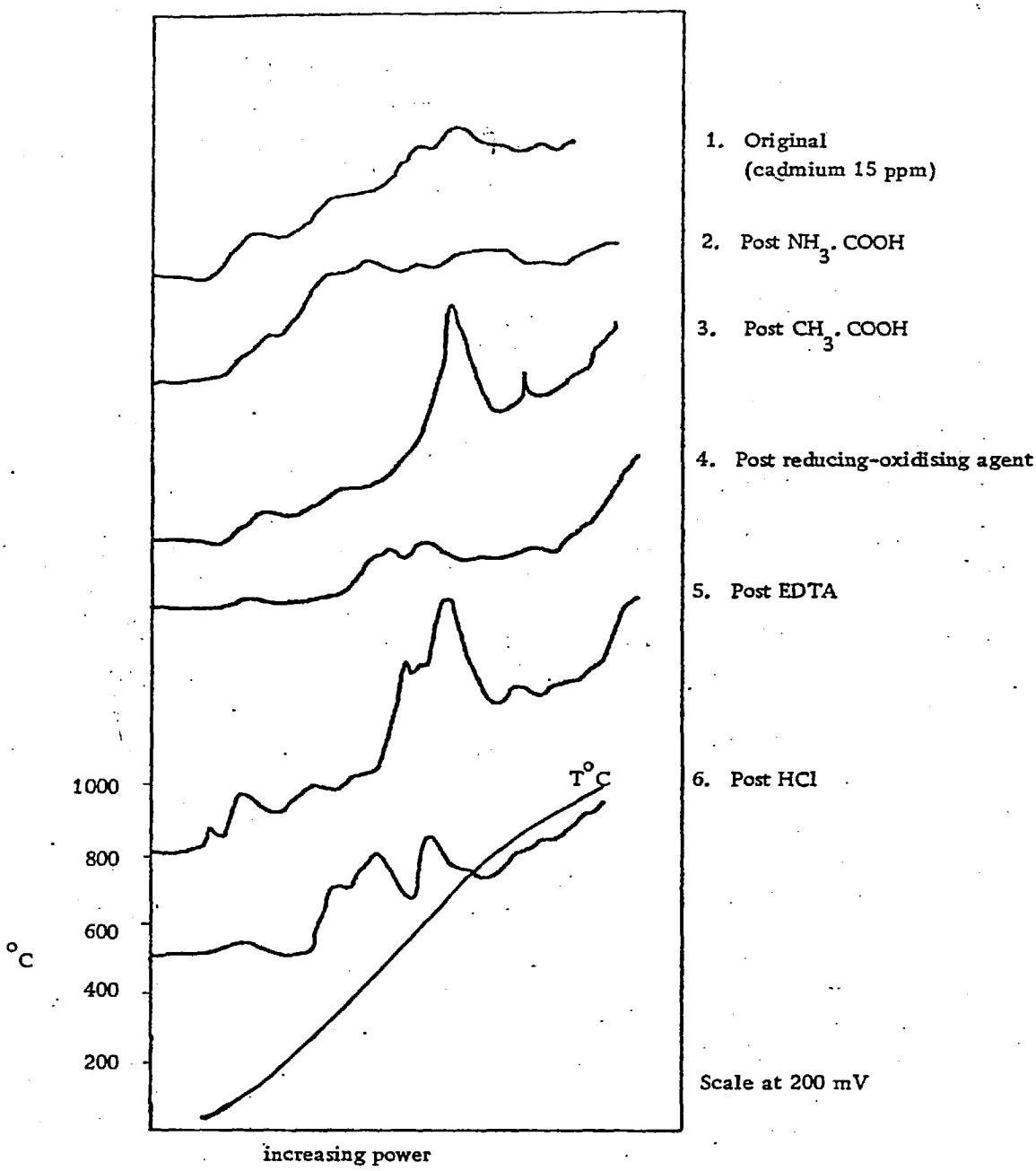


FIGURE 12.2 POST CHEMICAL EXTRACTION TEVPs STREAM SEDIMENT, TAWE VALLEY, SOUTH WALES

12.7 CADMIUM PRESENCE IN SOILS

12.7.1 TRAVERSE 1

A 19-point, 100m interval soil traverse taken from the Cray reservoir across to the head of the ridge which formed the easterly side of the upper Tawe Valley was found to contain only one sample with a cadmium content greater than 2.0 ppm and no samples with zinc levels greater than 104 ppm. In 11 cases where cadmium was noted to be present in differing amounts in the 0 to 15 cm. and 15 to 30 cm. soils, cadmium was higher in the topsoil on 7 occasions and higher in the subsoil in the remaining 4. In a topsoil sample with 3.0 ppm cadmium, zinc content was 85 ppm and subsoil content fell to 1.0 and 20.0 ppm respectively. In a further 8 samples no change between cadmium contents in topsoil and subsoil were recorded. In contrast 11 out of 15 subsoils displayed an increase in zinc content in subsoils compared with topsoils. It would seem to appear therefore, that any form of surface contamination East of the Tawe river was almost non-existent although when it did appear to be present zinc in particular had been leached from the topsoil into the subsoil (see location map, Figure 12.1).

12.7.2 TAWE VALLEY, TRAVERSE 2

Twenty-four small soil traverses were taken in the Tawe Valley where erratic presences of metals in sediments have already been noted. These were rather different in character from the Cray reservoir samples with topsoil contents of cadmium, zinc and lead reaching 60.0, 800.0 and 300.0 ppm respectively, on occasions significantly greater in content than subsoil levels and resultantly indicating surface contamination. A detailed explanation of four of these traverses, the localities of which are shown in Figure 12.1, will serve to indicate the habit of these three heavy metals in soils.

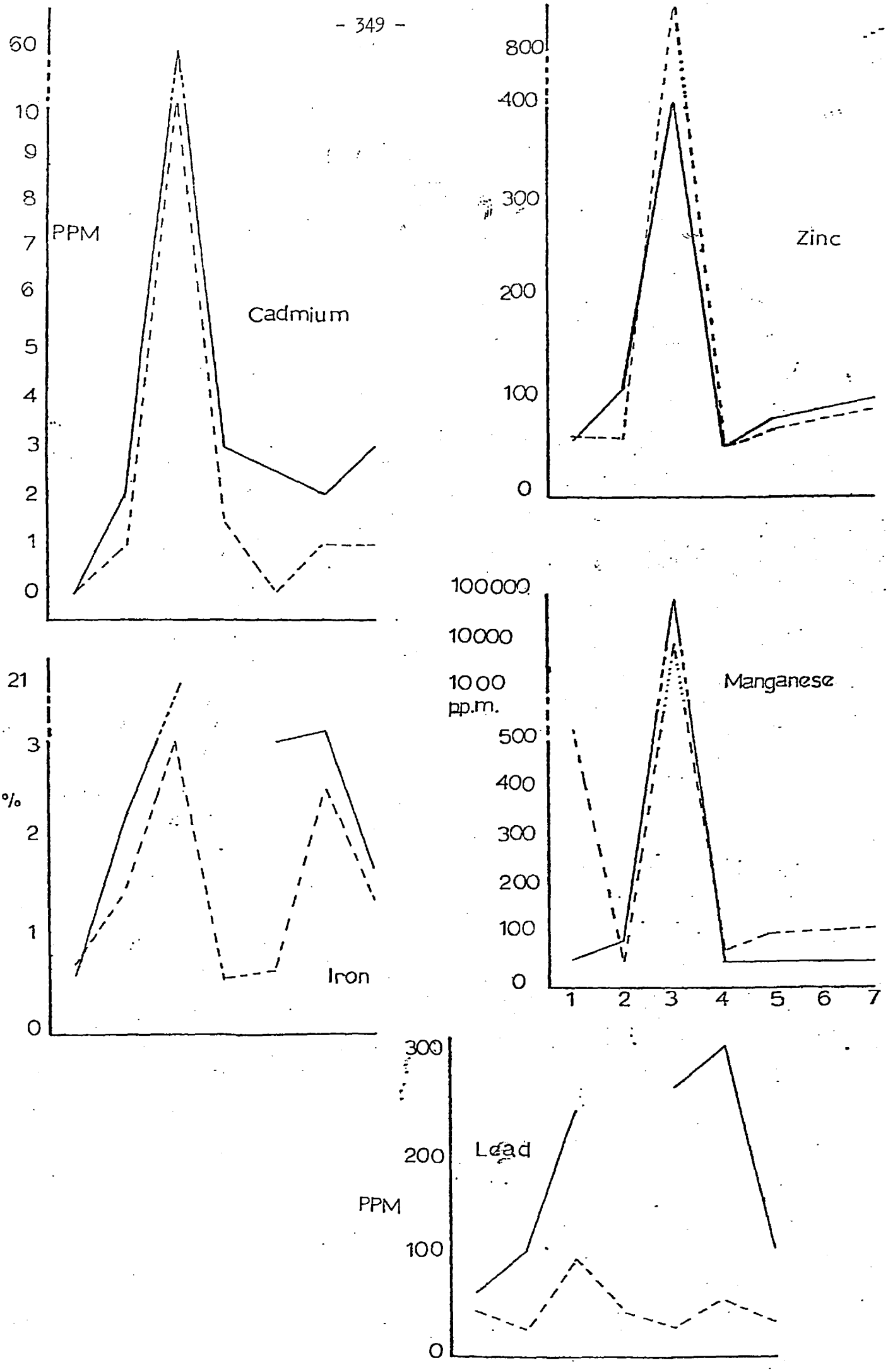


Fig. 12.3 Trace element content in topsoils and subsoil of Tawe traverse 2, South Wales.

In traverse 2, Figure 12.3 soils at 0 to 15 and 15 to 30 cms were sampled at seven sites, each at a distance of 10m apart across a high-altitude, southward facing marshy hollow from which rose a small tributary stream of the River Tawe. Samples at sites 1, 6 and 7 were collected from dry, well-drained soils either side of a central depression, the lowest point of which was marked by sample site 3. In the topsoil from the well-drained banks, cadmium and zinc were virtually undetectable although notably the lower horizon contained even less metal content. Manganese, however, had been leached into the subsoil where it concentrated at depth. Iron, on the other hand, displayed no such capacity to leach out of one horizon in preference to the other, although overall, levels were low, barely reaching 0.5%. Within the waterlogged depression metal contents rose considerably. Cadmium increased from not being detected to a level of almost 60.0 ppm in the topsoil and 10.0 ppm in the subsoil of sample site 3; lead increased from 50 ppm in the well-drained soils to almost 250 ppm, whilst zinc rose in the topsoil to about 400 ppm and in the subsoil to 860 ppm. In the same topsoil manganese rose to 8.0% and iron to 21.1%.

12.7.3 TRAVERSE 10

In traverse 10, Figure 12.4, the strike was taken deliberately across a southward exposed and marshy spring-source which was underlain by Carboniferous Limestone. The sample sites were located in four areas, each 20m apart. The 0 to 15cm topsoils were a series of dark-brown to black peaty clays and the 15 to 30 cm subsoils varied from cream-coloured sandy clays to brown sandy clays. Drainage on sites 1, 2 and 3 appeared to be permanently impeded whilst site 4 was dry and well-drained. Cadmium and lead were always present in greater concentrations in the topsoils of the three marshy sites. Manganese and iron levels also indicated a build-up in the topsoils of sites 1 to 3 and a marked decrease

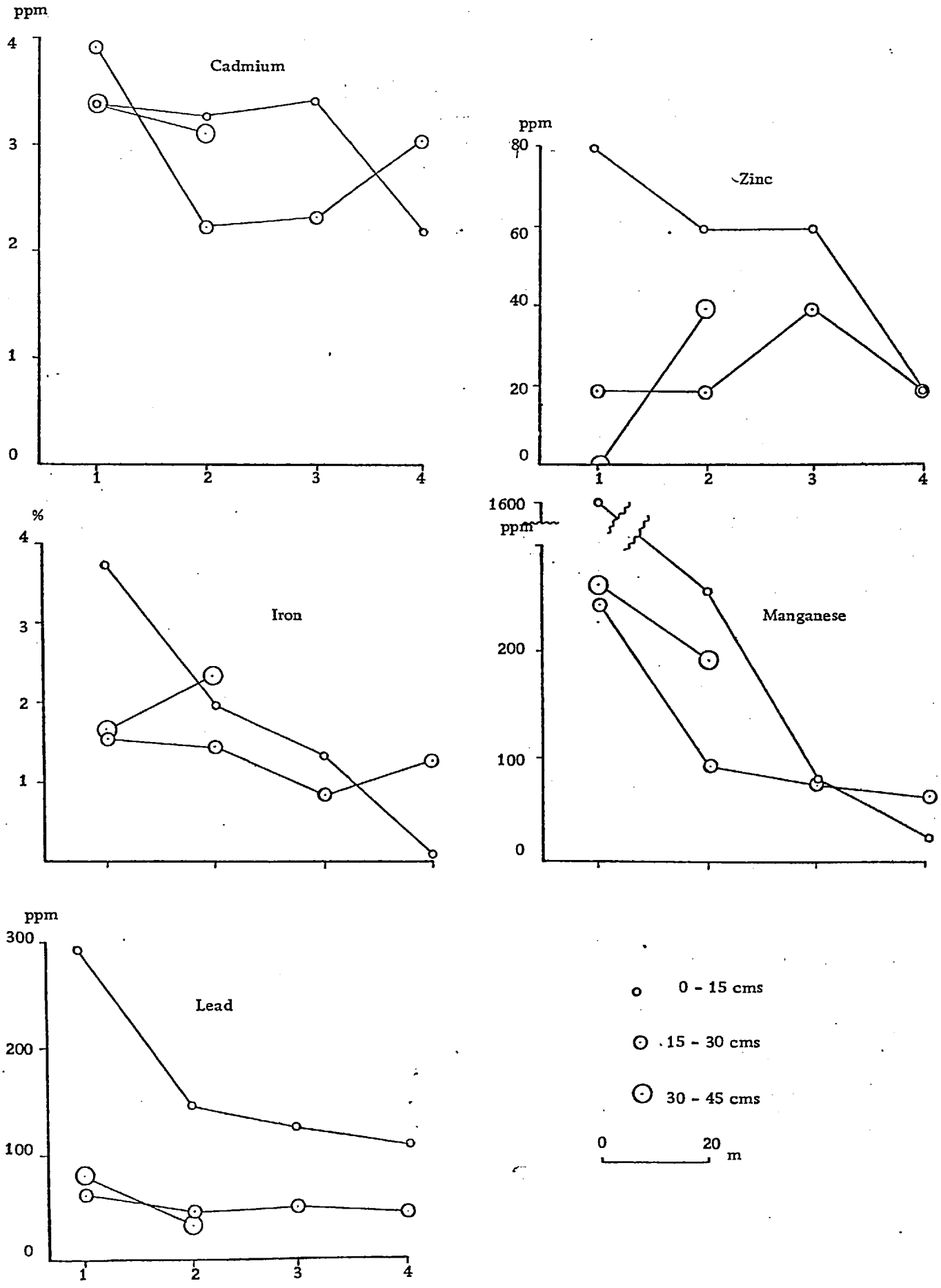


FIG. 12.4 PRESENCE OF TRACE ELEMENTS IN SOIL TRAVERSE 10, SOUTH WALES

in presence towards site 4 where both elements, in the process of leaching out of the topsoil, were more enriched in the subsoil. Zinc also displayed a decrease in topsoil metal content towards site 4 where the better-drained conditions had caused it to leach and enrich down profile.

12.7.4 TRAVERSE 18

Traverse 18, Figure 12.5 was taken at an altitude of 1500 ft. parallel to and near the top of the prominent high ridge West of the River Tawe. The topsoils appeared to be moderately well-drained and consisted of dark brown to brown loamy peats merging into pale brown to light brown loams at 30 cms. No cadmium was detected in any of the samples. Zinc, lead and manganese were present in greater amounts in the 0 to 15 cm horizon than in the 15 to 30 cm horizon and in addition, lead and manganese were strongly enhanced in two peaty surface soils collected to a depth of 2 to 3 cms (at sample sites 2 and 4). The analysis of the 2 to 3 cm surface soil from site number 4 was as follows (in ppm, 0 to 15 cm topsoil analysis in parenthesis); lead 355 (55), zinc 25 (42), manganese 24,000 (2500), and iron 12,000 (86,000). A combination of the detection of less zinc in the 0 to 3 cm surface soil than was found in the 30 cm subsoil and the absence of cadmium could indicate that either cadmium and zinc have been easily mobilised and dispersed out of the soils or that no cadmium and only small quantities of zinc were ever deposited.

12.7.5 TRAVERSE 20

Traverse 20 consisted of a series of 14 sampling sites taken over a distance of 250m across the suspected path of a large fault in order to detect a possible fault-line mineralisation source. The soil types varied from black to dark reddish-brown peats and sandy peats in the topsoil horizon and pale brown to dark-reddish-brown loams in the subsoil horizon. Iron and manganese were generally enhanced in the subsoils,

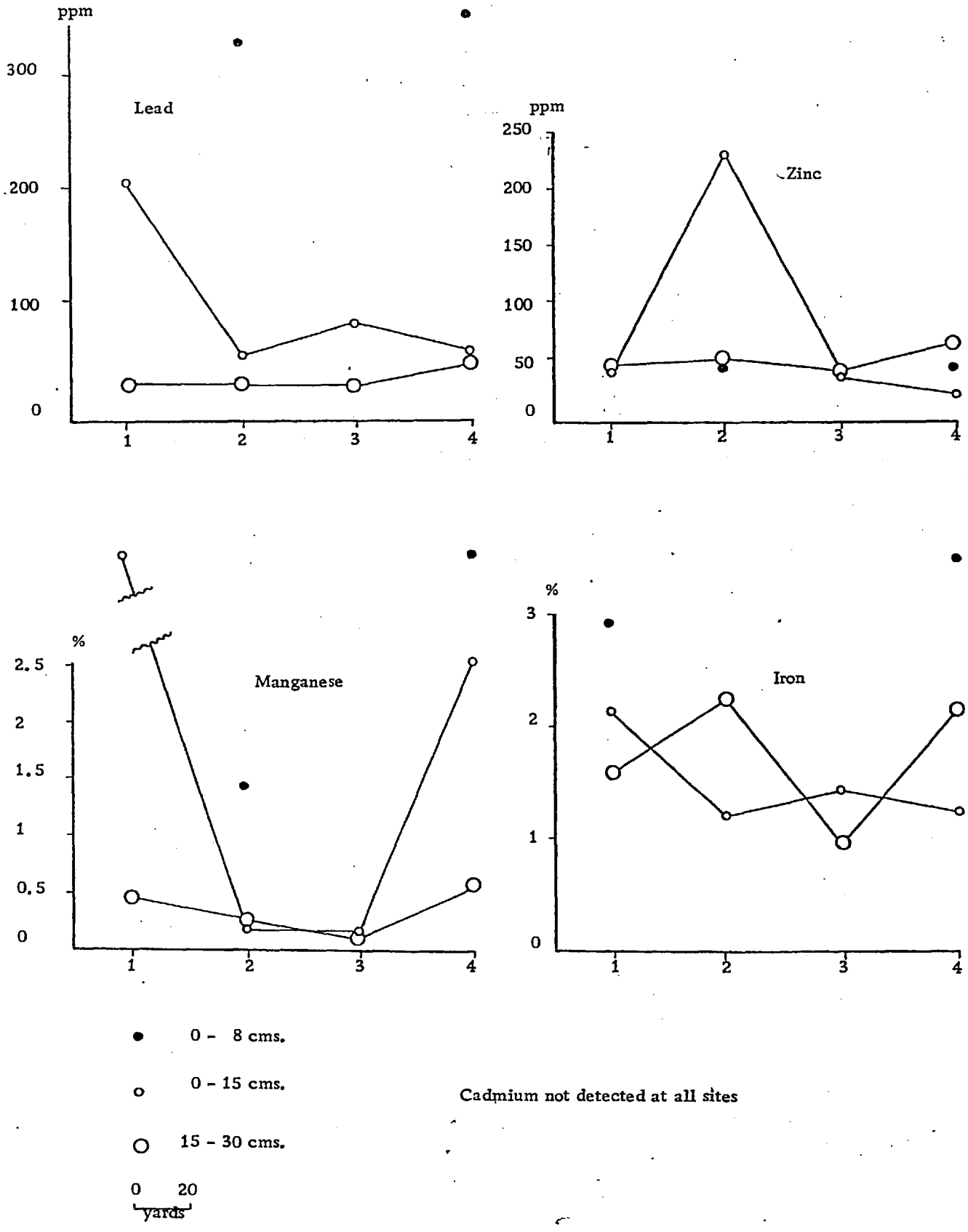


FIG. 12.5 TRACE ELEMENT PRESENCE IN SOILS OF TRAVERSE 18 , SOUTH WALES

especially at sample points 2 and 6 (see Figure 12.6), although their content was low. Conversely cadmium, zinc and lead were all enhanced in the topsoil reaching maxima in the same samples, notably 4, 7 to 8 and 11. Colour indicies of the soils, determined using a Munsell soil colour chart have been added to Figure 12.6. In sample 10, a topsoil which was dark brown in colour, cadmium presence was not detected whereas the metal content rose to 2.0 to 3.0 ppm in soils which varied in hue from very dark grey to black (samples 4, 7 and 13). The only sample which contained detectable cadmium in the subsoil (1.0 ppm) was described as very dark grayish brown in colour, whereas the remaining subsoils were reddish grey and brown in colour. The organic carbon content of the samples appeared therefore to be an important factor in the retention of heavy metals. The virtual non-existence of cadmium, zinc and lead in the subsoils was taken to be ample evidence to suggest that a metal source from mineralised faults is not a feasible explanation for the presence of anomalous metal content in topsoils. It is suggested therefore, that the source of cadmium to the surface soils in the Tawe Valley area of South Wales was aerially borne particulate matter channelled by the valleys in the upper air masses from the zinc refineries of Avonmouth and Swansea. These particulates deposited in the surface-oxide rich highlands of the Black Mountains.

12.8 CADMIUM RELATIONSHIP IN SOILS WITH THE ELEMENTS ZINC, LEAD, IRON AND MANGANESE

The background mean cadmium content in soils was calculated to be 1.1 ppm (number of samples, 71), which is a twofold enrichment of the average cadmium content in soil reported by Green (1959). In order to statistically relate the cadmium presence in soils with the four other analysed elements, the total set of soil samples with 207 specimens was subdivided into three on the basis of cadmium content. Those samples

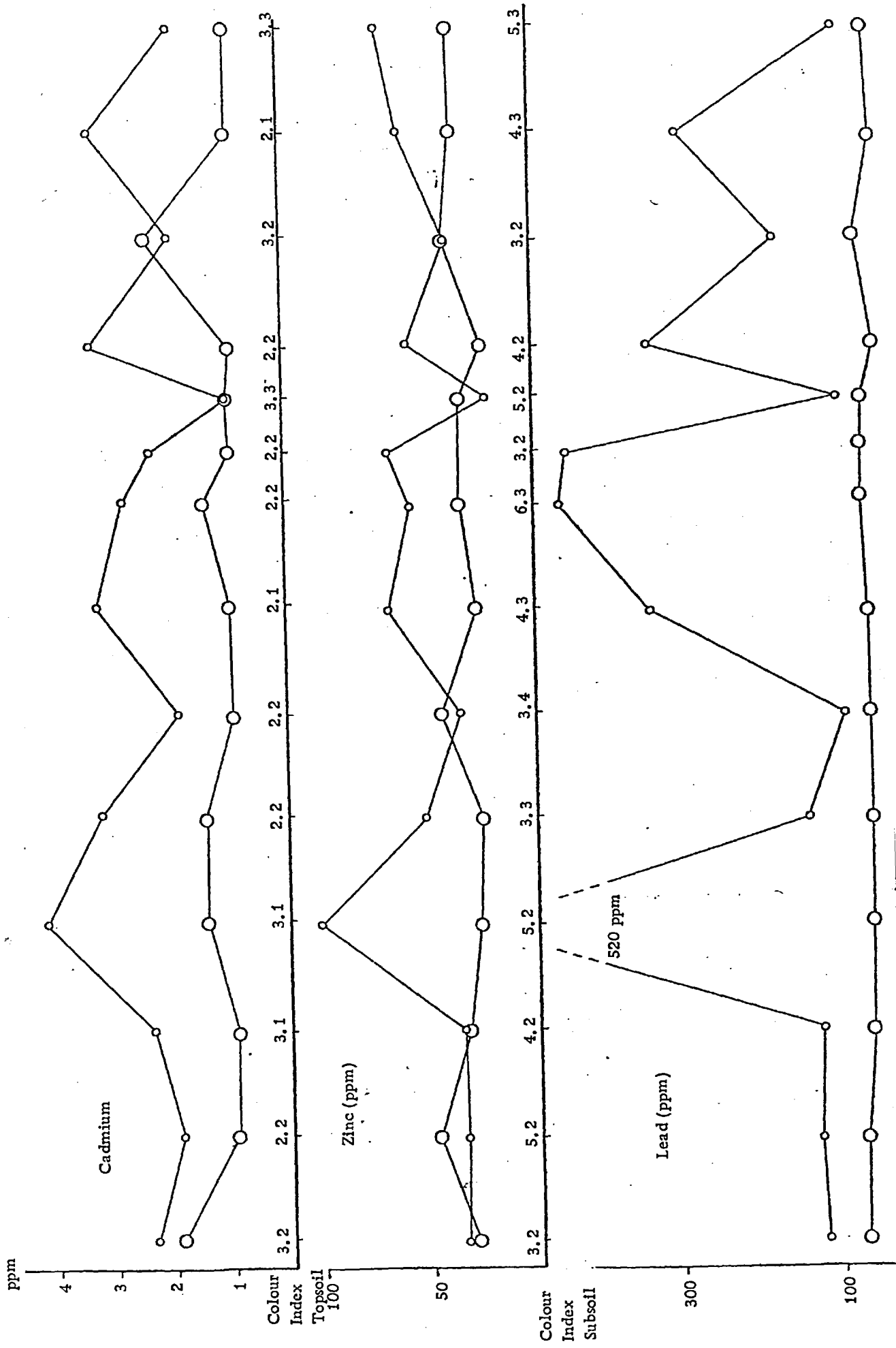


FIG. 12.6 TRACE ELEMENT PRESENCE AND MUNSELL COLOUR INDICIES FOR SOILS OF TRAVERSE 20, SOUTH WALES

Continued .....

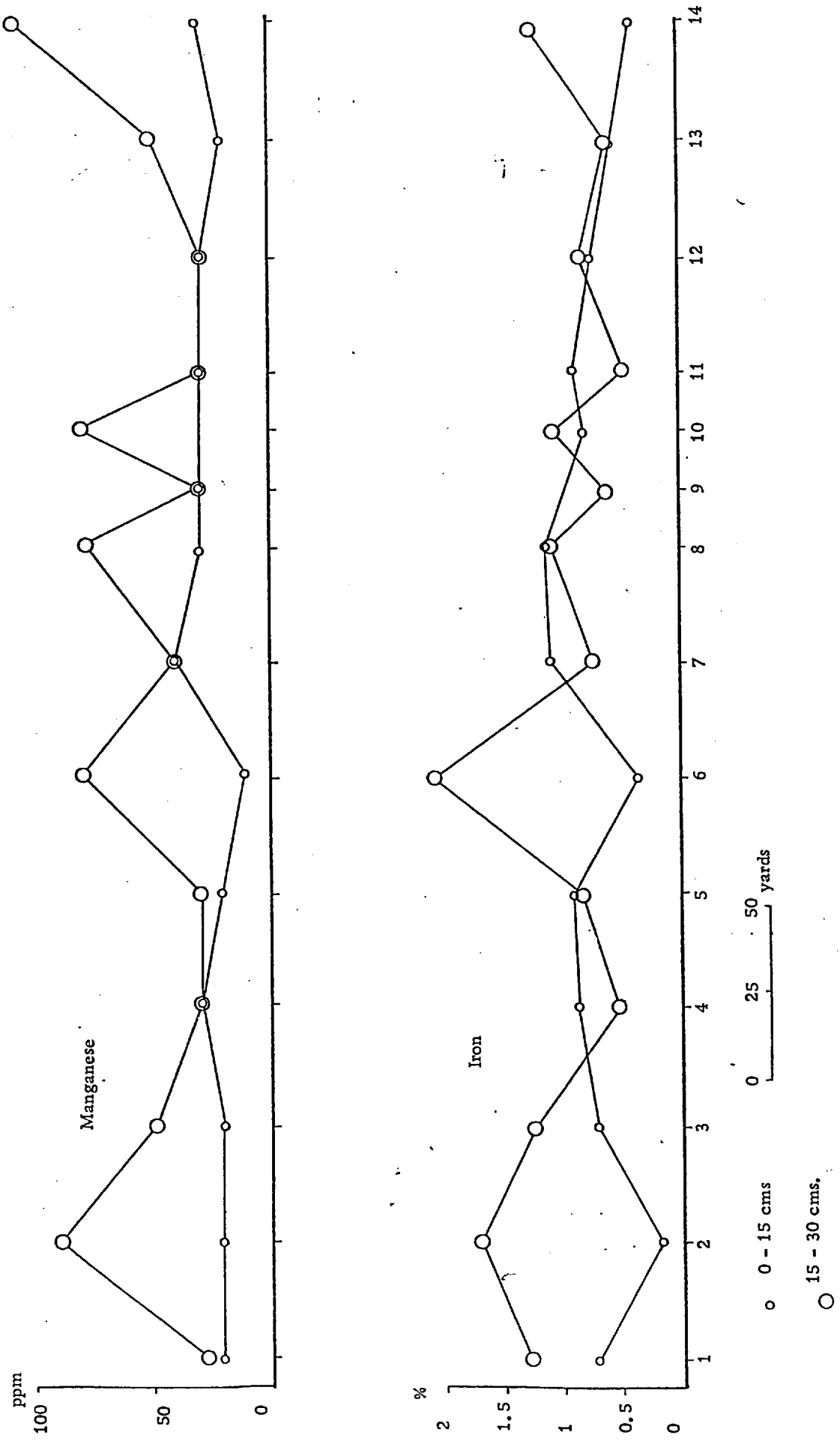


FIG. 12.6 Continuation TRACE ELEMENT PRESENCE IN SOILS OF TRAVERSE 20, SOUTH WALES

with less than 2.0 ppm cadmium were considered as background cadmium soils, those with between 2.0 and 5.0 ppm were considered to be anomalous cadmium soils, whilst those soils with greater than 5.0 ppm cadmium were regarded as strongly anomalous cadmium soils. The mean contents of zinc, lead, iron and manganese, in addition to cadmium in each of the sub-divided sets of samples can be seen in Table 12.4. The effect, for example, of cadmium enriching twofold in anomalous cadmium soils in comparison to background cadmium soils was reflected in a doubling of lead presence and a fourfold increase in zinc presence (compare Tables 12.4.2 and 12.4.3). These increases may be directly associated with an eightfold enhancement in manganese presence and a doubling of iron presence. Likewise, a threefold enrichment in mean cadmium presence, to almost 8.0 ppm in strongly anomalous soils (Table 12.4.3) compared with anomalous soils (Table 12.4.4) was reflected in a doubling of the presence of both zinc and lead to means of 367 ppm and 257 ppm respectively. Although total manganese levels in the strongly anomalous soils did rise, they did so by a matter of only 25% to a mean of 839 ppm. Mean iron levels in the strongly anomalous soils fell 12% to 2.35%.

In the correlation matrix of five variables for total soils (Table 12.4.1) cadmium correlated strongly (at $P = 0.001$) with zinc (correlation coefficient, $r = 0.56$) and lead ($r = 0.54$). The correlation coefficients of cadmium with manganese and iron were only weakly positive at levels of significance, $P = 0.01$ and $P = 0.05$ respectively. Following the subdivision of soils according to cadmium content, new correlation matricies were computed and are listed in Tables 12.4.2 to 12.4.4. In the set of samples representing background cadmium soils, where mean cadmium content was just over 1.0 ppm, it is perhaps not surprising that correlations with manganese and iron in particular were very poor. This set of samples included many analyses with

TABLE 12.4 CORRELATION MATRICLES OF FIVE VARIABLES FOR SOILS, SOUTH WALES

TABLE 12.4.1. TOTAL SOILS Number of Samples, N = 207

	Manganese	Iron	Lead	Cadmium	Zinc
Manganese	-	.50	.18	.30	.42
Iron		-	.39	.20	.51
Lead			-	.54	.51
Cadmium				-	.56
Zinc					-
Mean metal content	149	1.58	77.6	1.8	78.5

Levels of significance
P .001 = .25
.01 = .18
.05 = .14
(for N = 200)

TABLE 12.4.2. BACKGROUND CADMIUM SOILS N = 71

	Manganese	Iron	Lead	Cadmium	Zinc
Manganese	-	..69	-.01	-.28	..27
Iron		-	-.12	-.18	.44
Lead			-	.53	.21
Cadmium				-	.19
Zinc					-
Mean metal content	87	1.24	62.8	1.06	44.2

Levels of significance
P .001 = .38
.01 = .30
.05 = .23
(for N = 71)

TABLE 12.4.3 ANOMALOUS CADMIUM SOILS N = 141

	Manganese	Iron	Lead	Cadmium	Zinc
Manganese	-	.36	.05	.46	.33
Iron		-	.29	.47	.21
Lead			-	.36	.55
Cadmium				-	.32
Zinc					-
Mean metal content	688	2.72	137.1	2.68	173.3

Levels of significance
P .001 = .28
.01 = .21
.05 = .16
(for N = 150

TABLE 12.4.4 STRONGLY ANOMALOUS CADMIUM SOILS N = 19

	Manganese	Iron	Lead	Cadmium	Zinc
Manganese	-	.24	-.42	.39	.04
Iron		-	.30	.61	.26
Lead			-	.24	.05
Cadmium				-	.53
Zinc					-
Mean metal content	839	2.35	256.0	7.94	366.9

Levels of significance
P .001 = .67
.01 = .55
.05 = .43
(for N = 19)

All data by atomic absorption in parts per million (iron in percent)

barely detectible cadmium which could be regarded as analytically unreliable (see appendix, pages 403-413).

Correlations between cadmium, manganese and iron improved considerably in the anomalous cadmium soils (see Table 12.4.3) where the correlation coefficients at a level of significance, P = 0.05, were 0.46 and 0.47 respectively. In the strongly anomalous cadmium soils cadmium correlation with iron was 0.61 with P = 0.01 (Table 12.4.4). The corresponding r value for manganese did not attain a level of significance better than 0.05. It would appear therefore that in those soil situations where cadmium levels were raised the association of cadmium with hydrous iron oxides in particular (which were visibly present in marshy environments) was of some importance in the retention of cadmium. Added enrichment of cadmium in the strongly anomalous cadmium soils was accompanied by some iron loss and manganese gain within the soils, changes which caused a marked deterioration in correlation coefficients between the two elements and cadmium (see Table 12.5.4). Nevertheless the cadmium:iron correlation was still the most significant relationship in the matrix and it must be assumed that the poorness in correlation between variables in the last set of samples was in part a factor of the relatively small population within it, wide ranging manganese and iron presence and selective enrichment of one or more elements.

When cadmium was greatly enhanced in soils its correlation with zinc was most marked (r = 0.53, P = 0.05, Table 12.4.4). Conversely correlation between cadmium and zinc was poorest when contents of both elements were at their lowest levels. In the total soil set of samples zinc correlated better with manganese and iron than did cadmium (Table 12.4.1) and this is a direct result of moderately good zinc:manganese and zinc:iron associations in 'background cadmium' soils. Low level zinc precision on atomic absorption analysis was considerably improved over the poor precision of low level cadmium analyses.

TABLE 12.5.1 CORRELATION MATRIX OF FIVE VARIABLES FOR SUBSOILS FROM THE SOUTH WALES REGION

	Manganese	Iron	Lead	Cadmium	Zinc
Manganese	-	.35	.46	.39	.31
Iron		-	.33	.07	.07
Lead			-	.63	.56
Cadmium				-	.66
Zinc					-

Number of samples, N= 60

Levels of significance, P .001 = .4078
P .01 = .3248
P .05 = .2500

TABLE 12.5.2 CORRELATION MATRIX OF FIVE VARIABLES FOR TOPSOILS FROM THE SOUTH WALES REGION

	Manganese	Iron	Lead	Cadmium	Zinc
Manganese	-	.54	.15	.57	.45
Iron		-	.42	.55	.56
Lead			-	.45	.40
Cadmium				-	.65
Zinc					-

Number of samples = 62

Levels of significance, P .001 = .40
.01 = .32
.05 = .25

In the anomalous cadmium soils, zinc associated with iron and manganese oxides, but did not correlate as highly as these elements did with cadmium. The greater ease with which cadmium adsorbs onto colloidal matter than zinc, primarily as a result of its greater ionic size was undoubtedly a controlling factor in the better cadmium:manganese and iron associations.

12.9 RELATIONSHIP OF CADMIUM WITH ZINC, LEAD, IRON AND MANGANESE IN TOPSOILS COMPARED WITH SUBSOILS

The two lists shown in Table 12.5 represent the correlation matrices of elemental presence in topsoils 0 to 15 cms and subsoils 15 to 30 cms.

As in Table 12.4.1 of the previous section the strongest positive correlation coefficient in both topsoils and subsoils was between cadmium and zinc where the coefficients were almost identical ($r = 0.65$, $P = 0.001$; $r = 0.66$, $P = 0.001$ respectively). In contrast all other correlation coefficients were markedly different in the two horizons. All correlations with iron were distinctly better in the topsoils compared with the subsoils and likewise, all correlations with manganese (with the exception of lead) were better in the topsoils. All correlations with lead (with the exception of manganese) improved in the subsoil horizon (see Tables 12.5.1 and 12.5.2).

In the topsoil matrix cadmium correlated strongly with manganese and iron at $r = 0.57$ and $r = 0.55$ ($P = 0.001$) respectively. Correlation with lead was moderately strong, $r = 0.45$, $P = 0.001$. Cadmium correlations deteriorated in the subsoil with manganese and iron coefficients falling to $r = 0.39$ ($P = 0.01$) and $r = 0.07$ ($P = 0.05$) respectively. The cadmium relationship with lead at depth improved to $r = 0.63$ ($P = 0.001$).

The presence of iron and manganese oxides in the surface soils was seen therefore, as essential to the entrappment of cadmium (and zinc). Lead was mobilised down-profile alongside manganese and achieved a certain degree of stability in the subsoil horizon. Sufficient cadmium was also taken down profile possibly also with the manganese oxides to result in a strong positive lead:cadmium correlation.

12.10 SUMMARY CONCLUSIONS ON THE IDENTIFICATION OF CADMIUM FORM IN CONTAMINATED SOILS BY A METHOD OF THERMALLY EVOLVED VAPOUR PROFILES (TEVP)

Section 11.6 page 312, which dealt with the identification of cadmium species from aerially polluted soils provides the interpretive background from which the following conclusions are drawn.

Soils were divided into three groups according to the nature of their environment of formation; waterlogged soils, moderately-drained soils and well-drained soils.

In the three waterlogged soils no change was noted in cadmium species at depth, although the decrease in total cadmium content with depth resulted in a marked reduction in subsoil TEVP peak area (see figure 11.13, page 329).

The dominant topsoil peak was formed by cadmium expulsion resulting from the high temperature breakdown of clay mineral lattices, although in addition, the two peaks formed by release of cadmium from organic complexes and release of cadmium from iron and manganese oxides were unusually well-developed. At depth the high temperature clay-cadmium species eventually disappeared (presumably through leaching out) and cadmium peaks dissociated from re-ordered iron-manganese

oxides and organocadmium complexes dominated the graph. The appearance of a tiny peak at 930°C was the result of cadmium release from dissociating sulphides which formed at depths. Little cadmium was present overall in an adsorbed form, although such associations may have attained some greater prominence in the upper subsoil at 15 to 30 cms (see graph 2, Figure 11.3 page 294).

In moderately drained soils, represented in Figure 11.14, graphs 1 to 3, the principal topsoil peak at 325°C was caused by release of cadmium associated with iron oxide colloids. Peaks which represented release of cadmium from organic matter and within the lattices of clays were still present but were not as important as in waterlogged soils. At depth, leaching firstly caused the removal of colloidal clays and, eventually, iron oxides with the result that in the lower subsoil, only the organometallic compound was retained. In the vapour profile study on cadmium in well-drained soils, graphs 4 to 5, Figure 11.14, page cadmium associated equally with iron-manganese compounds and organic carbon. With humification at depth the cadmium-carbon peak remained in isolation as leaching primarily diminished the importance of the iron oxide-cadmium association.

12.11 IDENTIFICATION OF CADMIUM FORM IN CONTAMINATED SOILS BY THE USE OF AQUEOUS CHEMICAL EXTRACTIONS

The theories behind the use of aqueous chemical extractions and the expected action of each of the five extractants used and their interpretation is given in detail in chapter 8.

Cadmium presence in stream sediments was almost totally accounted for by association with manganese oxides and cation-exchange clay mineral sites. In soils, cadmium adopts similar positions but in addition

26 to 32% of total available metal was fixed more strongly (absorbed) within growing clay mineral lattices and formed hydrochloric acid soluble sulphides (see Table 12.6). Clay mineral associations accounted in total for up to 75% of total available cadmium partitioning in the topsoils and only up to 26% of total cadmium partitioning in the subsoils. The association of cadmium with iron-manganese oxides accounted for 21% of total cadmium in the topsoils and 66% of total cadmium in the subsoils. It must be assumed therefore that considerable quantities of cadmium in strong clay-mineral lattice associations which formed in the topsoils have been removed from the sub-soils by leaching. The formation of sulphides at depth can be gauged by studying the percentages of total iron soluble only in hydrochloric acid and residual after acid extraction. In addition to forming pyrite iron may also be substituting into the lattices of the growing sulphides of lead and zinc and in the matricies of clays.

Strong associations of cadmium with organic matter existed in the topsoils. Up to 41% of the total available cadmium in the topsoils which has been partitioned amongst the inorganic constituents of the rocks, may be removed by EDTA. The effectiveness of EDTA at depth was comparitively insignificant.

Finally, only 1.0% of total cadmium was in a simple, adsorbed from in the topsoils. Readily exchangeable iron and manganese oxides, which temporarily form in the topsoils accounted for 30% and 13% respectively of the total amount of these metals in the soils. 33% and 77% respectively of the total available iron and manganese however, form stable oxide forms in the topsoils and it was within these forms that cadmium was retained.

TABLE 12.6.1

Simplified Metal Associations	Cadmium	Zinc	Lead	Manganese	Iron
1. Adsorbed	1	2	N.d.	13	30
2. Inter-layer clay/carbonate	43	38	18	7	N.d.
3. Iron-manganese oxides	21	19	45	77	33
4. Clay lattice/sulphides	32	40	30	N.d.	28
5. Pyrite lattice/residual organics	3	1	7	4	9
6. Broad-based organics (EDTA extractable)	41	38	55	46	N.d.

Number of samples, N = 4

TABLE 12.6.2

Simplified Metal Associations	Cadmium	Zinc	Lead	Manganese	Iron
1. Adsorbed	N.d.	1	N.d.	4	N.d.
2. Inter-layer clay/carbonate	N.d.	11	34	11	1
3. Iron-manganese oxides	66	22	N.d.	30	1
4. Clay lattice/sulphides	26	47	27	21	53
5. Pyrite lattice/residual organics	8	19	39	34	45
6. Broad-based organics (EDTA extractable)	10	11	N.d.	23	N.d.

Number of samples, N = 1

In both tables, values are means of 'percent of total available metal extracted'.

For error estimation, see table 8.1.

For explanation of extractants used in determining associations 1 to 6, see Table 8.2.

N.d. = not detected

TABLE 12.6 THE BEHAVIOUR OF TRACE ELEMENTS IN TOPSOILS (TABLE 12.6.1) AND SUBSOILS (TABLE 12.6.2) FROM THE SOUTH WALES REGION BASED ON AQUEOUS CHEMICAL EXTRACTIONS

12.12 CONCLUSIONS REGARDING CADMIUM PRESENCE AND FORM IN THE STREAM SEDIMENTS AND SOILS OF SOUTH WALES

The study of stream sediments in South Wales indicated two centres of cadmium anomaly; one within a 7 km radius of Swansea and a second 35 kms from Swansea in the Southward facing uplands of the Black Mountains and Brecon Beacons. Comparison of sample plot scatters for pairs of variables indicated that the 'outside cluster' samples for five pairs, including cadmium:zinc and manganese:iron were geographically located in a small upland area at the source of the River Tawe where manganese oxide precipitation in stream beds abounded (compare Table 12.7 and Figure 12.1). Using aqueous chemical extractions it was concluded that cadmium was associated in stream sediments primarily with precipitated manganese oxides and secondarily in the cation exchange sites of clay minerals. Of the three cadmium associations identified in the thermally evolved vapour profile study, that removed by the reducing-oxidising mixture and which was considered to depict cadmium expulsion from iron and manganese oxides, dominated strongly. The remaining two peaks were formed by cadmium expulsion from dissociating carbon compounds and from the thermal destruction of pyritous minerals. The substitution of cadmium into clay minerals and into sulphides would have taken place during the course of soil profile development before processes of predominantly mechanical dispersion carried the host minerals into the drainage system.

In soils, cadmium was shown to be enhanced generally wherever poorly-drained soils permitted the precipitation of iron oxides. In exceptional circumstances organic-rich topsoils in southward-exposed, high-ground localities were the hosts for erratic surface contamination and enhancement. Traverses taken over known fault lines indicated that fault-plane mineralisation was absent from the area, whilst rock sampling failed to provide an adequate source of metal for the soils. Surface contamination was thought to have been caused by the upper air movement of heavy-metal rich particulate matter from the zinc smelters of Avonmouth and Swansea.

TABLE 12.7 CORRELATION MATRIX FOR FIVE VARIABLES IN SOILS FROM THE NORTH WALES REGION

	Manganese	Iron	Lead	Cadmium	Zinc
Manganese	-	.30	.37	.44	.25
Iron		-	.30	.20	.47
Lead			-	.37	.25
Cadmium				-	.26
Zinc					-
Mean metal content	596	3.49%	96.8	1.08	94.3

Number of samples, N = 71

Levels of significance, P .001 = .38
.01 = .30
.05 = .23
(for N = 71)

An increase in cadmium presence in strongly anomalous soils was reflected in an improvement in the correlation coefficient between cadmium and iron, and cadmium and zinc. Separate correlation studies on cadmium in topsoils and subsoils and its relationship to zinc, lead iron and manganese, indicated that the presence of iron and manganese oxides in the surface soils was essential to the retention of cadmium. However, it was concluded from the study with chemical aqueous extractions that up to 75% of the total available cadmium in topsoils was related to the presence of clay minerals both as substituents in the growing clay lattices and as exchanged cations. Only about one fifth of total remaining cadmium associated with the iron-manganese oxides. The dominance of iron-manganese oxide cadmium associations in subsoils was taken to indicate that most of the cadmium in the clay mineral forms had been dispersed out of the subsoils by leaching. Strong associations of cadmium with organic matter were indicated in the topsoils whilst associations of cadmium with the forming sulphides in subsoils was thought likely. Surface adsorption was of practically no significance in the retention of cadmium.

The identification of cadmium forms by the use of the TEVP method confirmed that the dominant topsoil cadmium form in waterlogged soils was as a substituent in the growing clay mineral lattices. However, release of cadmium from iron-manganese oxides and from cadmium-carbon complexes were also of importance. In moderate to well-drained soils the principal cadmium peak was associated with cadmium release from iron-manganese oxides. At depth in all soils the high temperature clay-cadmium form was no longer present, having been removed by leaching and in the lower subsoils the cadmium-carbon form dominated.

12.13 LOCATION, GEOLOGY AND SOILS OF THE DENBIGHSHIRE AREA, NORTH WALES

The Denbighshire study area is located near the town of Nantglyn in the Denbighshire Moors at an average altitude of 1200 ft. above sea level, 21 km East of Llamrwst and 16 kms west of Clwydian Range in Flintshire. The underlying bedrock belongs to the Wenlock Series of the Silurian and consists geologically of a series of grits, sandstones, flaggy siltstones and mudstones. The soils of the disected Nantglyn area are a series of silty-loams, and loams classed as low base status brown-earths derived from Silurian shale drift. Most of the streams sampled originate on the heather moors to the South, which consist of podzolised soils with poor or impeded drainage initiated by the formation of subsoil iron pans. The peaty gleyed podzols which result show occasional weathering and movement of ferric oxide at or near the surface and in addition the development of characteristic grey and pale-coloured subsoils. Low biological activity at the surface of podzolised soils leads to the accumulation of organic matter and the eventual development of humus. The rainfall in the Denbighshire area ranges from 32.2 inches per annum at Denbigh, to over 55 inches per annum in the area of the moors.

12.14 CADMIUM IN THE STREAM SEDIMENTS OF DENBIGHSHIRE

The mean cadmium content of four stream sediments sampled around the mineralised area near Llanrwst in the Conway Valley was 70.0 ppm with a range of 12.0 to 140.0 ppm. To the East of the mining region on the high moor area to the Southwest of Nantglyn, 23 out of 59 stream sediments were found to be anomalous by containing greater than 4.0 ppm cadmium (see map Figure 3.5, page 46 and location map Figure 12.7). The mean cadmium content of the area was found to be 4.9 ppm with a range of 1.0 to 33.0 ppm.

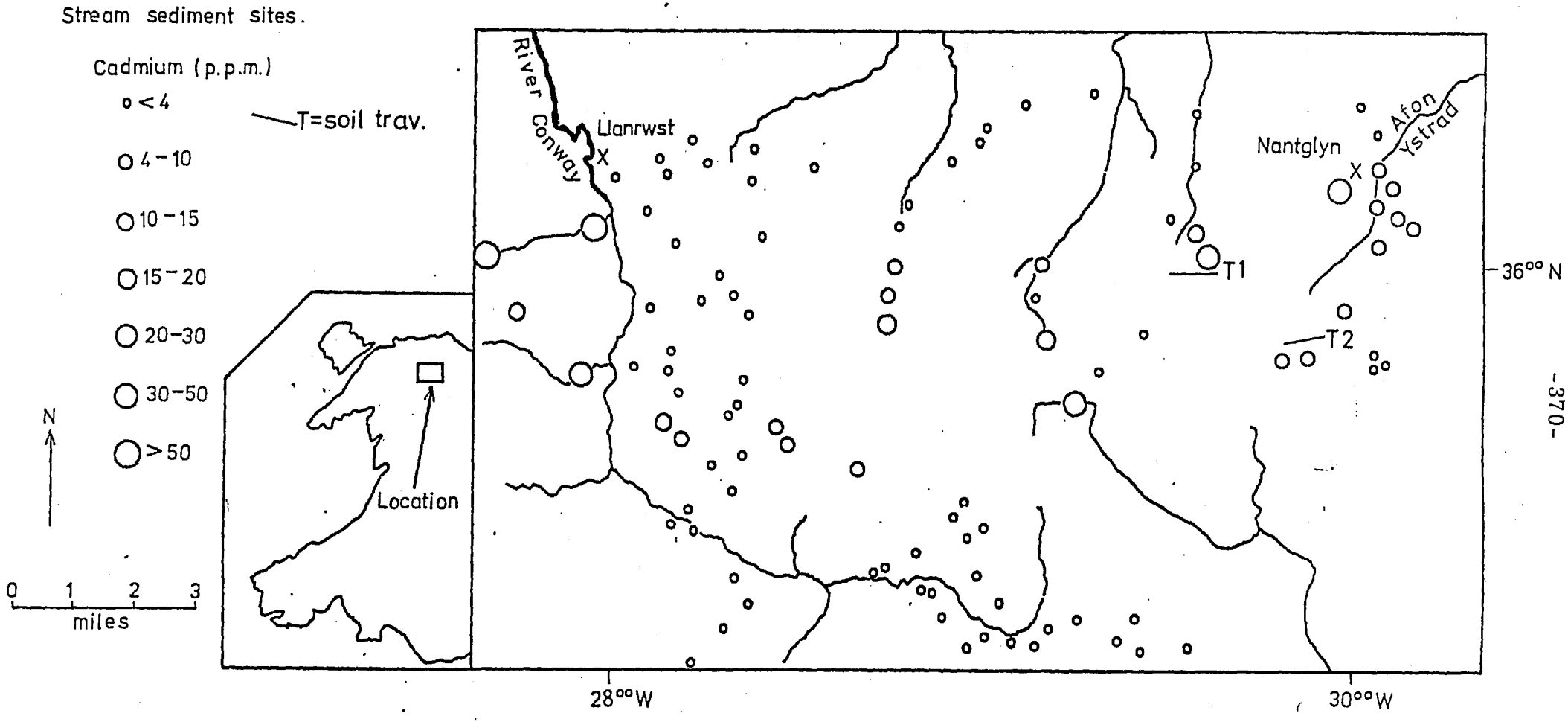


Figure 12.7 Geographical location of North Wales area with location of stream sediment sites.

12.15 METAL PRESENCE IN THE SOILS OF DENBIGHSHIRE

12.15.1 TRAVERSE ONE

Eight sites were samples in the 400 m long traverse from map reference (M.R.)W2980, N3571 to 2984, 3571. The well-drained humic surface soils graded into pale brown and greyish-brown topsoils at a depth of 2 cms. and these became increasingly more sandy and wet to a depth of 30 to 45 cms. Cadmium was not detected in any of the samples. Zinc, iron and manganese were present in higher quantities in the subsoil than the topsoil (see Figure 12.8) whilst lead was present in consistently greater amounts in the topsoils. With the exception of cadmium, the soils contained slightly greater amounts of zinc, lead, manganese and iron than the average soil of the South Wales area.

12.15.2 TRAVERSE TWO

Traverse two was made for 150 m across a prominent swampy area from M.R. W2998, N3589 to 3002, 3589. The surface clays, heavily waterlogged in places released clouds of iron-rich material when disturbed. Resultant iron content of the topsoils was later found to be as high as 12.0%. The soils at either end of the traverse (sites 1 and 8, Figure 12.9) were collected from dry, well-drained banks and accordingly iron, manganese and zinc were present in greater concentration at depth than at the surface. Cadmium was not detected in the soils of the dry banks. Iron content in the soils of the waterlogged area peaked either side of a central and moderately well-drained island (sites 5 and 7 Figure 12.9). Zinc and cadmium displayed no tendency for enrichment in either topsoils or subsoils and concentrations of both increased in sample site 6, along with lead, when both iron and manganese contents of the soils were low.

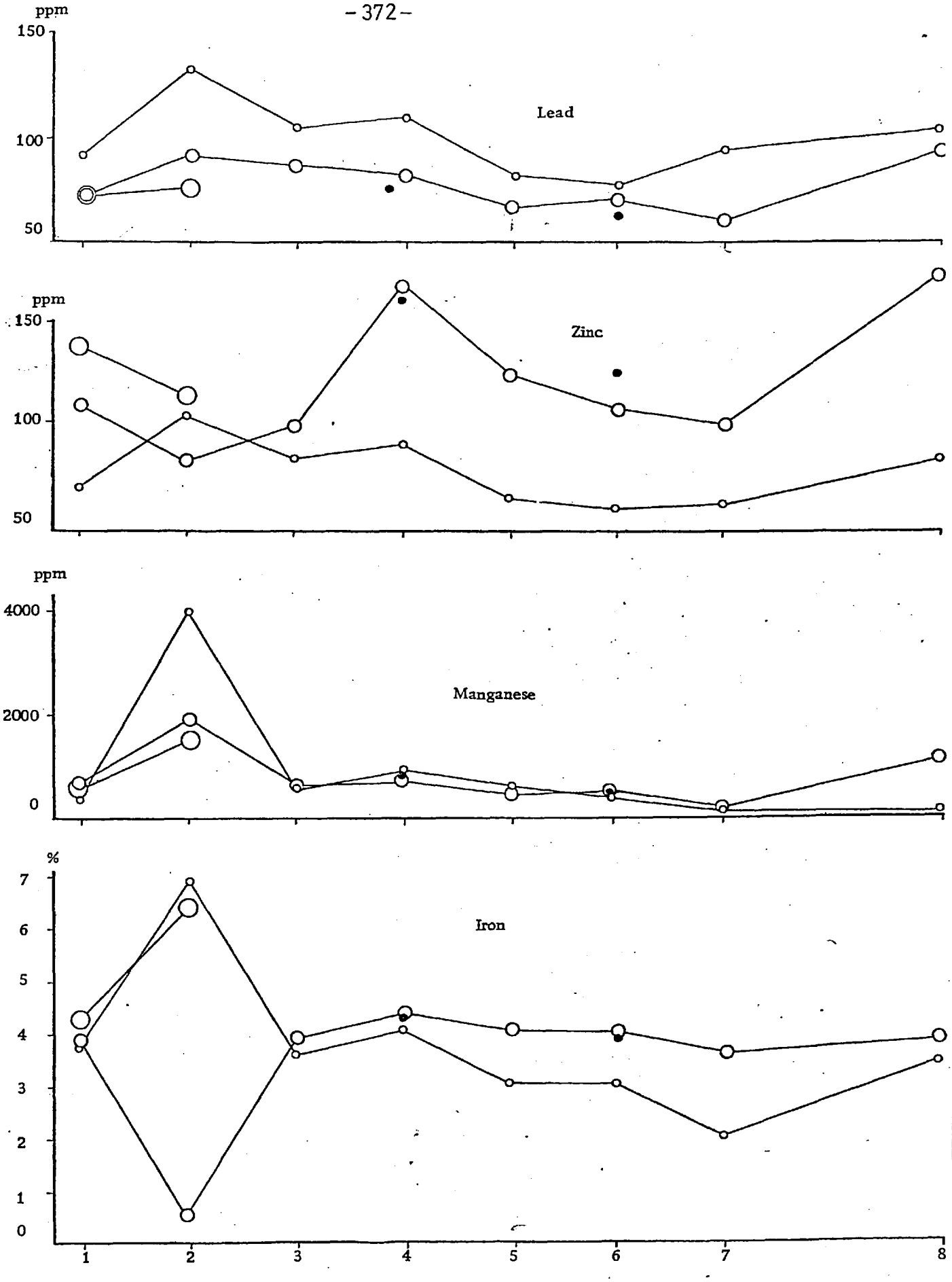


FIG. 12.9 TRACE ELEMENT PRESENCE IN SOILS OF TRAVERSE 1, NORTH WALES

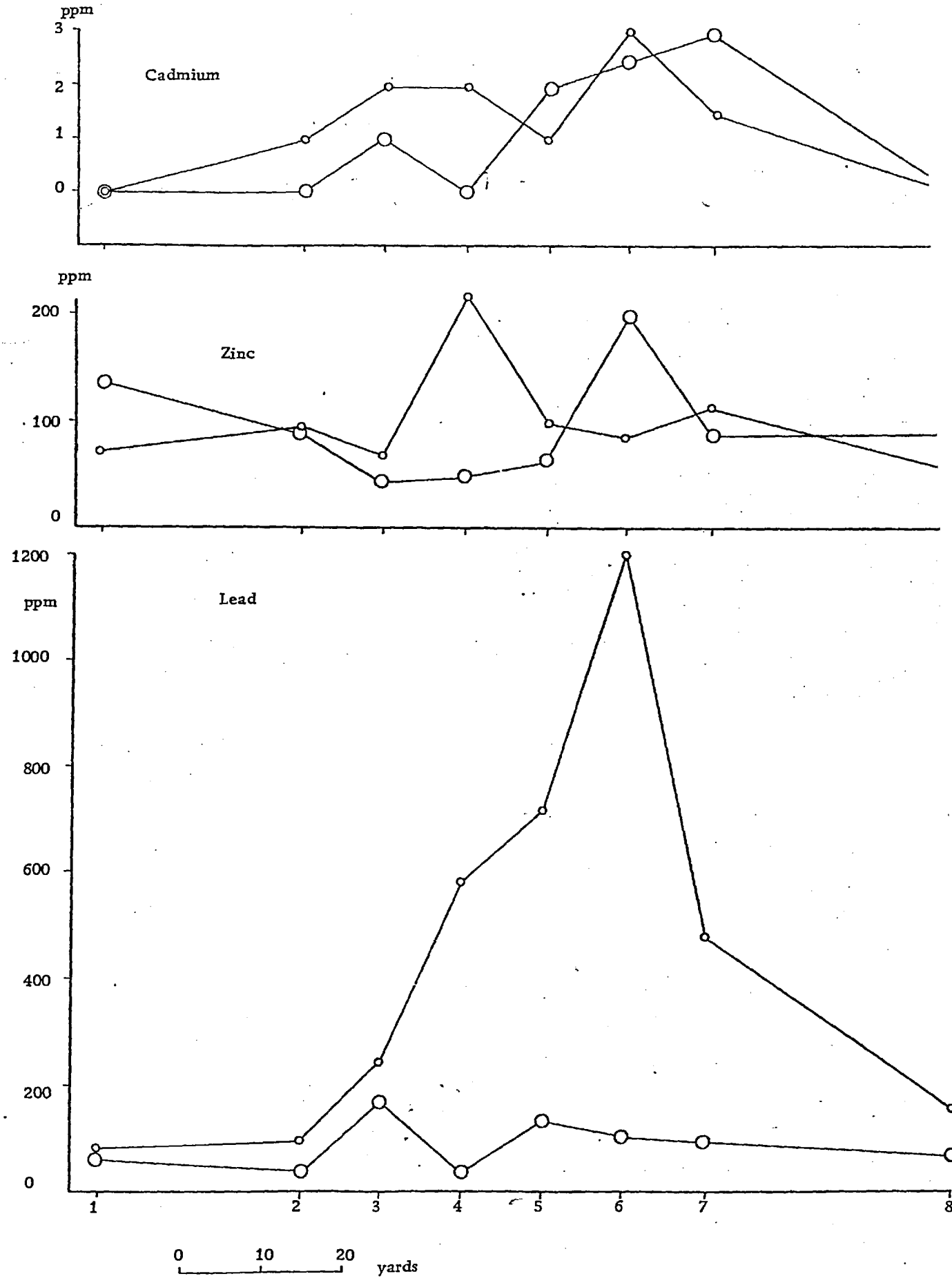
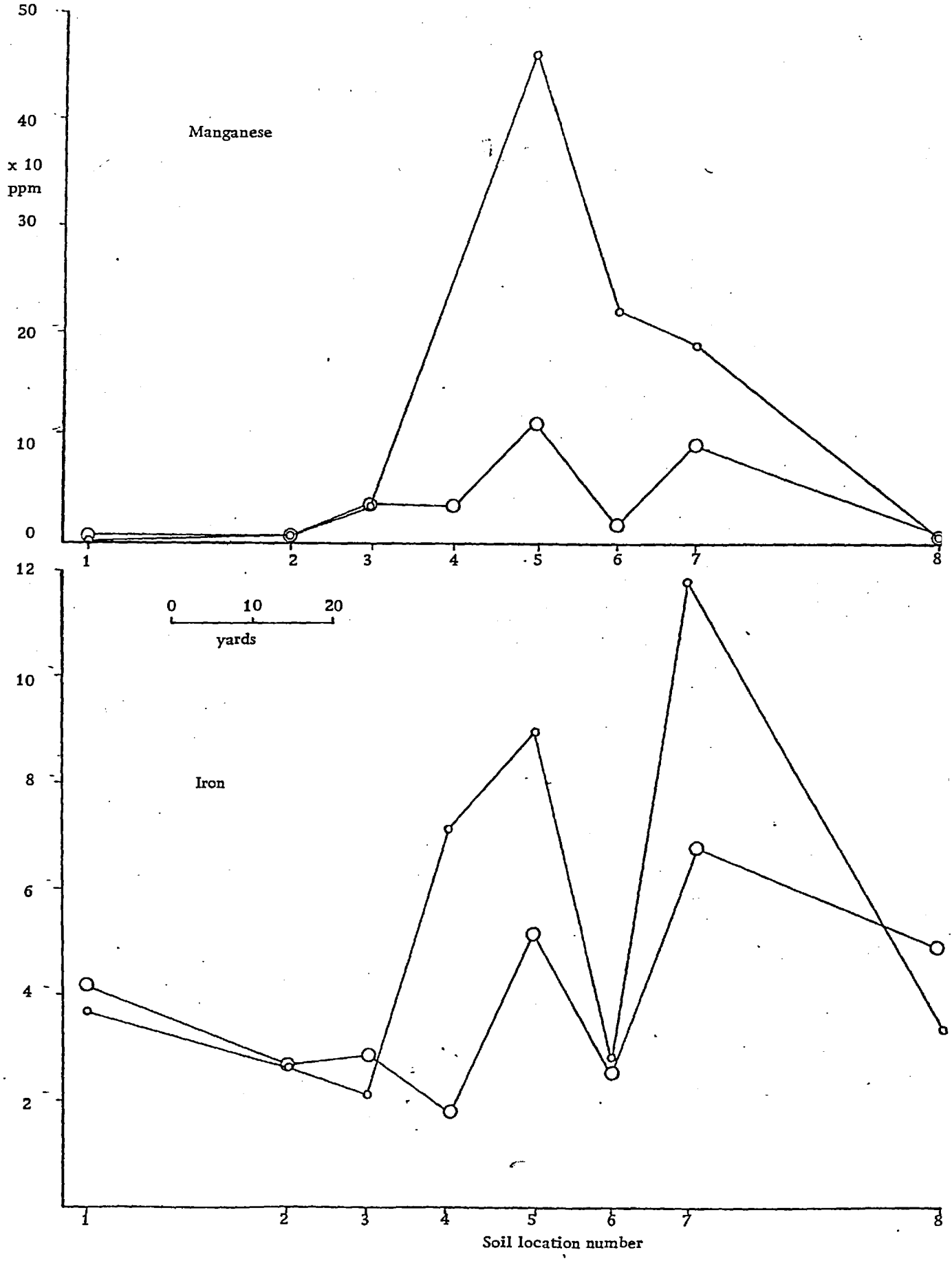


FIG. 12 9 continuation TRACE ELEMENT PRESENCE IN SOILS OF TRAVERSE 2, NORTH WALES



o 0 - 15 cms.

O 15 - 30 cms.

FIG. 12.9 TRACE ELEMENT PRESENCE IN SOILS OF TRAVERSE 2, NORTH WALES

Continued .....

In conclusion, of the heavy metals analysed in soils only lead was concentrated in the topsoil. On the rare occasions when cadmium was present in soils it did not appear to be specially concentrated either in topsoils or subsoils. Zinc on the other hand, was found in greater concentrations in the subsoils of the traverses which suggested that the metal source was either from the underlying geology or in weakly mineralised faults or joints within the rock. Cadmium was not detected in 5 samples of local shale although the samples were found to contain an average 104 ppm zinc and 36 ppm lead.

12.16 CADMIUM RELATIONSHIP IN SOILS WITH THE ELEMENTS ZINC, LEAD, IRON AND MANGANESE

The mean cadmium content of 71 North Wales soils was just over 1.0 ppm which was similar in amount to that cadmium content calculated for background cadmium soils in South Wales. Cadmium correlated moderately strongly with manganese ($r = 0.44$, $P = 0.001$, see table 12.7), weakly with lead and poorly with iron and zinc. Zinc, on the other hand, correlated well with iron ($r = 0.47$, $P = 0.001$).

12.17 SUMMARY OF CADMIUM PRESENCE IN THE SOILS AND SEDIMENTS OF DENBIGHSHIRE

In comparison to the mean metal contents of the South Wales soils the presence, in the soils of Denbighshire of, on average, a higher cadmium\zinc ratio suggests that the soils of North Wales are relatively cadmium deficient. Likewise, the analysis of a small population of rock samples in the area indicated that the bedrock was deficient in cadmium. Nevertheless cadmium-anomalous stream sediments were

present in the drainage channels surrounding the heather moor upland near Nantglyn although analysis of cadmium in soils was inconclusive. However, from the evidence of zinc presence in soils it appears that the source of the zinc was from the bedrock and it does seem unlikely that any further source of metal solely rich in cadmium could have been available for dispersion into the drainage channels. It is suggested therefore that the effect of humic acid rich groundwaters from the moors' peat on undiscovered cadmium-bearing shales, or even weakly mineralised faults could readily mobilise and disperse cadmium into the surface drainage system where cadmium (if the good correlation between manganese and cadmium in soils can be extrapolated to sediments) could be retained by freshly precipitated oxides.

CHAPTER 13

13 SUMMARY AND CONCLUSIONS

13.1 INTRODUCTION

This thesis has been concerned with the identification and study of localities in England and Wales in which anomalous amounts of cadmium have been detected in stream sediments over a wide and persistent area. The primary sources of cadmium in the environment indicated by this study are: industrial emissions, metallic sulphides and metal-enriched black shales.

The anomalous stream sediment patterns for cadmium (i.e. greater than 4 ppm) identified on the preliminary 1 to 1 million scale Wolfson Atlas map of England and Wales can be broadly divided into three classes: those relating to areas of mining activity or mineralization (e.g. the Buxton-Ashbourne region of Derbyshire) those correlated with the presence of cadmium-using industries (e.g. the Swansea and Neath Valleys of South Wales) and those which may indicate cadmium-enriched underlying geology (e.g. the Bowland Forest region of Lancashire).

The following recommendations made in the SRC report on Cadmium in the Environment were considered:-

1. Contributions to the environment from the air.
2. The presence, availability and mobility of cadmium in different environments.
3. The chemical forms of the element in natural materials.
4. The inter-relationships of cadmium with other elements.

13.2 CONTRIBUTIONS TO THE ENVIRONMENT FROM THE AIR

The mean cadmium content in rock samples representing the geology of the South Wales study area was 0.3 ppm and in no samples did the cadmium content exceed 1.5 ppm: thus eliminating the sedimentary

bedrock as a possible source of anomalous soil and stream sediment cadmium.

Of the 77 samples of stream sediment collected from the source of the River Tawe area, half contained anomalous cadmium contents (greater than 4 ppm) and one contained 44 ppm. In the correlation matrix for all sediments cadmium correlated well with zinc ($r = 0.81$, $P = 0.001$) and moderately well with manganese ($r = 0.37$, $P = 0.001$) and lead ($r = 0.36$, $P = 0.001$). In the matrix for samples with at least 5 ppm cadmium, the metal correlated well with zinc ($r = 0.66$, $P = 0.001$) and significantly with manganese ($r = 0.45$, $P = 0.001$).

The dominant behaviour of cadmium in stream sediments was firstly, to be retained by precipated manganese oxides (45% of total cadmium) and secondly, to substitute into the exchange sites of clay minerals (39% of total cadmium).

Thermally-evolved vapour profiles of a stream sediment indicated that no clear metal-associated component existed. The action of the manganese-specific reagent however, effectively removed all but a minor content of cadmium from the samples. Of the remaining minor cadmium associations, one was with carbon compounds whilst a second was within the structure of pyritous minerals.

The mean background cadmium content in 71 soils from South Wales was 1.1 ppm. In the correlation matrix for anomalous cadmium soils the coefficients between cadmium and manganese and iron were 0.46 and 0.47 respectively ($P = 0.05$). In the matrix for strongly anomalous cadmium soils, the correlation with iron was more significant ($r = 0.61$, $P = 0.01$) and the highest in the matrix. Correlation between cadmium

and zinc was most marked when cadmium was greatly enhanced at levels exceeding 5 ppm ($r = 0.53$, $P = 0.05$). Cadmium appeared to have a greater affinity for adsorption onto colloidal matter than had zinc.

Cadmium was not detected in any well-drained topsoils taken in the Tawe Valley 1 km. south of the river source: no surface contamination of note was found east of the Tawe Valley. However, in soils collected from waterlogged and southward facing depressions at the river source, cadmium was detected in concentrations up to 60 ppm in topsoils and 10 ppm in subsoils. In better-drained conditions zinc, iron and manganese, in addition to cadmium, leached downprofile. Lead values in the humic top two centimeters of a contaminated soil exceeded the whole topsoil concentration of 55 ppm, sevenfold. The virtual non-existence of cadmium, zinc and lead in subsoils collected over the path of a known and prominent mineralised fault-plane was interpreted to mean that these were not potential sources of metal.

The anomalous concentrations of cadmium in stream sediments and topsoils of the Upper Swansea Valley was taken to be proof of the presence of cadmium in the higher air masses emanating from the Lower Swansea Valley smelter which had been chanelled up-valley by prevailing north-easterly and subsequently deposited in an area where heavy annual precipitation favoured surface oxide formation. Although a Welsh Office report (cited in the Guardian in October 1975) stated that, 'there is no apparent risk to human health from atmospheric pollution in the Swansea, Neath and Port Talbot industrial areas of South Wales', the continued presence of considerable quantities of the metal in soils monitored over the course of three seasons suggests that aerial pollution and hence some risk to human health does exist. The inference of epidemiological interest is that long-term, low-level exposure to cadmium from

environmental sources may result in its accumulation in soils to levels at which toxic effects might result. Fortunately the area of cadmium enhancement is very sparsely populated by man and animals, and in cases of excessive enhancement the greater proportion of the metal was in a relatively immobile and hence harmless form.

13.3 THE PRESENCE, AVAILABILITY AND MOBILITY OF CADMIUM IN DIFFERENT ENVIRONMENTS

Ten out of twenty-six sets of black shales rock samples of various ages were found to be minor element enriched on the basis of an Element Enrichment Index (page 93) greater than 115: those collected from the Carboniferous E2 age Dove Shales and the P1 age Bowland Shales were most enriched. 73% of the 15 samples of the latter group exceeded the minimum enrichment value for cadmium of 11 ppm. Of the wide geological range of samples considered, only those of Carboniferous age were found to be significantly enriched in cadmium. Thirty-four sets of black shale samples were analysed by atomic absorption for cadmium, and of these, five contained greater than the 11 ppm enrichment value. Three of these were from the Bowland Shales, one from the Edale Shales and one from the Onecote Shales: all were from the d4 Millstone Grit Formation. A sample of E1 age Bowland Shales contained 219 ppm cadmium. The mean concentrations of cadmium in 35 Permian Marl Slate specimens was 6.2 ppm (median 3.5 ppm) with a range from not detected to 73.5 ppm.

The preference of cadmium for predominantly shale sedimentation periods was seen to be a function of sediment particle size. In addition cadmium was enhanced in sediments following the occurence of marine bands in the sequence. Pyrite was found to contain up to 4 ppm cadmium.

Samples of calcareous concretions were found to contain no detectable cadmium, whilst their pyritic outer skins contained up to 22 ppm cadmium. The detritus in the hollow centre of one nodule contained 11 ppm cadmium.

As cadmium concentrated in shales it became relatively more enriched than zinc. It was suggested that in the moderately oxygenated and metal-rich zones of aeration, sufficient sulphur was not available in the form of sulphide to precipitate both zinc and cadmium, and furthermore that during mobilisation in the course of diagenetic compaction, cadmium would have been more susceptible to retention by colloidal materials than zinc, leading to its relative enrichment.

In soils collected over the Lower Worston Shales in the Bowland Forest area of Lancashire, cadmium, lead and zinc content increased with increasing depth: it was postulated that this was caused by the presence of undiscovered mineral veining. Further comparisons of topsoil and subsoil metal contents for this region indicated that the source of higher metal contents in the subsoils was the Bowland Shale bedrock. Paucity of cadmium content in soils in general suggested that extensive mobilisation and dispersion of the metal had taken place. Enhancement of cadmium in soils was found to occur over metal-rich bedrock when deep weathering and strongly impaired drainage conditions (preventing mobilisation) coincided. Such enrichment of cadmium was a comparitively uncommon event: even mildly acidic waters leaching through black shale soils would encourage mobilisation of the metal. The grand mean for cadmium in all the Bowland black shale rock samples was 12.3 ppm; but for all soils from the region was only 1.8 ppm. The grand mean for rocks of the Onecote area was 8.9 ppm, whilst that of soils was 2.4 ppm. The ratio of mean soil to rock cadmium (indicating the degree of metal mobilisation) for Onecote was 3.7 and 7.0 for Bowland. In a sample

of soil from the River Dove area 50% of the total cadmium was found to be in a sulphide form, confirming the assertion that epigenetic mineralisation accounted for a major part of cadmium partitioning in samples of the area. The grand mean of cadmium in rocks of the Dove region was 6.4 ppm whilst that for soils was 3.3 ppm (giving a ratio of 1.9) and stream sediments in this region were commonly anomalous. The grand mean of all Edale Shales was 7.6 ppm, whilst that of all Edale soils was low (1.6 ppm). The ratio of soil:rock cadmium was comparitively high at 4.7.

Where organically and clay-bound cadmium predominated, as in Bowland and Edale, dispersal of cadmium from soils was more marked than in the remaining areas of Onecote, and Dove where epigenetic sulphide forms were more resistant to weathering.

Soils which have developed upon rocks with metal of syngenetic origin contained cadmium which firstly, adopted clay mineral exchange sites, secondly, was found in stable forms of manganese oxides and thirdly, was influenced by the presence of organic matter. Almost no cadmium was adsorbed or related to readily exchangeable oxides. Soils which have developed on epigenetically metal-rich rocks, contained cadmium which was predominantly in a sulphide form.

In Britain Visean age rocks outcrop over an area of almost 5,000 square kilometers: the three areas studied, Bowland, Edale and Onecote/Dove, represented 8.7% (419 km^2) of the total Visean area of mid-north England. 5.1% (244 km^2) of the total Visean outcrop in England can be assumed to comprise metal-rich black shales. The amount of cadmium which is directly potentially available to plants developed on such shales is 1.4 to 7.6% of total cadmium in the three areas. However, in soils overlying metal-rich black shales,

considerably more cadmium was found to be present. The potentially hazardous nature of cadmium in soils is emphasized by the fact that cadmium can be much more readily taken up into plants than zinc or lead principally by processes of adsorption through, and accumulation in, the roots of plants. Increased adsorption has been demonstrated (Wakeley, 1973) when low phosphate, acidic soil conditions develop. If such acidic conditions should develop, with the onset of poor drainage conditions, cadmium could be released from rock and soil matrices and made available to plants and grasses in the area - thus constituting a potential hazard in the natural food chain. If acidic conditions were capable of releasing cadmium from its adsorbed, clay, carbonate and oxide forms, 5.1% of the 5,000 km^2 area of Visean outcrop in England would have available from 4.0 to 6.5 ppm cadmium (Edale and Bowland figures respectively).

13.4 THE CHEMICAL FORM OF THE ELEMENT IN NATURAL MATERIALS

Despite variations in physiochemical conditions which must have existed in each of the Central Province black shale depositional environments, the behaviour of cadmium during diagenesis and sedimentation was similar in each. The element participated mainly in the formation of sulphides. Of equal, but lesser, importance were the association of cadmium in secondary iron and manganese precipitation, and the formation or retention of stable cadmium-carbon compounds. Variation occurred in lower energy sites where inter-layer cation substitution in clays and surface adsorption have been shown to exist. Conditions could also exist whereby cadmium substituted into growing carbonate lattices. Until the lower energy categories were considered, little differentiation could be made between the three sets of samples of the Central Province basin.

In the shales of Onecote, 70% of the total extractable cadmium was removed by the three strongest extractants and represented that metal which was contained in the iron-manganese oxides, as substitutes in the clay minerals and pyrite lattices, as sulphides and as a constituent of residual kerogen. In the shales of Edale and Bowland 75% and 71% of total extractable cadmium respectively, were so contained.

The overall cadmium content in 276 Culm Measures rocks was found to be 1.3 ppm. Most of the 32% of total extractable cadmium removed by HCl and identified in the rocks of Cornwall as the most dominant form, was contained in sulphides. The remainder of the total metal was almost fully divided amongst the iron-manganese minerals, the reconstituted micas and the adsorbed components.

In both samples considered in the post-extraction thermally-evolved vapour profile study, carbonate and sulphide forms have been identified. The hypothesis was presented that cadmium was incorporated into carbonate structures outside the realm of reducing conditions, where cadmium may have been precipitating as sulphide, and washed in as environmental conditions became more agitated. In the absence of pyrite (sulphide) formation in the basin, cadmium was associated with widely diversified types of organic material.

Removal of almost all the cadmium present in a stream sediment by the reducing-oxidising agent was taken to indicate that manganese oxides dominated in the retention of cadmium. Subordinate peaks at 470 and 615^{o}C were formed by the release of cadmium from organic and pyritous structures respectively.

A study of principal plasma peaks confirmed that the most dominant cadmium peak in early (predominantly argillaceous) P1 times was low to medium in temperature (100-500°C): those in the Pendleside sandstone phase showed great temperature fluctuations, whilst the principal peaks of the predominantly arenaceous Upper Bowland Shales (E1) were dominantly high temperature (500-900°C). The presence of a cadmium-carbon peak at 500-600°C was persistent. High total cadmium content in samples correlated with high temperature-dominant (sulphide) peaks. The stable form of cadmium was seen to be the sulphide.

In the Upper Booth traverse at Edale, medium to high temperature peaks predominated in the earlier E2B stage, whilst low to medium temperature peaks dominated in the younger E2C stage and medium temperature peaks dominated in theyoungest H stage rocks. Total extractable cadmium increased in samples collected above most of the marine bands. It was suggested that enrichment occurred when metal-enriched top-waters came into contact with stagnant and stratified bottom waters following aeration and turbulence. Sulphide formation in Edale however, was found to be a relatively uncommon event. In contrast to cadmium's mobile and 'free'form of entry into the Bowland basin, here it entered partly in a detrital form within the lattices of clay minerals. In addition, the rate of sedimentation appeared to be too rapid to allow for in situ mineral weathering and the subsequent provision of soluble cadmium. Carbon and clay cadmium-species dominated.

All samples from the Culm Measures, Cornwall, had dominant cadmium-carbon peaks at 500-600°C and subordinate adsorbed cadmium peaks at 100-190°C. The formation of sulphides was seen in samples with 5 ppm or more.

In the thermally-evolved vapour profiles of waterlogged soils from South Wales, four cadmium species were observed in the topsoil related to cadmium dissociation from (1) iron-manganese oxides (335^{o}C); (2) structures of decomposing organic complexes (550^{o}C); (3) the breakdown of cadmium-containing clay minerals (805^{o}C) and (4) a relatively unimportant, low temperature adsorbed form. The formation of montmorillonite-type clays with high cation exchange capacities in poorly-drained soils was of primary importance. In the subsoils the cadmium-carbon peak dominated. At depth cadmium-oxide gels stabilised and decomposed at higher temperatures; and sulphides were detected. Large decreases in subsoil TEVP area compared with that of topsoils indicated the degree of downprofile leaching which was taking place.

In profiles of moderately drained soils, the cadmium-iron oxide association dominated although the metal also associated within clay lattices, in organic materials and as adsorbants. At depth all but a broad low organic-cadmium form were removed.

In the TEVPs of well-drained soils iron-manganese oxides scavenged most topsoil cadmium and were readily leached out at depth. Organo-metallic complexes appeared to be less mobile than colloidal oxide forms: stabilisation during humification was apparently taking place. Cadmium-clay forms, so common in waterlogged soils were barely detectable in well-drained soils. The presence of cadmium predominantly in waterlogged topsoils was thought to be a function of the presence of suitably wet conditions for the formation of iron-manganese oxides.

13.5 THE INTER-RELATIONSHIPS OF CADMIUM WITH OTHER ELEMENTS

The aluminium\silicon ratio decreased as basins became more clay-rich. In Edale and in the Culm, where Al\Si ratios were low, the percentage of total cadmium associated with the clay minerals rose. In Bowland, the highest average total cadmium content in sets of samples coincided with a high Al\Si ratio and, in addition, high calcium content. The presence of a low Al\Si ratio alone (indicative of a clay-rich sediment) was therefore not considered to be the only controlling factor in the process of cadmium enhancement. As total aluminium increased in the kaolinite-rich Onecote samples, so the content of cadmium adsorbed onto the surfaces of the aluminium-rich clay mineral groups illite and kaolinite increased. Cadmium inclusion in magnesium-rich minerals in Onecote suggested that the pH of the environment of weathering was nearly neutral, in contrast to that of Bowland, where a strong cadmium: aluminium correlation suggested a more acidic environment of weathering. In Bowland therefore, more cadmium mobilised from the weathering site in a soluble or easily adsorbed form, whereas in Onecote, cadmium was more detrital in nature upon entering the basin of deposition. Partial decay of clay minerals in the disequilibrated basin of deposition released cadmium and made it available for readsorption. A strong disequilibrium in the Edale basin led to the formation of highly adsorptive aluminium-rich clay minerals.

A negative relationship between a wide range of total carbon concentration and adsorbed cadmium in Cornwall, Bowland and parts of Onecote indicated that the presence of organic matter as an adsorbant was of some importance. EDTA extractable cadmium was significantly

positively correlated with total carbon in Cornwall samples and positively, but poorly correlated in Edale and Bowland. A positive correlation was found between total carbon and carbonate cadmium in Bowland Shales, confirming that cadmium was in part non-detrital in nature substituting from solution within carbonate precipitating in mildly acidic environments.

A weak positive correlation between hydrochloric and insoluble cadmium and total iron indicated that cadmium probably entered into the growing lattices of pyritous minerals. Up to 5 ppm cadmium may have entered the pyrite structures in the Bowland area, whilst up to 2-3 ppm may have entered pyrite in the Onecote-Edale areas.

13.6 FURTHER CONSIDERATIONS OF METAL SOURCE AND ENHANCEMENT PROCESSES

Cadmium has commonly been enhanced in black shales by a factor of 50 to 60 times that of the crustal average of 0.2 ppm. The source of metal to the enriching black shale environments of the Carboniferous era may have been the mineralisation associated with the Armorican earth movements. The lead-zinc lodes of the Alston block of the North Pennines cut chiefly Yoredale rocks of the Carboniferous: a period when the Upper Bowland Shales were being deposited in stagnant basins. Cadmium may have been made directly available for sulphide precipitation and the formation of organo-metallic complexes, as mineralising solutions entered the environment of deposition through fissures in the Visean rocks, or may have been supplied from weathered and exposed bedrock of earlier Carboniferous age. If the conditions of sedimentation became highly reducing, for example on sediment burial, it is postulated that insecure adsorbed and oxide-scavenged cadmium forms may be remobilised by expelled pore waters into younger strata where sulphides (pyrite etc.) were actively forming. The concentration of cadmium in

pyritous bands surrounding diagenetically formed calcareous and oxide concretions was a demonstration of the elements' post depositional mobility within a sediment. Cadmium which is not precipitated by chalcophile action may emerge above the sediment-water interface for further adsorption and deposition. During more vigorously oxygenated periods of the depositional cycle part of the depositing carbonaceous matter broke down to form CO_2 instead of the H_2S commonly formed during more oxygen starved periods. Cadmium expelled from sediments undergoing diagenesis at such times, or entering the basin in a soluble form from fissures or from weathering hinterland could substitute into growing carbonate lattices for the physically similar calcium ion.

13.7 RECOMMENDATIONS

Cadmium is a cumulative poison. The long term effect of low-level intake of cadmium has still to be fully assessed before any possible link between such symptoms as hypertension and environmental conditions can be over-ruled. It is accordingly recommended that further study should be carried out on the availability of cadmium to the food-chain in those geographical regions which have been identified as cadmium enriched - principally those 250 km^2 of Visean black shale outcrop. Cadmium uptake in plants, possibly on a seasonal basis should be studied in detail in those areas where cadmium-enriched bedrock and sources of metallic sulphides are known. In addition, continual monitoring of the atmosphere in certain areas where airborne cadmium from smelters is known, like Avonmouth and Swansea, is recommended; rising metal trends in air and the responses of organisms may thus provide an early warning system for impending human ill-health.

The urgent need to strictly and regularly monitor working atmospheres in factories using cadmium-rich materials and to instil an

awareness amongst workers and management of the dangers of using the metal without due caution has been demonstrated in a report cited in the Sunday Times of December 1975: a possible correlation had been drawn between high cadmium levels in the air of a Glasgow factory and a strong incidence amongst cadmium-solder using coppersmiths, of kidney damage and abnormal blood pressure ten times above the national average.

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APPENDIX: SAMPLING AND ANALYTICAL METHODS

A1 INTRODUCTION

The regional geochemical stream sediment reconaissance of England and Wales on which this thesis is based forms part of a programme carried out by the Applied Geochemistry Research Group to prepare a geochemical atlas of the country, financed by the Wolfson Foundation. The sampling of the 49,500 stream sediments was carried out in 1969 by two-man teams sampling road or track intersections with tributary drainage at a density of one per square mile (1 per 2.6 km^2). Selected anomalies for cadmium were followed up for this study with more detailed stream sediment, soil and rock sampling.

A2 SAMPLING

The stream sediment sampling followed the technique described by Hawkes and Webb (1962). Duplicate samples of sediment collected near midstream were given identifying numbers and geographically located by the allocation of national grid co-ordinates. The samples were dried overnight at about 80°F, gently disaggregated and sieved to minus-80 mesh (less than 204 microns) in preparation for decomposition by a nitric-perchloric acid mixture (described in section A.3.2).

Soils, prepared in the same way were collected along traverses at varying intervals, usually between 20, 150 and 1,000 feet. Soils were composited from up to four sub-soils taken from the top 15 cms. and depths 30-45 cms, 45-60 cms and 60-75 cms, over a rectangular grid of about five square meters in area.

Rocks sampled according to the procedure mentioned in section 5.2 were pulverized in a jaw-crusher to small chip size and ground to minus-80 mesh powder in a steel or agate Tema mill. The mill was cleaned periodically with fine white sand and, after each run, with acetone.

A3 ANALYTICAL TECHNIQUES

A3.1 INTRODUCTION

The major sources of error in geochemical analysis were fully described by Miesch (1967) and include analytical imprecision and sampling variability. With the atlas data it is generally regarded that the estimation of analytical precision offers a potentially greater source of error to the final result, than does variability in sampling.

The analytical techniques used to provide the data for this thesis have been developed at the Applied Geochemistry Research Group. Two fundamental methods of rapid routine analysis of geochemical materials were used: the more precise and reproducible atomic absorption spectrometry and the more productive but less precise direct-reading spectrographic technique (not used for 'atlas' data) known as system C. Other analytical techniques used included micro-wave, argon-plasma emission, x-ray diffraction, colorimetric analysis, flameless atomic absorption spectrophotometry and the use of a carbon-hydrogen analyser.

A3.2 ATOMIC ABSORPTION SPECTROMETRY

The use of the atomic absorption spectrometer in geochemistry is described in detail in the text of Angino and Billings (1967). The determination of cadmium, zinc, lead, iron and manganese was carried out

on a Perkin-Elmer 403 model spectrometer. Absorption measurements were converted to concentration by calibration graphs. Preliminary studies were undertaken to test the efficiency of sample decomposition by various acid mixtures including nitric, perchloric and hydrofluoric acids before the following attack, as a consequence of its chemical effectiveness and uncomplicated procedure, was adopted: a mixture of Analar nitric to perchloric acids (4+1, 5ml.) was added to a 0.25 gm homogenised sample in a lipped test-tube and the acid slowly evapo rated to dryness over an air-bath. The residue was leached with 10 ml of molar hydrochloric acid which also was used to prepare the standards.

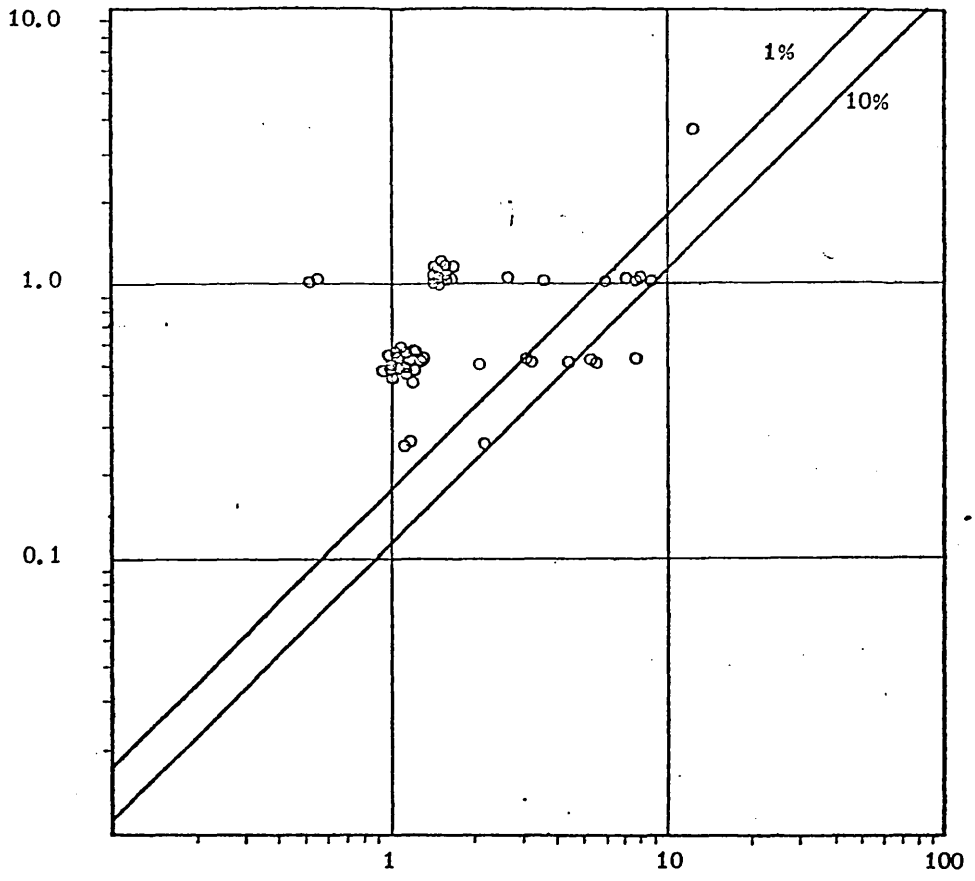
Analytical control was maintained by both the repeated analyses of known natural standards and the use in batches of duplicate pair analyses at a frequency of one in ten. The analytical precision was generally better than $\pm$10% at the 95% confidence level. A measure of the precision so obtained for low cadmium, and high cadmium concentrations in samples is shown graphically in appendix figures, 1.1 and 1.2 respectively. This method of analytical control, developed by Howarth and Thompson (1973), demonstrates the poor analytical reproducibility of cadmium in shales containing less than 5 ppm.

A3.2 DIRECT-READING SPECTROGRAPHIC TECHNIQUE:SYSTEM C

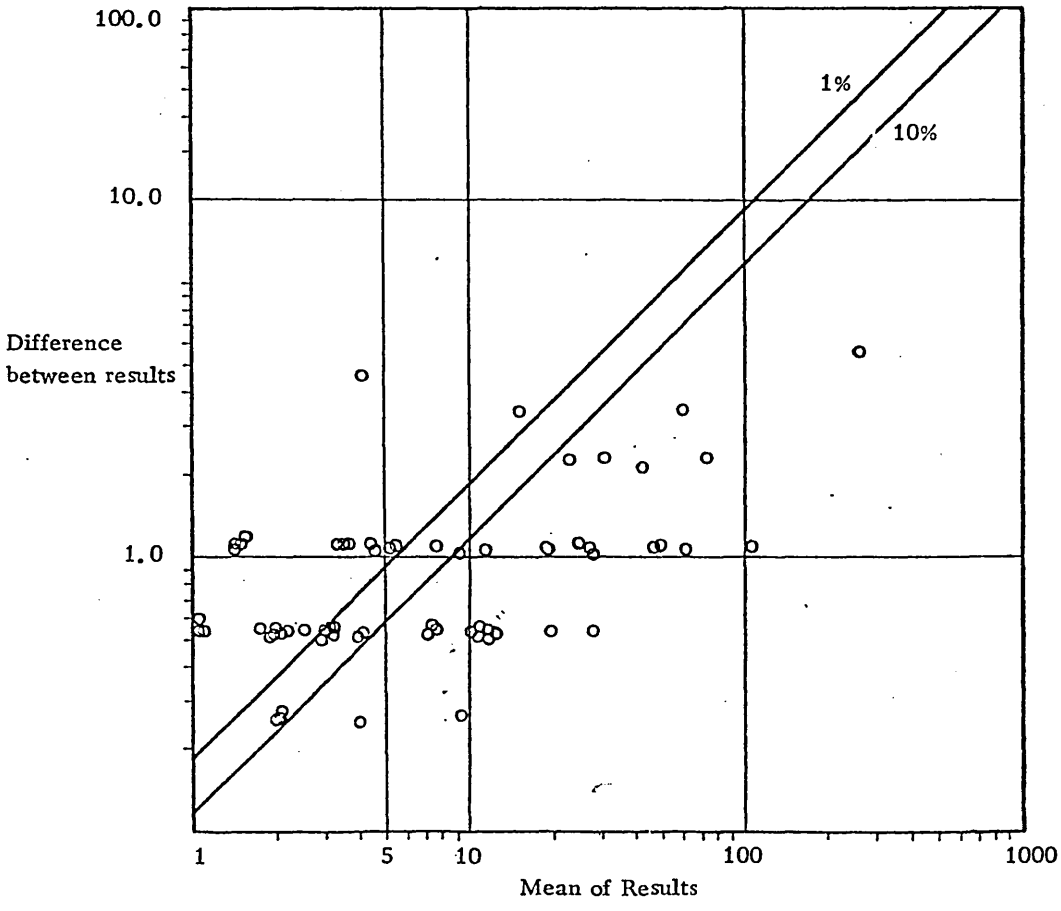
System C is a combination of a direct reading spectrographic technique and a computer program which converts the 'raw' output into element concentrations. The method and principles are described in detail in the users guide to system C (Applied Geochemistry Research Group, June 1973).

Ten gram samples of sieved rock powder were ignited for three hours at 450^{o}C (to remove moisture and decompose organic

1. Cadmium Range 10^{-1} - 10 ppm



2. Cadmium Range 1 - 100 ppm



In a set of duplicate measurements, the precision of measurement is 10 percent at the 95 percent confidence limit when the indicated proportion of points falls above the diagonals.

APPENDIX FIGURE 1 PRECISION CONTROL CHART FOR REPRODUCIBILITY OF CADMIUM ANALYSED BY ATOMIC ABSORPTION

material) and homogenised at 2:3 ratio with a carbon/sodium fluoride buffer mixture. A part of the sample was then packed into a hollow-topped carbon electrode and arc activated: arc conditions and the finer operational nuances are detailed in the forementioned technical communication. Calibration for each element is checked by the repetitive activation of standard 'calibrators' of pure silica, a trace element standard and a major element standard. Background and drift corrections, calculated from the study of repetitive calibrator determinations during each day were applied by the operating analysts. Batch precision was gauged by the analysis of up to 15 duplicates during the analytical day. A statistical analysis was made on the duplicate pair results on the basis of a pre-determined standard of precision. Limits of detection and the useful analytical range of the elements determined is presented in appendix Table 1. Precision and the range of element concentration over which duplicate pair precisions have been computed are shown in appendix Table 2.

A3.3 MICRO-WAVE INDUCED ARGON PLASMA EMISSION

This system described in detail in Chapter 9 and based on the method described and developed by Meyer and Leen (1973), was used for the detection of cadmium vapour evolved from heated samples of soil, sediment and rock. The method was characterised by referring to emission profiles from various natural materials, differential thermal analysis curves for natural and synthetic materials and profiles produced by Meyer and co-workers during the development work on the system.

A3.4 MERCURY DETERMINATION

Mercury determination of soil and rock samples were carried out using a double-cell, flameless atomic absorption spectrophotometer and a method described by James and Webb (1964).

APPENDIX

TABLE 1 SYSTEM C, D. R. SPECTROMETER: USEFUL ANALYTICAL RANGE

	Detection Limit	Upper Limit
Fe	0.1	15.0
Mn1	40.0	500.0
Mn2	500.0	10000.0
Cu	2.0	1000.0
Pb	5.0	1000.0
Zn1	10.0	1000.0
Cd	1.5	100.0
Ag	0.3	100.0
Mo	1.0	100.0
V	5.0	1000.0
Co	2.0	1000.0
Ni	2.0	1000.0
Cr	1.0	1000.0
Ga	0.2	100.0
Sn	2.0	1000.0
Ti	10.0	20000.0
Be	0.5	100.0
Mg	0.1	5.0
Ca	0.1	25.0
Sr	10.0	1000.0
Ba	1.0	1000.0
K	0.1	10.0
Li	3.0	1000.0
Al	0.7	15.0
Sc	2.0	100.0
Si	4.0	46.0
Bi	0.4	1000.0
As	2.0	1000.0

APPENDIX

TABLE 2 PRECISION OF ELEMENTS IN D.R. SPECTROMETRY

Element	Precision 95% C.L.	Range means ppm $^{+}_{-}$%
Ti	$^{+}_{-}$17.6	732-6555
Mn I	$^{+}_{-}$ 9.7	57.5-994.0
Mn 2	$^{+}_{-}$10.0	64 -4314
Ag*	$^{+}_{-}$56.1	-0.2-+13.5
Ba	$^{+}_{-}$22.3	142.3-8097.6
Be	$^{+}_{-}$16.2	-0.2-+14.2
Co	$^{+}_{-}$17.1	4.4-56.5
Cr	$^{+}_{-}$27.7	14.4-441.9
Cu	$^{+}_{-}$7.9	21.2-239.9
Ga	$^{+}_{-}$14.8	1.9-29.9
Mo	$^{+}_{-}$23.8	0.9-40.0
Ni	$^{+}_{-}$15.9	9.8-361.0
Pb	$^{+}_{-}$ 7.7	3.9-859.2
Sc	$^{+}_{-}$14.3	5.4-17.5
Sr	$^{+}_{-}$34.8	7.5-209.5
V	$^{+}_{-}$13.6	134-946
Zn	$^{+}_{-}$33.5	45-182
Cd**	$^{+}_{-}$47.6	1.8-8.7
Fe^{+}	$^{+}_{-}$21.1	1.4-8.8
Mg^{+}	$^{+}_{-}$15.3	0-1.2
Ca^{+}	$^{+}_{-}$ 4.5	0.1-9.41
K^{+}	$^{+}_{-}$21.4	0.3-3.85
Al^{+}	$^{+}_{-}$34.5	2.8-18.0
Si^{+}	$^{+}_{-}$ 4.8	5.1-31.88
Li	$^{+}_{-}$17.3	0.5-335.9
Sn	$^{+}_{-}$56.1	-3.9-+14.6

Precision in $^{+}_{-}$% at 95% confidence level. By median difference method of Thompson & Howarth (Analyst, 1973)

* Ag by method of Garrett, 1969

NUMBER OF PAIRS USED

** The precision of reproducibility for Cd is thought to be $^{+}_{-}$10% at P=0.05, when Cd is present in amounts 5 ppm

A3.5 MOLYBDENUM DETERMINATION

The molybdenum determination was based on the colorimetric method of Stanton (1966) which uses the reagent toluene dithiol after a fusion with potassium hydrogen sulphate. Organic matter together with molybdenite and other sulphides, when present, were oxidised by the addition of potassium nitrate to the fusion. Black shale samples containing large amounts of organic matter and sulphides were decomposed by a nitric/perchloric acid attack for the first stage of the analysis.

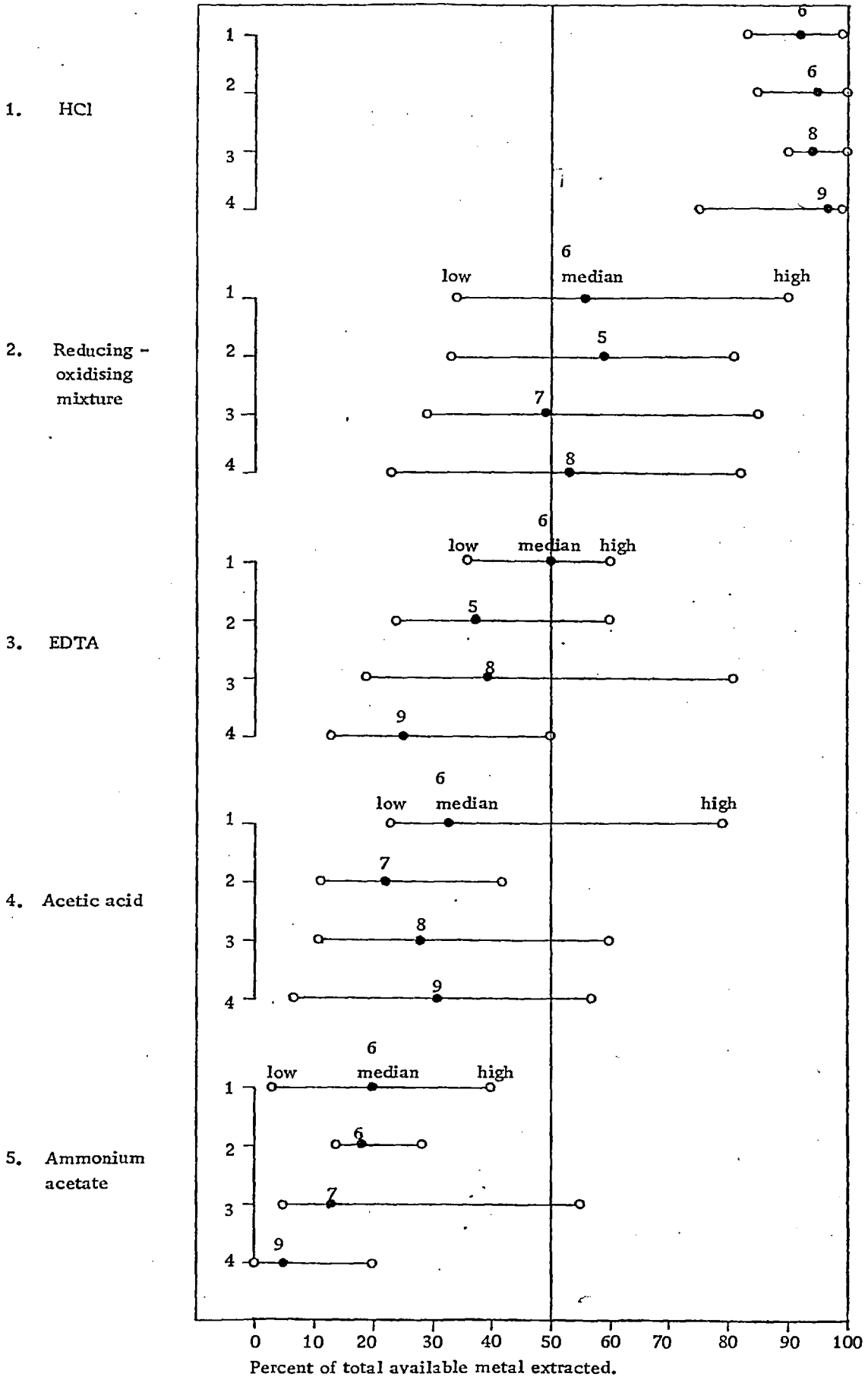
A3.6 CARBON DETERMINATION

Analysis for total carbon concentration, rank by reflectivity measurement and hydrocarbon identification using gas chromatograms were carried out by the Organic Geochemistry Unit of the university of Newcastle-upon-Tyne.

Carbon was analysed by an Aminco carbon and hydrogen analyser using the principle of total combustion and oxidation at 1000^{o}C followed by the determination of resultant carbon dioxide, after the removal of all other degradation products. Two pure standards with concentrations of 1.45 and 1.85% carbon were used to calibrate the instrument.

A4 THE USE OF AQUEOUS CHEMICAL EXTRACTIONS

The chemical extractants used in cadmium speciation experiments are described in section 8.2. The range and median values of 'percent metal removed, of total' by each of the five extractants is shown graphically in appendix Figure 2.



1. Culm, Cornwall, 2. Edale, 3. Onecote, 4. Bowland.
Numbers of samples in each extraction noted above median value.

APPENDIX FIGURE 2. RANGE AND MEDIANS OF CADMIUM EXTRACTED BY FIVE METHODS FROM ROCK SAMPLES OF VISEAN AGE.

A5 DATA HANDLING

Data was stored on punch cards prior to processing on a CDC 6400 computer at the computer centre, Imperial College. For the production of the cadmium atlas map (Figure 3.1) on which this thesis was originally based, atomic absorption analyses for 49,500 stream sediments were plotted as greyscale maps using the computer line-printer for read-out. The values for geochemical data tended to be noisy owing to sampling and analytical errors, so the PLTLP1 plotting program (Howarth, 1971) was extended by its author to incorporate local moving average smoothing in the final maps.

The GESTAT program (Garret, 1967) was used for the computation of means, variances and standard deviations as well as the inter-element correlation matrix and associated matrix of Student's t values.

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