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The occurrence and economic potential of nodular monazite in south-central Wales

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R T Smith, D C Cooper and D J Bland

BRITISH GEOLOGICAL SURVEY

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SUMMARY

Review of all Mineral Reconnaissance Programme panned concentrate data confirmed that very high (>5000 ppm) levels of cerium, caused by the presence of nodular monazite, are characteristic of samples collected from catchments containing sedimentary rocks of Upper Cambrian to Silurian age deposited in the Welsh Basin. The largest panned concentrate anomalies (>1% Ce) are associated with rocks of Upper Ordovician age and the most extensive area containing these very high values is in south-central Wales, near Newcastle Emlyn.

Follow-up panned concentrate sampling in this area showed that cerium anomalies caused by nodular monazite extend from tributary drainage into the main river systems and, in the Afon Teifi, persist for over 20 km into the estuary near Cardigan. Levels of monazite in stream sediment locally exceed minimum grades exploited in placer deposits, reaching 1.65% in the <2 mm (sand, silt and clay) fraction of the samples collected. Consequently it is recommended that further work is undertaken to assess the concentrations of monazite and other heavy minerals in river and estuarine sediments, dune sands and beach deposits associated with the Afon Teifi and other rivers draining Upper Ordovician and Lower Silurian sedimentary rocks deposited in the Welsh Basin. Few other heavy resistate minerals were recorded in the sediments collected from the Afon Teifi, but the placer deposit potential of some other monazite-bearing estuarine sediments in Wales is likely to be enhanced by the presence of additional economic minerals, notably gold.

Mineralogical studies of nodular monazites found in the rocks of the Newcastle Emlyn area showed that they have very similar properties to those described from Central Wales, Belgium, France and Spain. They occur in mudrocks subjected to low-grade metamorphism, are less than 2 mm in size, ovoid to discoid in shape, dark grey in colour, and have a prominent inclusion fabric indistinguishable from the host-rock. The nodules are characterised by a low thorium and high europium content compared with monazites of igneous origin, and are compositionally zoned with LREE-rich rims. However, the monazites from the Newcastle Emlyn area have some distinctive properties: they are notably smaller and more ragged, and commonly contain more inclusions than those from Central Wales. They contain lower thorium and higher europium levels than many other nodular monazites, and display complex chemical zonation with up to seven concentric zones, 10–100 μm wide, distinguishable within a single nodule.

In contrast to Central Wales, where nodules are concentrated in Llandovery-age hemipelagic mudstone horizons showing considerable enrichment in REE, nodules appeared to be dispersed in the mudstone-dominated succession of the Newcastle Emlyn area. Bulk analysis of these nodule-bearing rocks showed that they do not contain unusually high overall levels of REEs and no evidence of stratabound REE enrichment was found in the survey area. The concentrations of nodules recorded both here and in the hemipelagic mudstones of Central Wales suggest that an economic deposit of nodular monazite in bedrock is unlikely to exist in Wales.

It is believed that the nodules formed by post-depositional, pre-metamorphic diagenetic growth under physico-chemical conditions that are poorly understood, but which involved at least local saturation of REE with respect to REE phosphate coprecipitation in the pore-fluids. Under the anoxic conditions likely to have prevailed during early diagenesis, REE may have been released from iron-manganese hydrous oxides and other phases, and fixed by phosphate released during the decomposition of dispersed organic matter.

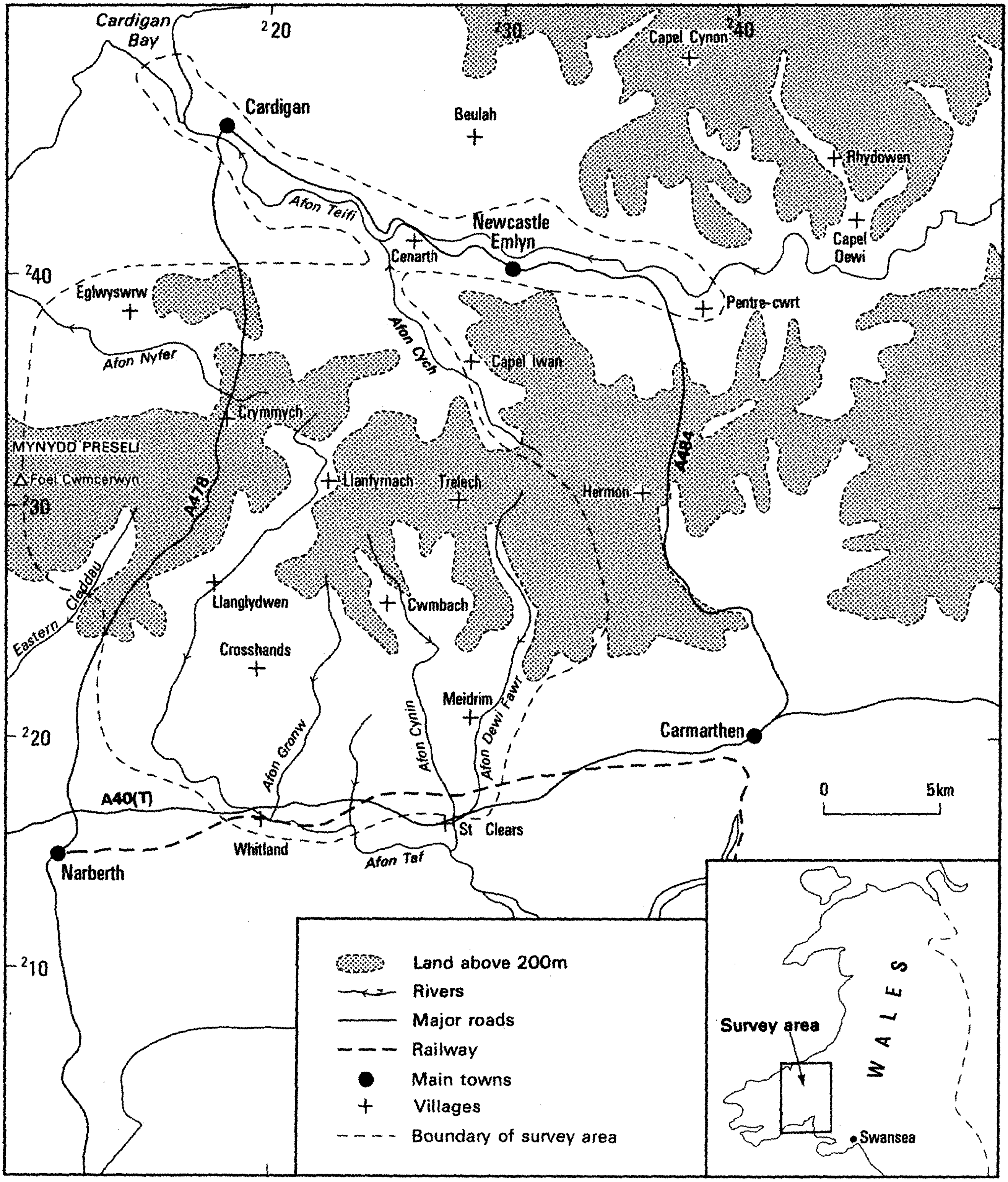

Figure 1 Location of the survey area

INTRODUCTION

This report describes work carried out in the Newcastle Emlyn area of south-central Wales (Figure 1), to determine the economic potential of nodular monazite concentrations found in the stream and river sediments of this area and other parts of Wales by Mineral Reconnaissance Programme (MRP) surveys.

Previous work related to the occurrence of nodular monazite

Nodular monazite was first recorded in the UK from the mineralogical examination of panned concentrates collected during MRP drainage surveys. These concentrates, produced from the <2 mm sediment fraction, contained very high levels of cerium, but <150 μm (100 mesh) stream sediment samples collected from the same sites showed only weakly elevated cerium levels and much poorer geochemical contrast. The anomalous cerium values in panned concentrates had a distinct regional distribution pattern with very high (c. 1% Ce) values restricted to catchments draining Lower Palaeozoic rocks of the Welsh Basin, apparently derived from clastic, mudstone-dominated, sedimentary successions of Upper Cambrian to Silurian age. Similar clastic sedimentary successions of Lower Palaeozoic age in Britain deposited in other basins, such as those exposed in the Lake District and southern Scotland, generated only normal background values, as did volcanic sequences within the Welsh Basin (Cooper and Read, 1984).

Follow-up mineralogical studies showed that the cerium anomalies were caused by a grey, nodular form of monazite with physical and optical properties quite distinct from those of igneous monazites (Cooper et al., 1983; Read et al., 1987). The nodules were grey in colour and, typically, discoid to ovoid in shape. They possessed an inclusion fabric of low-grade metamorphic minerals identical to those of the host rock, and occurred in a limited size range (maximum frequency at 0.5–0.7 mm in Central Wales; Read, 1983). Chemical analysis of the nodules showed that they were characterised by low levels of thorium and high europium when compared with monazites of igneous origin. Electron microprobe studies showed that the nodules were zoned with rims highly enriched in LREE (Read, 1983). The nodules proved difficult to detect in rock outcrops (Read, 1983) but a detailed study associated with 1:10 000 scale mapping showed that in Central Wales they were concentrated in anoxic hemipelagic mudstone horizons within a sandstone-mudstone turbidite succession (Milodowski and Zalasiewicz, 1991). Investigation of mineralogical, textural and chemical features indicated a pre-cleavage or diagenetic origin for these nodules and it was suggested that they formed by precipitation, initially of rhabdophane, within the anoxic hemipelagites from upward-migrating REE-enriched pore-fluids during diagenesis (Milodowski and Zalasiewicz, 1991).

The occurrence of nodular monazite with close physical and chemical similarities to those of the Welsh Basin is not restricted to Britain, and recent work in particular has described several occurrences in other parts of Europe. For example, it has been reported in sedimentary rocks of Cambro-Ordovician (Burnotte et al., 1989) and Devonian age (Limbourg, 1986) in Belgium, from the Ordovician and Dinantian of Brittany (Donnot et al., 1973) and from the Ordovician of Spain (Windle and Nesbitt, 1993). Other worldwide sources of authigenic monazite include shales and siltstones of Precambrian to Cretaceous age in Alaska, USA, Morocco, Madagascar, USSR and Gabon, stanniferous placers in Siberia and Zaire, and monazite placers in Taiwan, Niger, Bolivia, Canada, Pakistan, Thailand, Bangladesh, and Peru (Overstreet, 1967; Matzko and Overstreet, 1977;

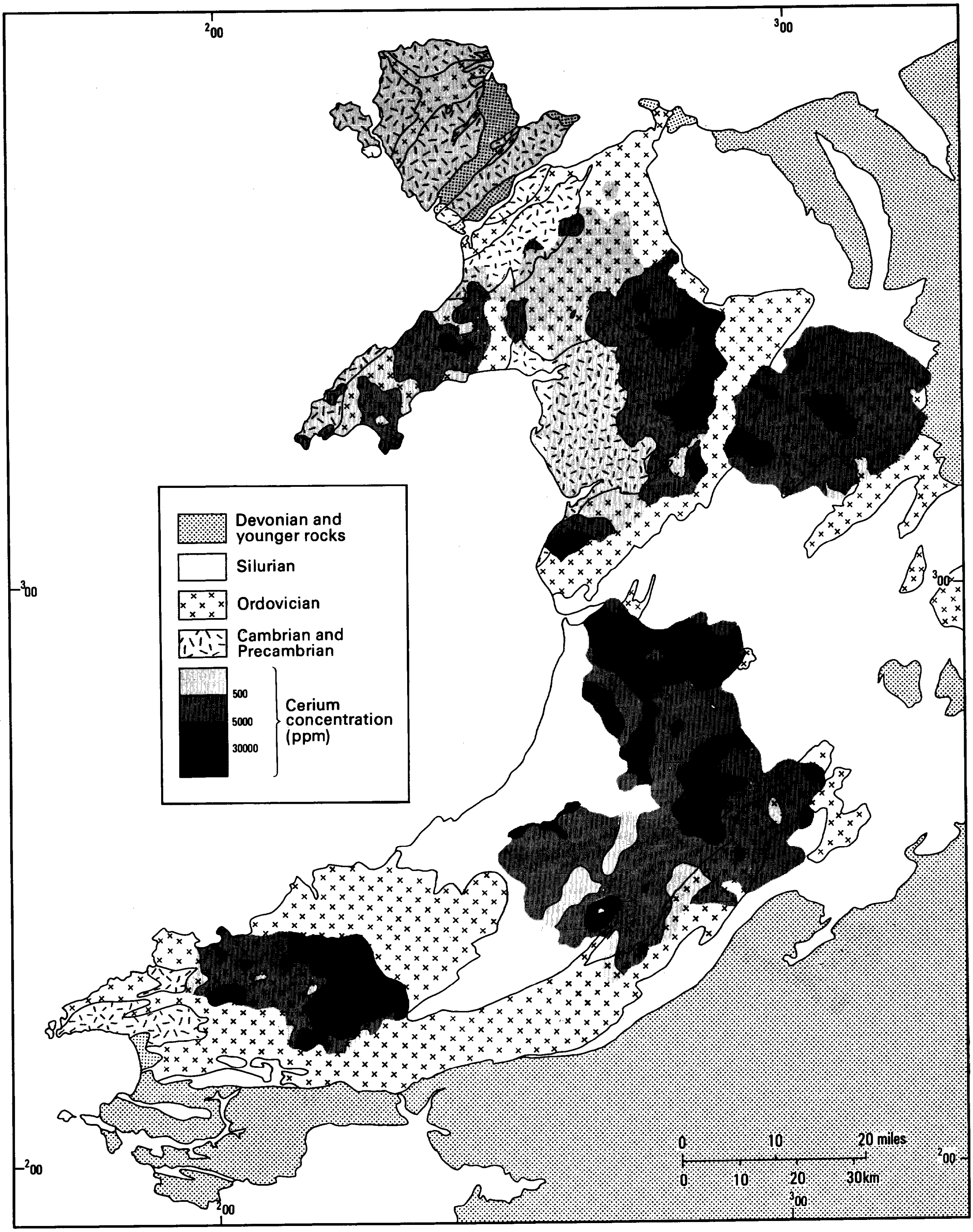

Figure 2 Contoured plot of cerium levels in panned concentrate samples collected in Wales superimposed on a simplified geological map

Rosenblum and Mosier, 1983). Detailed studies in some of these areas have demonstrated the broad compositional similarity and texture of the nodules wherever they are found, but local differences in occurrence are also evident. For example, in Central Wales the nodules are concentrated in specific horizons (hemipelagic mudstone) whereas in other areas, such as Belgium (Burnotte et al., 1989) and Spain (Windle and Nesbitt, 1993), they appear to be distributed throughout the succession.

The distribution of nodular monazite in Britain

A comprehensive review of all the available data for cerium in panned concentrates was undertaken to assist in the selection of a favourable area for an investigation of the economic potential of the monazite nodules. This review, which involved the retrieval of data from the MRP database and the preparation of computer-generated maps, included MRP datasets acquired since the work of Cooper and Read (1984). Summary statistics for selected MRP survey areas and sub-areas are given in Table 1 and a contoured plot of the cerium data for Wales (produced from interpolation of the raw data to a regular grid by a weighted average method using the UNIRAS software package) is superimposed on a simplified geological outline map in Figure 2.

The results confirmed the findings of earlier work in showing the restriction of highly anomalous levels (>1%) of cerium in panned concentrate to the Lower Palaeozoic rocks of the Welsh Basin. In Anglesey, the Lake District, and southern Scotland the absence of high cerium values in panned concentrates (Table 1) was assumed by Read et al. (1987) to reflect an absence of nodular monazite in the Lower Palaeozoic rocks of these areas, and led them to suggest that the source rocks of the Welsh Basin exerted an important control on nodule formation, or that unusual physico-chemical conditions existed in the Welsh Basin for long periods of time during the Lower Palaeozoic.

Outside Wales, the only other area of Britain in which elevated cerium values in panned concentrates can be reliably attributed to nodular monazite is Exmoor. Mid to Upper Devonian Ilfracombe Beds containing monazite derived from the weathering of Lower Palaeozoic sedimentary rocks of Wales were considered by Read et al. (1987) to be the most likely source of these nodules, on the basis that they were petrographically and physically indistinguishable from the Welsh monazites. However, more recent work has shown that nodules with these characteristics are of widespread occurrence in sedimentary rocks of different ages and provenance, so it is possible that the Exmoor monazites formed in situ and are not derived from the Welsh Basin. The maximum concentration of cerium in panned concentrates from the Exmoor area is an order of magnitude lower than in samples from Wales (Table 1), so the Exmoor area was not selected for more detailed assessment during this investigation.

In Wales, it is apparent from the regional variation pattern (Figure 2) that monazite nodules are widespread and not restricted to a single horizon or lithostratigraphic unit. However, clear evidence that stratigraphy exerts an important influence on nodule distribution is provided from the Harlech Dome. In this area a pronounced change occurs from uniformly low cerium values in catchments over the Lower–Middle Cambrian (Harlech Grits Group) to moderately high levels over the mudstone-dominated Upper Cambrian (Mawddach Group) and very high levels in catchments draining shales and mudstones of Upper Ordovician age around the eastern periphery of the Dome (Cooper and Read, 1984). The distribution of the highest values (>3% in Figure 2) is distorted by some of the early data (pre 1984) for the Berwyn Dome, Snowdonia and part of Central Wales being subject to an upper calibration limit of 1% Ce. However, despite this restriction and the incomplete areal coverage, a general association of high values with clastic sedimentary rocks of Upper Ordovician and Lower Silurian age is evident.

Table 1 Summary of cerium data, in ppm, for panned concentrates collected in Wales and selected areas of England and Scotland

Area	Samples	Median	Range
Anglesey	490	50	<21-660
Lleyn Peninsula	416	*380	<21-32100
Snowdonia	170	140	30->10000
Harlech Dome			
Harlech Grits Group	141	53	<21-490
Mawddach Group	177	692	<21-8500
Caradoc-Ashgill	121	2990	44-140000
Berwyn Dome	399	2015	89->10000
Central Wales	488	1600	50->10000
Preseli Hills and adjacent areas			
Reconnaissance[1]	384	5270	37-137000
This survey[2]	31	21702	973-105123
Exmoor	809	85	212-6100
Lake District			
Skiddaw Group	5	170	130-300
Southern Scotland	585	44	<21-171

* Geometric mean

[1] Samples collected in the Preseli Hills reconnaissance survey (Cameron et al., 1984) and, subsequently, in adjacent areas.

[2] Samples collected in the follow-up survey reported below.

Selection of the survey area and scope of the investigation

More detailed analysis of the cerium data for panned concentrates from each sampled area in Wales suggested an association of the highest cerium values with mudstones of Upper Ordovician age. It was also evident from these data that the largest sampled area with very high values is in south-central Wales, and that this anomalous area is unclosed to the east and north (Figure 2). Mineralogical work carried out during the reconnaissance survey of the Preseli Hills (Cameron et al., 1984) showed that nodular monazite was the cause of the cerium anomalies in this area. Anomalous levels of As, Ba, Cu, Pb, and Zn are also present in the dataset and these were attributed to vein-style base-metal mineralisation and mudstones containing higher than average levels of these metals. Prior to this survey, no follow-up investigation of the cerium anomalies had been undertaken.

The highest cerium values recorded (up to 13.7%) occur in the east of the reconnaissance survey area, around Llanfyrnach (Figure 1). The anomalous area, unclosed to the east and north around Newcastle Emlyn, includes parts of the Afon Teifi and Afon Taf river systems with catchment areas of about 1000 and 550 km^2 respectively. In their headwaters both rivers erode Ordovician and Silurian mudstone and siltstone successions, while superficial deposits in the lower reaches of these catchments, including river alluvium and reworked fluvio-glacial material, represent favourable environments for the deposition of heavy mineral placers. Estuarine deposits, characterised by a considerable thickness of laminated silt, clay, fine sand and, in the case of the Teifi estuary, coarser dune and beach sands, represent further probable sites of heavy mineral accumulation.

Because of the potential for the concentration of monazite in a number of different environments and the high levels that appear to be present in drainage over large areas, it was concluded that the Newcastle Emlyn area was worthy of further investigation to aid assessment of the economic potential of nodular monazite in Wales. Guided by the cerium distribution pattern in reconnaissance drainage samples, a limited programme of follow-up exploration was undertaken to:

(i) establish whether an enriched bedrock source(s) of monazite exists within the anomalous area and, if so, whether it might form an economic deposit;

(ii) evaluate the characteristics of monazite dispersion from tributary drainage into the main river channels and assess the potential for accumulation in down-stream alluvial deposits;

(iii) indicate the possibility of monazite placer concentrations occurring in the estuarine deposits of the main river systems;

(iv) determine the composition and mineralogy of the monazite and compare and contrast it with other occurrences.

Sampling of dune, beach and deep channel deposits was not attempted during this exercise.

Location, physical features and previous work in the survey area

The area investigated covers about 1200 km^2 of rural south-central Wales bounded by Cardigan Bay in the north-west and Carmarthen Bay in the south. It includes the southerly flowing Afon Taf drainage system and much of the catchment of the westerly flowing Afon Teifi (Figure 1). Between these two major valleys relief is characterised by a low plateau, for the most part lying between 50 and 250 m OD, incised by a dense network of fast flowing streams. In the north-west of the area the highest ground is formed by the east–west ridge of the Preseli Hills rising to over 500 m. Many valleys, mature in their upper reaches, show evidence of rejuvenation with the development of nick-points, waterfalls and steep-sided gorges. These provide some of the best exposures but elsewhere, due to extensive till, head and soil deposits, outcrop is generally very sparse and restricted to a few road and railway cuttings, and quarries. Despite high rainfall, soils over the plateau area are relatively free draining and neutral to mildly acid, except in valley bottoms where clay-rich deposits give rise to poorly drained gley soils. Peat and peaty gleys cover only small areas of the highest ground on the Preseli Hills and, locally, some flat-lying hill-tops.

The relatively sparse population is concentrated in the two market towns of Carmarthen and Cardigan. A dense network of minor roads and tracks connects smaller towns, villages and farms, providing easy access everywhere except to the highest ground over the central part of the Preseli Hills. Intensive livestock farming is the principal land use, supplemented by arable cropping over the more fertile, flat-lying ground of the main valleys and coastal platform. Small, but numerous forestry plantations are confined to the steep slopes of deeply-incised minor valleys. Slate quarrying was formerly an important activity, especially in the shales and slates of middle and upper Ordovician age in the Cardigan and the Crymmych–Llanfyrnach districts, but many of the smaller quarries and trials have now been filled in and grassed over.

Published geological, geochemical and geophysical maps for the survey area are available at regional scales (>1:250 000). Geological maps at 1:50 000 scale exist for only the Haverfordwest (sheet 228) and Carmarthen (sheet 229) areas. Complete geological coverage is available at 1:250 000 scale on BGS map sheets 51N 06W (Lundy) and 52N 06W (Cardigan Bay). Regional geophysical (gravity and magnetic) data are available from BGS in digital and hard-copy formats. The results of a regional geochemical survey of England and Wales are contained in the Wolfson Geochemical Atlas (Imperial College, 1978), but these are of little value to this investigation since the rare-earth elements and pathfinder elements for monazite, such as thorium and uranium, were not determined. The BGS Geochemical Survey Programme sampled the area in 1993 but the data are not yet available.

GEOLOGY

The area consists of basinal clastic sedimentary rocks comprising an interbedded sequence of dark graptolitic shales, turbidite mudstones and volumetrically subordinate siltstones and sandstones of Ordovician and Lower Silurian age. Apart from coastal sections the area is geologically one of the least known in Wales, due in part to the poor exposure. No comprehensive modern geological overview exists for the area and the more detailed geological information in this report is based on the publications of Evans (1945), Cope (1979), Anketell (1987) and McCann (1992). These authors have established and described the stratigraphic succession and structure in different parts of the survey area, the most modern work being based on coastal sections in the north.

Regional tectonic setting

From the late Precambrian to the end of the Lower Palaeozoic much of Wales evolved as a structurally controlled marginal basin along the south-eastern flank of the Iapetus Ocean (e.g. Dewey, 1982; Kokelaar et al., 1984a). The basin, founded on immature continental crust, is bordered to the south-east by the Midland Platform and to the north-west by the smaller Irish Sea Platform. The south-east margin of the basin lies along the Welsh Borderland fault system and its projected southern continuation. These north-east trending sub-parallel structures exerted an important control on sedimentation, facies changing over a distance of less than 15 km from deep-water (basinal) graptolitic shales to offshore (shelf-to-slope) mudstones and siltstones and near-shore calcareous sandstones and mudstones at the south-eastern margin. In the west, the Irish Sea Platform was an active detrital source area between early Cambrian and late Ordovician times. The main basin persisted throughout the Lower Palaeozoic and was characterised towards its centre by prolonged deposition of pelagic graptolitic mudstones with substantial periodic incursions of turbidite-dominated sandstone, siltstone and mudstone sequences. An estimated 13 km of sediment accumulated towards the centre and a maximum of 5 km near the margins of the basin (Kokelaar et al., 1984b). The sequence is dominantly marine, but a basin-wide change to non-marine facies is preserved in the Lower Devonian, heralding basin inversion and the Acadian (end-Caledonian orogenic event. The basin was tectonically active throughout its history, culminating in the Acadian event and resulting in locally intense folding and thrusting, cleavage development, anchizone metamorphism and strike-slip faulting (Roberts et al., 1991).

Volcanism from several major centres in the early and middle (Arenig to Caradoc) Ordovician, and in the early Silurian in South Wales, was a major feature of basin development. Volcanism occurred mainly along complex and relatively narrow grabens which marked the sites of deep and steep crustal fractures (Kokelaar, 1988). Remnants of the igneous activity are prominent in the Lleyn, Snowdonia, Harlech Dome, Central Wales and Pembrokeshire. Geochemical data are consistent with Ordovician volcanism in a supra-subduction zone marginal basin (Bevins et al., 1992), whilst the lower Silurian mildly alkaline volcanism has dominantly within-plate characteristics (Thorpe et al., 1989).

Towards the south-east, the rocks of the basin are progressively affected by Variscan orogenic events, the 'Variscan front' passing across Carmarthen Bay, to the south of the survey area (e.g. Freshney and Taylor, 1980; Hancock et al., 1981). Variscan deformation in the south of Wales, which extended through the Carboniferous to merge with Permo-Trias basin formation (Woodcock, 1984), was accompanied further north by re-activation of Caledonian structures.

Stratigraphy

Ordovician: Arenig

The oldest rocks exposed in the survey area are of Arenig age and form a more or less continuous east–west, 3–5 km wide, belt from Carmarthen westwards to the Preseli Hills. Basal conglomeratic units and mudstones and siltstones with occasional pebble horizons of the Ogof Hen Formation pass upward into dark mudstones and a turbidite succession, the Carmarthen Formation (Cope, 1979). The basal deposits represent a transgressive arenaceous shelly facies up to 300 m thick and the upward succession shows features indicating progressively deepening marine conditions. On the flanks of the Preseli Hills, Evans (1945) records a succession of blue-grey to greenish grey mudstones, ashy mudstones and tuffs of Arenig (*Didymograptus extensus*) age, the Foel Tyrch Beds, on Crugiau Dwy, 3 km south of Crymmych. The Upper Arenig is represented by Tetragraptus Beds, dark mudstones with only sparse terrigenous material.

Ordovician: Llanvirn

The Lower Llanvirn, represented by *Didymograptus bifidus* beds, comprises a monotonous series of blue-black slates, shales and thin tuffaceous bands, likely to be over 300 m thick (Evans, 1945). These rocks outcrop widely in the Preseli Hills and to the east, forming much the valley of the Afon Taf and its major south-flowing tributaries. Despite eastward thinning, the rocks can be traced at least as far as the Carmarthen–St. Clears area (Williams et al., 1972).

The *Didymograptus bifidus* beds are succeeded by the acid and basic lavas and tuffs of the Fishguard Volcanic Group. The thickest development of the group is on Strumble Head, near Fishguard, where about 1.8 km is recorded. The group thins eastwards and Evans (1945) recorded

140 m of rhyolitic rocks on Foel Trigarn, close to the margin of the survey area west of Crymmych. Acid volcanic rocks predominate, basic extrusives being largely restricted to the Strumble Head area. The tuffs show evidence of both sub-aerial and sub-aqueous eruption. Extrusives are accompanied by high-level intrusives, with basic intrusions prominent in the Preseli Hills. Both calc-akaline and tholeiitic magmas are represented and these have chemical characteristics which suggest eruption in a back-arc basin setting (Bevins et al., 1992).

The uppermost 'ashy mudstones' in the Fishguard Volcanic Group pass either conformably or with a minor non-sequence into black, commonly pyritous, shales and mudstones yielding *Didymograptus murchisoni.* These Murchisoni Beds show marked eastwards thickening, and in the vicinity of Carmarthen thicknesses of about 700 m have been recorded (George, 1970).

Ordovician: Llandeilo–Caradoc

Marine mudstones of Llandeilo age to the east of the Preseli Hills are represented by the Hendre Shales, which Evans (1945) suspected to lie unconformably on both the Murchisoni Beds and Fishguard Volcanic Group in this area. McCann (1992) renames this sequence the Parrog Shales, restricting the term Hendre Shales to a formation outcropping in the Carmarthen–St. Clears area. The succession comprises monotonous interbedded grey, poorly fossiliferous, mudstones and siltstones often possessing a distinctive brown weathering surface due to the presence of framboidal pyrite. Apatite-rich concretions concentrated along bedding planes are attributed by Smith (1987) to diagenesis in an oxic environment. The conformably overlying Newport Formation, c. 200 m thick in the type section at Newport, west of Cardigan, consists of middle and upper Llandeilo turbiditic, fine to coarse-grained sandstones with locally abundant interbedded siltstones and mudstones (McCann, 1992). The inland extent of this formation is uncertain.

The Caradoc sequence at the eastern end of the Preseli Hills consists of the Mydrim Shales. The succession is exposed in the upper reaches of the Afon Taf near Crymmych. Here the succession consists of pale-weathering, blue-black shales and mudstones, locally crowded with poorly preserved graptolites. According to Evans (1945) the beds are from over 50 to 100 m thick. On the north coast, rocks of this age are divided into the Ceibwr Formation, consisting principally of parallel laminated mudstones about 50 m thick, and the Poppit Formation, a succession of intercalated fine to coarse sandstones, siltstones and mudstones (McCann, 1992). A thin but very distinctive black graptolitic shale of late Caradoc age occurs near Whitland and possibly in discontinuous outcrop to the east and west. On the basis of geochemical and mineralogical studies it has been equated with the organic-rich Nod Glas facies of central and North Wales (Temple and Cave, 1992).

Ordovician: Ashgill

Most of the central and northern part of the survey area is dominated by rocks of Ashgill age. In the Crymmych area, the Mydrim Shales are overlain unconformably by the arenaceous Clogue Slates, 150 m thick, carrying *Dicellograptus anceps,* and the Freni Fawr beds, a 300 m succession of interbedded turbiditic sandstones and mudstones, with a conglomerate consisting of sandstone, mudstone and shale pebbles in a silicified matrix at the type locality (Evans, 1945). To the east of Newcastle Emlyn, a lithologically similar succession is recorded by Anketell (1987). Grey banded mudstones with rare cross-laminated siltstone bands of the Tresaith Formation are followed by the sandstones, mudstones and gritty mudstones of the Llangranog Formation. In contrast, in the south of the area, rocks of Ashgill age comprise neritic sediments with conglomerates, thin sandstones, calcareous mudstones and fragmented outcrops of impure nodular limestones (the Shoalshook Limestone), indicating deposition in a relatively shallow-water environment.

Silurian: Llandovery

Rocks of Llandovery age form the eastern margin of the survey area. There are no abrupt lithological contrasts between the Ordovician and Silurian rocks, although the Lower Llandovery generally displays more pronounced facies variations with rapid changes in sandstone to mudstone ratio compared to formations above or below it. Faunal changes serve to define the boundary. Anketell (1987) mapped three formations in the area to the north and east of Newcastle Emlyn, principally on the basis of coastal exposures. The oldest, the Gaerglwyd Formation, 110 m thick in the type section, follows conformably unbedded grey mudstone of the Llangranog Formation, and consists principally of laminated dark grey mudstone, locally pyritic and homogeneous, with rare sandstones. These rocks pass conformably up into the Allt Goch Formation, which is characterised by well-bedded turbidite sandstones, up to 20 cm thickness, and siltstones. It is succeeded abruptly by pale grey mudstones of the middle Llandoverian Cefn Cwrt Formation, the youngest formation described from the survey area.

Structure

The Caledonian orogenic events generated east to north-east trending folds with a broadly axial planar cleavage. Folds are of different magnitudes, varying from regional structures with wavelengths of c. 12 km, to major folds with 3 km wavelengths and minor folds with wavelengths ranging from a few centimetres to a few metres (Anketell, 1987). The regional-scale folds from north to south are the Llangranog Syncline, Capel Cynon Anticline, Teifi–Llangeler Anticline, Central Wales Syncline and Tywi Anticline. These stuctures are not simple folds but comprise a faulted complex of fold structures. Folds are mostly upright or steep and south-east verging with steeply north-west dipping axial planes, their geometry being influenced to varying degrees by basement fractures (Woodcock, 1984). Along the Tywi lineament to the north-east of the survey area, near Llanwrtyd, north-west dipping thrust faults have been mapped, and near Carmarthen Cope (1979) records moderately dipping thrusts associated with the Caledonian folding which have produced thrust slices of Precambrian to Old Red Sandstone rocks. Similar thrust faults are shown on sections through the other major fold structures (e.g. Anketell, 1987). A progressive change in the direction of vergence from south-east to north-west occurs to the north of an east to north-east trending arcuate zone passing through the Capel Cynon area. This vergence divide, the Glandyfi tract, has been interpreted by Anketell (1987) as delineating the axis of the basin in central and South Wales. Fold plunge is mainly to the north-east except in the central part of the area where horizontal attitudes cause expansion of the Ashgill outcrop.

The major fold and fault zones, often forming distinctive linear features, exert a major influence on the pattern of outcrop. The Llangranog lineament, the most northerly within the project area, is typical. North-east of Cardigan it forms a well-defined structural feature 5–10 km wide characterised by a zone of high strain and involving both strike-slip and dip-slip movements. It has been interpreted as the surface expression of a deep basement fault with a significant strike-slip displacement (Woodcock, 1984; Craig, 1987). Faults, often sub-parallel and anastamosing, commonly display reverse, normal and sinistral oblique-slip on fault planes dipping south-eastwards. The effect on outcrop is demonstrated most clearly by the Pencader Fault Zone on the flanks of the Central Wales Syncline. By downthrowing to the east and cutting across the regional fold trace, it effectively determines the eastern boundary to Ashgill rocks in the survey area and preserves Llandovery rocks in the core of the Central Wales Syncline (Anketell, 1987).

Superficial deposits

Although this part of south-central Wales has undergone more than one episode of glaciation, deposits of glacial drift from the earliest Wolstonian period ('older drift' of Charlesworth, 1929), of mainly Irish Sea provenance, are only present in highly dissected and restricted outcrops. The outer limit of the latest Devensian (Weichelian) glaciation passes west of Carmarthen and south of Cardigan Bay, excluding much of the Preseli Hills and the catchment of the Afon Taf (Bowen, 1973). In these areas, 1–2 m of periglacial head deposits accumulated on valley sides during the preceding interglacial period from the reworking of earlier glacial material and the in-situ weathering of bedrock. During the Devensian, competing ice flows, one from the Irish Sea, and the other from the Welsh mountains to the east deposited a variety of glacial sediments including lodgement and solifluction tills, and fluvio-glacial sands and gravels. The most extensive meltwater deposits are found at Banc-y-Warren 2 km north-east of Cardigan where thicknesses of >40 m of laminated sands and interbedded gravels have been recorded (Harris and Donnelly, 1991).

Tills deposited by Irish Sea ice containing a high proportion of marine silt with shell fragments are well developed in coastal exposures near Cardigan Bay and south-east of Carmarthen. Further inland the deposits of the Teifi valley, for example, comprise up to 4 m of matrix-supported grey till with abundant mudstone-siltstone clasts of mainly local derivation. These lithologies were also observed to form an important constituent of the sand-size fraction in drift deposits throughout the area. Proglacial outwash and recent alluvial sands and gravels often overlie the tills to thicknesses of several metres on the main valley floors. Many of the pre-glacial valleys are choked by drift, sometimes causing dry meanders and spillways due to abandonment by post-glacial rivers.

Estuarine intertidal mud-flats and marshes composed of silt and clay-rich sediment grading seawards into coarser sand-grade material are developed extensively in Carmarthen and Cardigan Bays. In the former area a network of dendritic tidal channels has resulted in reworking of large areas of the flats at distances of up to 5 km from the coast. Colonisation of the highest flats has produced wide expanses of salt marsh flooded only by the highest tides. The extent to which these deposits and associated dune sand reflect fluvial as opposed to reworked glacial and interglacial deposits of partly marine origin is uncertain. Coastal exposures a few kilometres south-east at Broughton Bay, for instance, show a complex glacial stratigraphy with marine tills containing shell fragments overlying raised beach and head deposits, in turn overlain by soliflucted till, colluvium and blown sand (Harris and Donnelly, 1991).

GEOCHEMICAL DRAINAGE SURVEYS

Reconnaissance survey data, which contains analytical results for samples collected in the Trelach–Llanglydwen area (Figure 1) after the publication of Cameron et al. 1984, are described together with data for follow-up panned concentrates collected during this survey in the catchments of the Afon Taf and Afon Teifi. The follow-up sampling was necessary to allow a more detailed evaluation of the distribution of monazite in these river systems than was possible using the reconnaissance data alone.

Reconnaissance drainage survey data

All samples, including those obtained after the work reported in Cameron et al. (1984), were collected, prepared and analysed following the methods outlined in that report. Analytical data for 368 panned concentrate samples collected over an area of 355 km^2 during these reconnaissance surveys are summarised in Table 2. Included in the table are all the elements common to the reconnaissance and follow-up surveys. The complete dataset is available from the MRP database.

Table 2 Summary statistics for the chemical analyses of 368 panned concentrates collected during reconnaissance drainage surveys of the Preseli Hills and adjacent areas

Element	Mean	Standard Deviation	Percentiles 25th	 50th	 75th	 90th	Min.	Max.
Ni	55	31	35	47	64	98	8	188
Cu	44	128	11	17	28	69	<6	1451
Zn	160	505	97	128	155	184	35	9915
Zr	433	496	200	266	390	950	130	4270
Mo*	-	-	<2	<2	<2	3	<2	19
Sn	76	176	9	28	77	157	<9	2455
Ba	661	1328	352	495	650	920	<27	19299
Ce	19400	27700	730	5270	29400	63000	37	137000
Pb	219	1225	33	55	95	283	<13	21884
U*	-	-	<2	10	20	49	<2	116

* High proportion of data below the detection limit

Figure 3 shows the histogram and cumulative frequency plot (A) for the logarithmically transformed Ce in panned concentrate analyses from the reconnaissance dataset. Overall, the transformed data are negatively skewed, a feature which is more commonly associated with some major element distributions. Analysis of the cumulative frequency plot (Sinclair, 1976) suggests the presence of three approximately lognormal populations, and the absence of a distinct inflection between 200 ppm and 6.3% Ce indicates that a high proportion of the data is drawn from a single anomalous population, related to the presence of nodular monazite in the pans. At very high concentrations (>6.3% Ce), the data show some evidence of top-censoring, probably due to poor analytical sensitivity at very high concentrations.

A small number of very low Ce values, forming the lowest of the three discernible sample populations, are attributable to samples derived from Ordovician volcanic rocks and associated intrusions in the Preseli Hills. A higher population, with a high proportion of values in the range 125 to 200 ppm, is related to monazite-deficient lithologies in the sedimentary succession, notably coarse-grained arenaceous rocks of mainly lower Ordovician age.

Relative to panned concentrates, the cumulative frequency plot for Ce in <150 μm (100 mesh) stream sediments (B in Figure 3) shows little variation and poor geochemical contrast between sites known to contain abundant monazite and those with little or none. This is due to the relatively coarse grain size of the nodular monazite, which is largely screened out when producing the <150 μm fraction of the sediment.

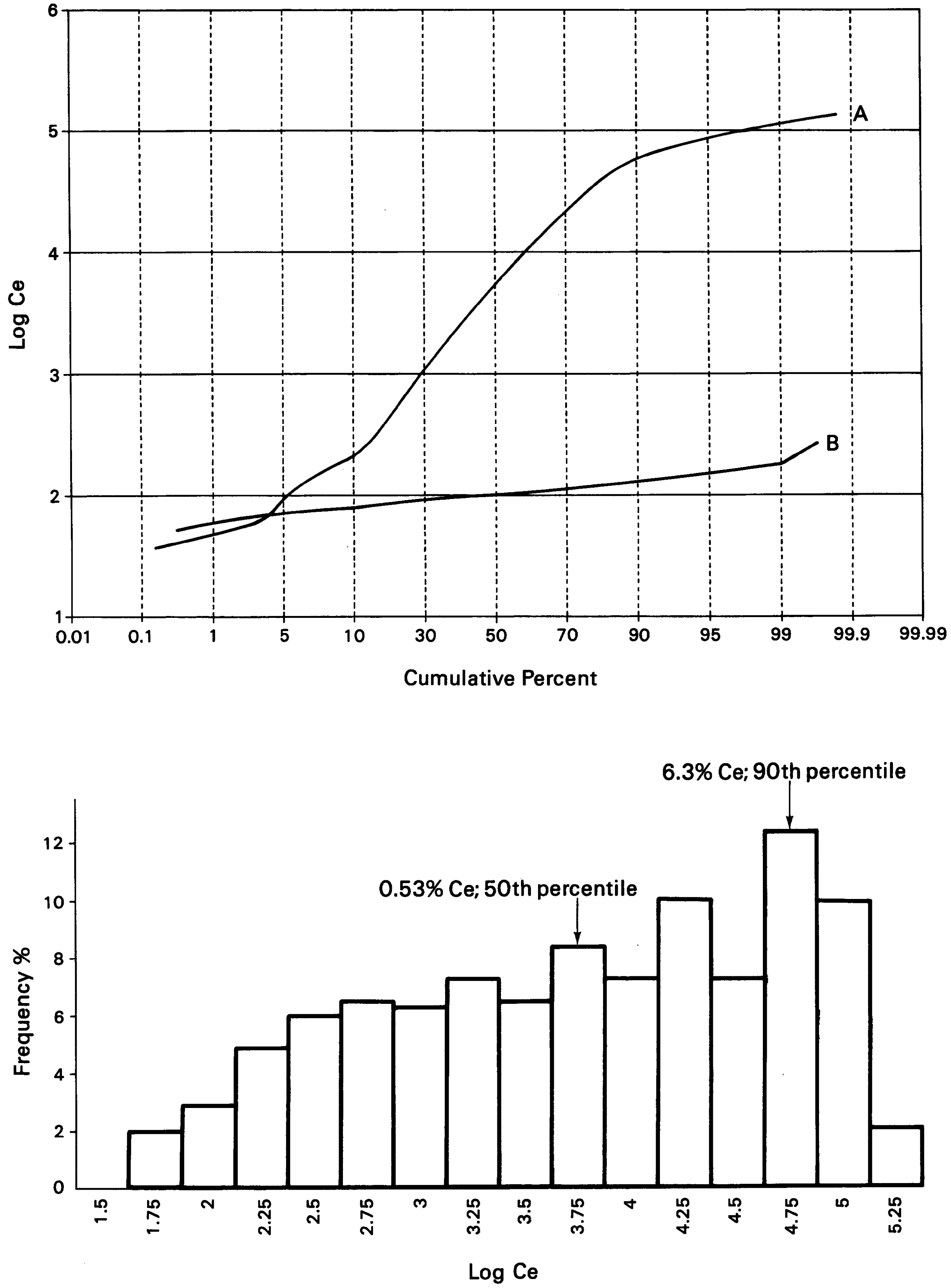

Figure 3 Histogram and cumulative frequency (A) plots of the cerium content in ppm of 368 panned concentrates collected during reconnaissance drainage surveys of the Preseli Hills and adjacent areas, and the cumulative frequency plot (B) for the cerium content in ppm of $<150\ \mu m$ fraction stream sediments from the same sites

Table 3 Summary of positive inter-element Spearman-rank correlations derived from the chemical analyses of 368 panned concentrates collected during reconnaissance drainage surveys of the Preseli Hills and adjacent areas.

Element	Correlation coefficient 0.2–0.4	0.4–0.6	0.6–0.8	>0.8
Ni	Cu, Ba, Pb	U	Ce	
Cu	Ni, Mo, Sn	Zn, Ba, Pb		
Zn	Mo, Pb	Cu, Ba		
Zr	Pb			
Mo	Cu, Zn, Pb			
Ba	Ni, Pb	Cu, Zn		
Ce			Ni	U
Pb	Ni, Zn, Zr, Mo, Ba	Cu, Sn		
Sn	Cu, U	Pb		
U	Sn	Ni		Ce

Because of the complexity of the data distribution, statistical treatment has been kept to a minimum and inter-element relationships were examined using a non-parametric statistical method (Table 3). Except for Ni and U, there are no significant correlations between Ce and other elements determined in the reconnaissance panned concentrate survey. The strong Ce-U correlation is explained by monazite incorporating U into lattice sites (Clark, 1984). The Ni-Ce correlation is considered to be spurious, caused by analytical interference from high Y concentrations in monazite-rich samples. The paucity of positive Ce correlations is consistent with the results of Cooper et al. (1984, 1985) who observed that Ce variation in panned concentrates from the Berwyn Hills and Harlech Dome was largely independent of the other elements analysed.

Distribution of Ce anomalies

Spatial distribution of the Ce levels in panned concentrates from the reconnaissance survey is illustrated in Figure 4 using solid circles proportional in radius to element concentration. To improve resolution and aid interpretation, values exceeding the 90th percentile (>6.3% Ce) are shown as hatched circles. The regional-scale anomaly on which this work is based lies mainly, but not entirely, over the outcrop of Ordovician sedimentary rocks of Llanvirn to Ashgill age. Since the high values extend to the margin of the reconnaissance survey area in the east and north, the full extent of the anomalous area is unknown, but it is estimated to exceed 200 km^2. Nearly all of the major headwater tributaries of the Afon Taf, including the Afon Gronw, Afon Cynin, Afon Cywyn and Dewi Fawr, which drain exclusively mudstones and shales of Ashgill age, contain percentage levels of Ce, many exceeding 6.3%. The largest anomalies (6.3–13.7%, Figure 4) are located in the Afon Tigen, a relatively small, fast-flowing stream with a catchment area of 6 km^2 which enters the Afon Taf at Llanglydwen [SN 1801 2676]*. Exceptionally high values in the range 12.2–13.7% Ce are recorded over a distance of 2.2 km in the lower two thirds of the stream section close to the faulted Caradoc–Ashgill junction. It is not certain whether these very high values are a product of the geology, weathering, erosional or depositional conditions in the stream catchment, but confirmation of the very high values in the follow-up survey (Figure 6) indicates that sampling bias caused by over-panning to a smaller than average concentrate size was not an important factor.

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* National Grid Reference

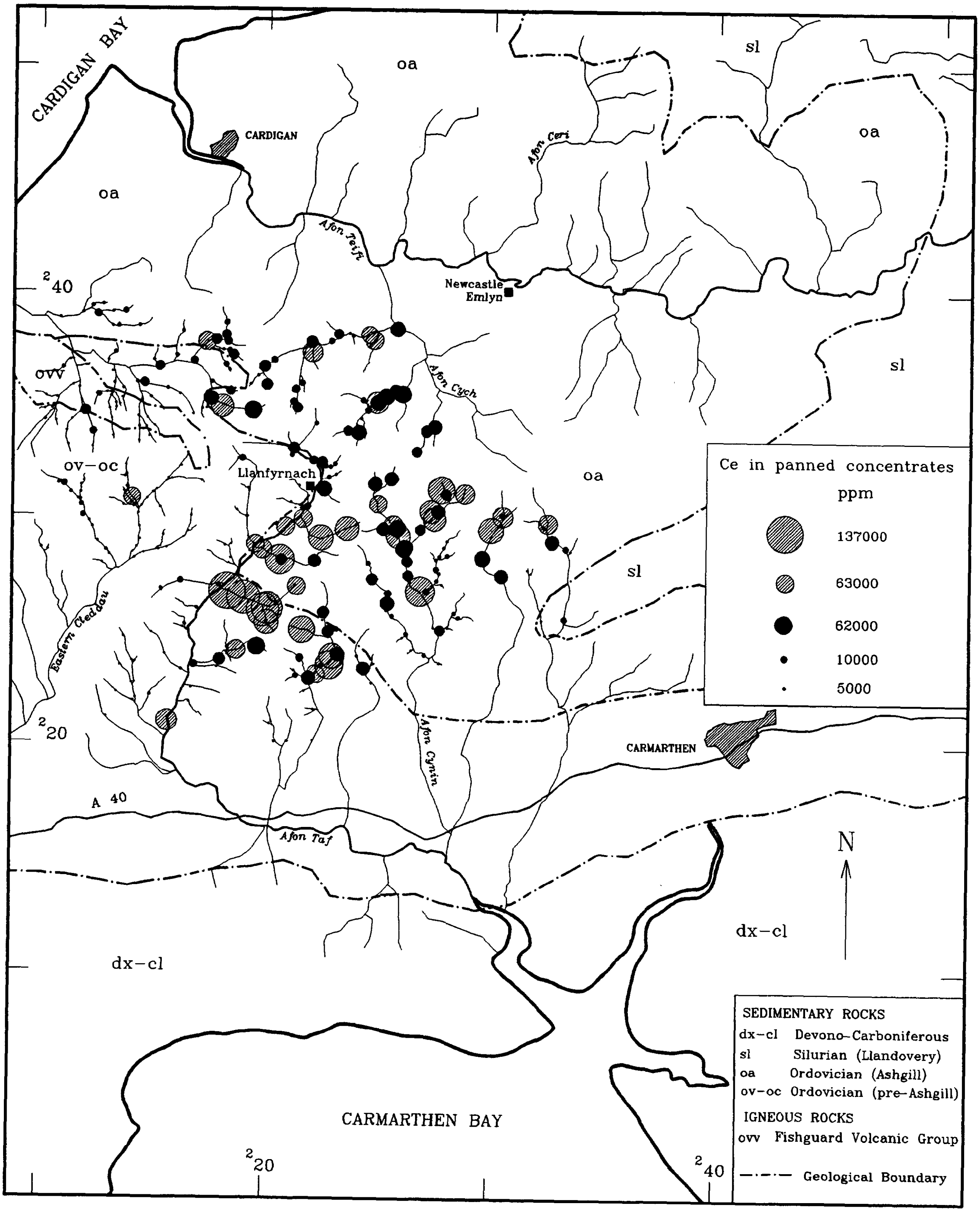

Figure 4 Geographical distribution of cerium in reconnaissance survey panned concentrates. The diameter of the circle denoting each sample point is proportional to the cerium content of the sample

Of the northward-draining tributaries of the Afon Teifi, only the Afon Cych with its entire catchment in rocks of Ashgill age was sampled. Here, persistently high Ce values extend downstream from the headwaters to the lowermost sample site 2 km above the confluence with the Afon Teifi (Figure 4).

A notable exception to the general association of high Ce levels in panned concentrates with catchments containing Ashgill rocks occurs in the Afon Sien [SN 26 24], a southward-flowing tributary of the Afon Cynin. Here, Ce values are lower in samples from 10 consecutive sites extending over a 4 km length of the river (range 940 ppm to 1.7%). Field observations suggest that the change in abundance of Ce may correlate with lithological variation, since a significant increase in the proportion of arenaceous clasts was noted in the sediments of this catchment.

Ce levels are distinctly lower towards the western margin of the survey area, and tributary drainage of the Afon Nyfer and Eastern Cleddau, flowing away from the high ground occupied by the igneous rocks of the Preseli Hills, contain the lowest Ce values in the project area. The igneous rocks, which contain levels of Ce typical of these lithologies, clearly exert a diluent effect on the high levels generated from the sedimentary rocks. This geochemical change coincides closely on a regional scale with the geology at outcrop, implying that glacial dispersion has made little impact on the distribution of Ce anomalies in drainage at this scale. Only a modest increase in Ce occurs as these streams traverse eastwards into Ordovician shales and mudstones of pre-Caradoc age. However, increased Ce levels over rocks of similar age in the lower reaches of the Afon Taf and Afon Gronw may reflect a significant component of stream sediment derived from more fertile Caradoc–Ashgill rocks, dispersed southwards by high-energy, headwater streams.

Hydrological factors, such as stream discharge conditions related to channel width, gradient, and flow velocity also appear to influence Ce abundance. The highest values tend to be located in high-energy, deeply incised channels, often floored by bedrock. Several low-order anomalies (<8000 ppm Ce) lying within the central anomalous zone are apparent in minor streams of less than 500 m in length or in the first 100–200 m of sluggish headwater streams. A common feature of these environments is the absence of active down-cutting, resulting in failure of the stream to erode bedrock. Under these low-energy conditions stream flow is generally insufficient to remove the fine fraction from the clay-rich drift and there is little evidence of the fluvial sorting necessary to produce a lag deposit of heavy minerals .

Trace elements in stream sediments and to a lesser extent in panned concentrates are often characterised by smooth anomaly decay patterns downstream of a single source (Hawkes, 1976). In marked contrast, the panned concentrate data from the Newcastle Emlyn area display a regional-scale Ce anomaly with no evidence of regular decay away from such a source. This behaviour is consistent with a very large, dispersed source from which Ce-bearing heavy minerals have been liberated during weathering and upgraded during fluvial processes.

Follow-up drainage survey

Sampling and analysis

Follow-up panned concentrate samples were collected using the same methodology as that employed in the Preseli Hills reconnaissance survey by Cameron et al. (1984), with the addition of weighing all size fractions.

Table 4 Estimated monazite content of alluvial sediment samples from the catchments of the Afon Teifi and Afon Taf

Sample No. RAP	Grid Ref. [SN]	2–50 mm Weight kg	<2 mm (dry) Weight kg[+]	Concentrate Weight g	% Monazite in <2 mm[*]	% Monazite in <50 mm
101	1802 2675	12.4	3.6	187	1.65	0.370
102	1922 2645	12.2	4.1	58	0.49	0.125
103	2725 2630	23.4	4.2	73	0.46	0.070
104	2725 2629	28.8	5.5	66	0.14	0.022
105	2695 1963	39.9	6.0	91	0.13	0.017
106	1630 2222	21.3	4.2	82	0.17	0.027
107	3408 4108	12.8	2.8	113	0.29	0.052
108	3391 4069	2.5	4.0	105	0.33	0.200
109	3746 4042	23.6	3.4	209	1.60	0.200
110	3742 4014	15.5	3.1	115	0.39	0.065
111	3895 3925	0.2	3.2	67	0.02	0.015
112	3875 3892	12.6	4.2	74	0.02	0.005
113	3541 4122	7.2	3.8	72	0.007	0.002
114	3168 4075	9.7	7.8	82	0.06	0.026
115	2595 4232	23.5	3.5	72	0.21	0.027
116	2303 4359	25.6	2.8	68	0.35	0.035
117	1864 1682	16.4	4.8	138	0.16	0.035
118	2248 1608	10.0	3.0	93	0.32	0.075
119	2250 1610	4.0	3.1	54	0.01	0.004
120	3093 4287	11.0	5.7	89	0.26	0.090
122	2588 4252	20.0	4.1	68	0.03	0.006
123	1897 4520	63.0	3.1	88	0.10	0.005
125	1618 4822	0.10	17.5	173	0.006	0.006
126	1586 4815	3.8	6.7	75	0.04	0.026
127	2090 1799	28.0	3.2	56	0.03	0.003
128	2775 1733	26.0	3.1	68	0.21	0.023
129	2910 1886	10.0	3.6	45	0.05	0.014
130	2910 1886	5.7	1.9	56	0.06	0.014
131	1641 4664	4.0	3.9	58	0.03	0.014
132	2672 3787	13.0	3.9	50	0.27	0.063
135	1758 4590	0.5	4.2	82	0.006	0.005

[+] Dry weight of <2 mm fraction estimated from the average water content of two 1 kg splits of <2 mm sediment dried at 80° C.

[*] Monazite content of dried <2 mm sediment calculated from the Ce content of the panned concentrates, assuming that these monazites contain 30% Ce, that all Ce is held in monazite, and that all monazite is retained in the concentrate.

Samples were collected from 31 stream and river sites (Table 4). Tributary streams were sampled normally within 200–500 m of the main river, but site selection was constrained by run-off conditions, prolonged heavy rain during the sampling programme limiting access in the larger streams and rivers to shallow water embayments close to the bank. At these locations samples were obtained by deep digging into shallow-water, bar-tail deposits and, where necessary, amalgamating sediment from several closely spaced sites. Elsewhere, sampling was undertaken from armoured gravel or cobble beds near to bar-heads and occasionally, for comparison purposes, from the sandy deposits in the bar-tail or eddy pools. In the smaller streams active (mid-channel) sediment was collected from as deep as possible in the stream bed (usually over the 30–60 cm interval). Sediment was wet screened through a 2 mm (8 mesh) sieve into a wooden pan after discarding any clasts larger than 5 cm diameter. After draining off excess water, the weights of wet >2 mm and <2 mm fractions were recorded. An average weight of 4.5 kg of <2 mm (8 mesh) wet sediment was then split into two roughly equal portions, each of which was panned to produce a concentrate averaging about 70 g. At some sites the panning operation was stopped at the 100–200 g level to avoid loss of monazite. The weights of the concentrates were recorded and two control tests were carried out to establish the average moisture content of the <2 mm unpanned material.

In the laboratory the panned concentrate samples were dried, mixed, and reduced by riffle splitting to approximately 50% of their initial weight before grinding in agate mills to yield a product in which >95% of the sample had a particle size of <30 μm. A 12 g subsample was further ground with 3 g of 'elvacite' binder prior to pelletising and analysis by X-Ray Fluorescence Spectrometry for a range of trace elements including Ce, La, Nb, Th, and Y (Table 5).

The accuracy of Ba and Pb XRF data from earlier surveys (Cooper et al., 1984; Cameron et al., 1984) was affected by interference from high concentrations of REE (Ce >c. 3000 ppm), but changes in machine parameters have eliminated this problem in these new data. Ni values in some monazite-rich samples were enhanced by up to 30% due to spectral overlap with the Y K-alpha peak, but the effect on this investigation is very limited (maximum reported Ni value in the samples analysed is 98 ppm; Table 5). Severe REE interference affected V, Cr and Co determinations (not reported). The maximum limit of calibration was not exceeded for Ce (20%), and was only exceeded for La (2.5%) in two samples. Limits of detection for La and Ce of 2 and 7 ppm respectively were well below the minimum reported values in these samples.

Based on the XRF data for cerium, material from four monazite-rich concentrates was analysed for the full range of REEs by Inductively Coupled Plasma Mass Spectrometry using a high-sensitivity analytical technique developed recently by the BGS Analytical Geochemistry Group (Appendix). To increase the proportion of monazite and to reduce the amount of other heavy mineral phases and composite grains, the samples were sieved to produce an enriched (0.5–1.0 mm) monazite fraction for analysis. Data for Gd (affected by La interference) and Ho (used as an internal standard) were not obtained.

Results

A summary of the analytical data for the panned concentrates is presented in Table 5 and significant positive Spearman-rank correlation coefficients are summarised in Table 6. The REE analyses of the monazite concentrates are listed in Table 7. Figure 5 illustrates Ce co-variation with other elements concentrated in monazite, and spatial distribution plots for Ce and Th are shown in Figures 6 and 7.

Site inspection of panned concentrates revealed substantial amounts of grey ellipsoidal monazite nodules at all sites where analytical values exceeded 1% Ce. In the upper reaches of the Afon Taf at Llanglydwen a few grains of coarse weathered galena were noted in the panned concentrate, possibly related to downstream dispersion from the old Llanfyrnach silver-lead mine workings (Foster-Smith, 1981). To the east of Llanglydwen, a grain of gold in a sample from the Afon Tigen confirmed an earlier observation of alluvial gold identified from this catchment in the reconnaissance survey. Dark heavy minerals, which include Fe and Fe-Ti oxides, were present in very small amounts (estimated as <2% of total heavy mineral fraction), and zircon was not observed except in samples from the Teifi estuary.

The dimensions of the regional-scale anomaly indicated by the results of the reconnaissance survey are increased considerably by the new data, and it is probable that the anomalous area extends at least as far as the Ordovician–Silurian boundary to the north-east of the Teifi valley (Figure 6).

Table 5 Summary statistics for the chemical analyses of 31 follow-up panned concentrate samples

Element	Mean	Standard Deviation	Percentiles 25th	50th	75th	90th	Min.	Max.
Ni	46.5	21.1	32	43	62	67	11	98
Cu	43.4	91.6	15	17	25	70	<2	471
Zn	126.7	42.5	94	128	150	165	50	258
Y	450.1	417.8	102	370	602	1069	27	1633
Zr	358.4	375.6	184	233	316	585	137	1735
Nb	43.6	28.4	19	35	57	85	14	111
Mo	-	1.5	<1	<1	1	3	<1	5
Sn	83.4	85.6	26	57	108	147	11	363
Ba	449.4	154.8	373	422	512	626	180	929
La	7405	8309	1245	4616	9478	20168	362	30480
Ce*	2.85	2.89	0.56	2.17	3.76	7.76	0.09	10.51
Pb	209.1	517.2	38	62	108	237	10	2738
Th	430.9	412.5	90	308	806	947	32	1608
U	39.5	32.7	12	30	60	98	2	116

* Values in per cent; all other values in ppm.
For individual determinations reporting below the detection limit, mean values have been calculated using the minimum detectable value.

A strong positive correlation exists between Ce and the Y, Nb, La, Th and U content of the samples (Table 6; Figure 5), reflecting the concentration of these elements in the nodular monazite. Except for the Ce-Ni correlation (which is due to analytical interference from Y), other inter-element correlations are much less strong, indicating that the process which resulted in the concentration of monazite had little influence on these elements. The statistically significant Cu-Pb-Zn-Sn correlations in the dataset are attributed mainly to variation caused by the presence of heavy detrital contaminant phases, although some contribution is also likely from the vein-style base-metal mineralisation recorded in the area.

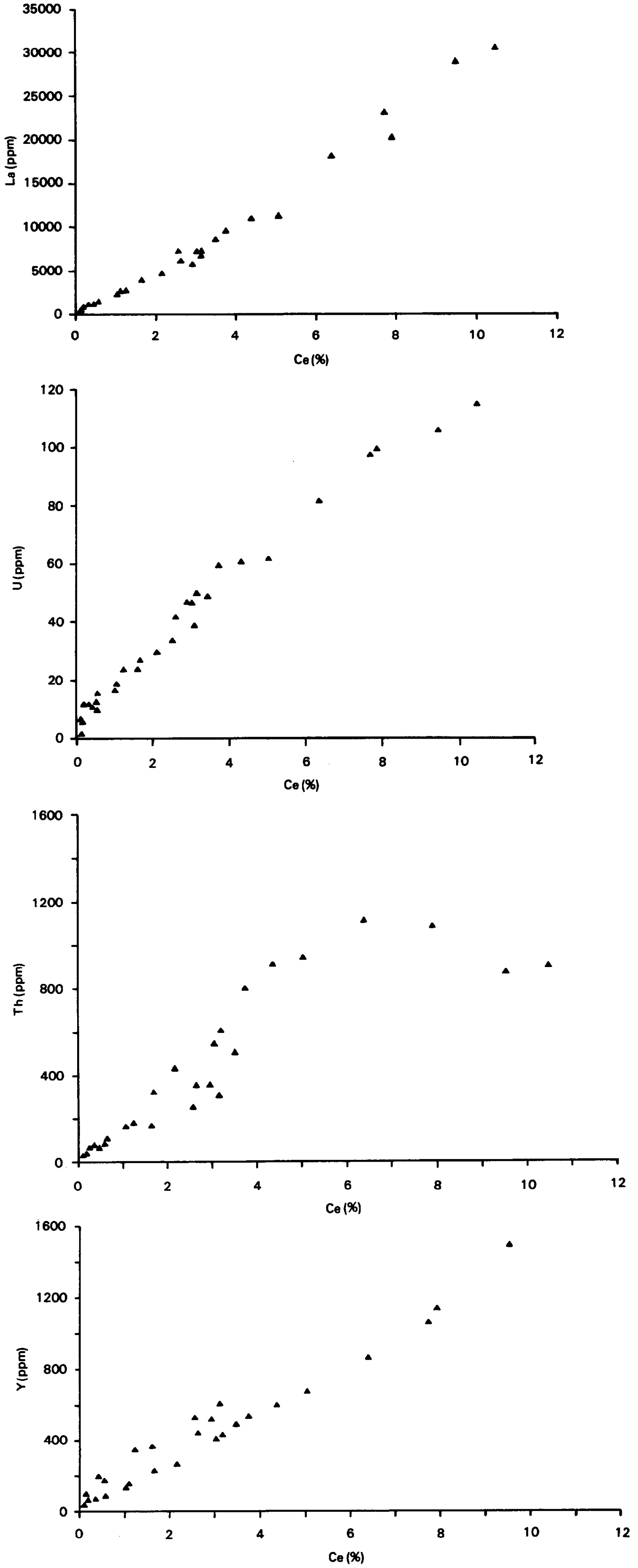

Figure 5 Plots of Ce v La, U, Th and Y content of 31 follow-up panned concentrates

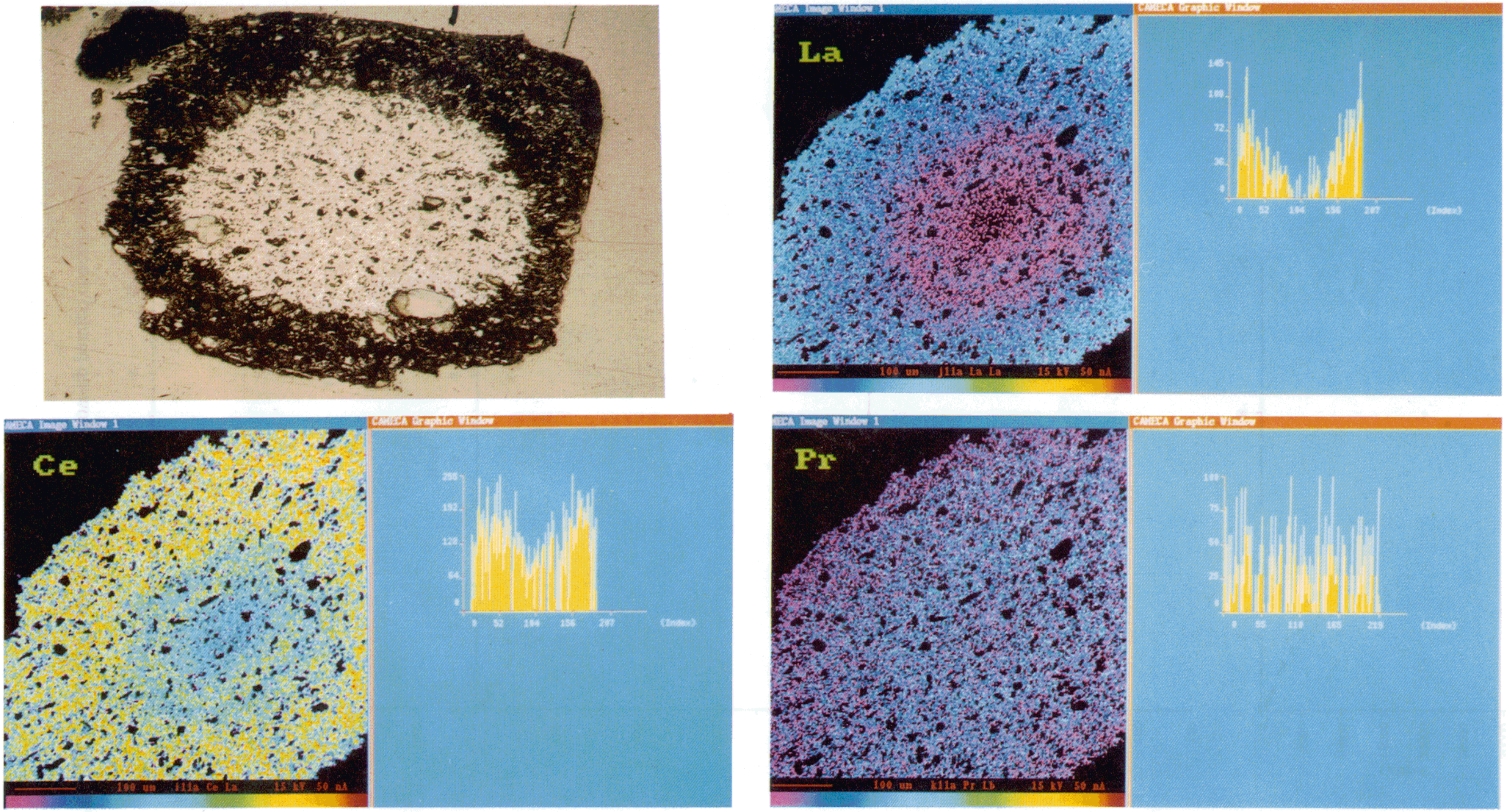

Plate 1 Microchemical maps and traverse plots showing the distribution of La, Ce and Pr in a monazite nodule from sample RAR11 [SN 1994 2671]. The sections are through the centre on the short diameter.

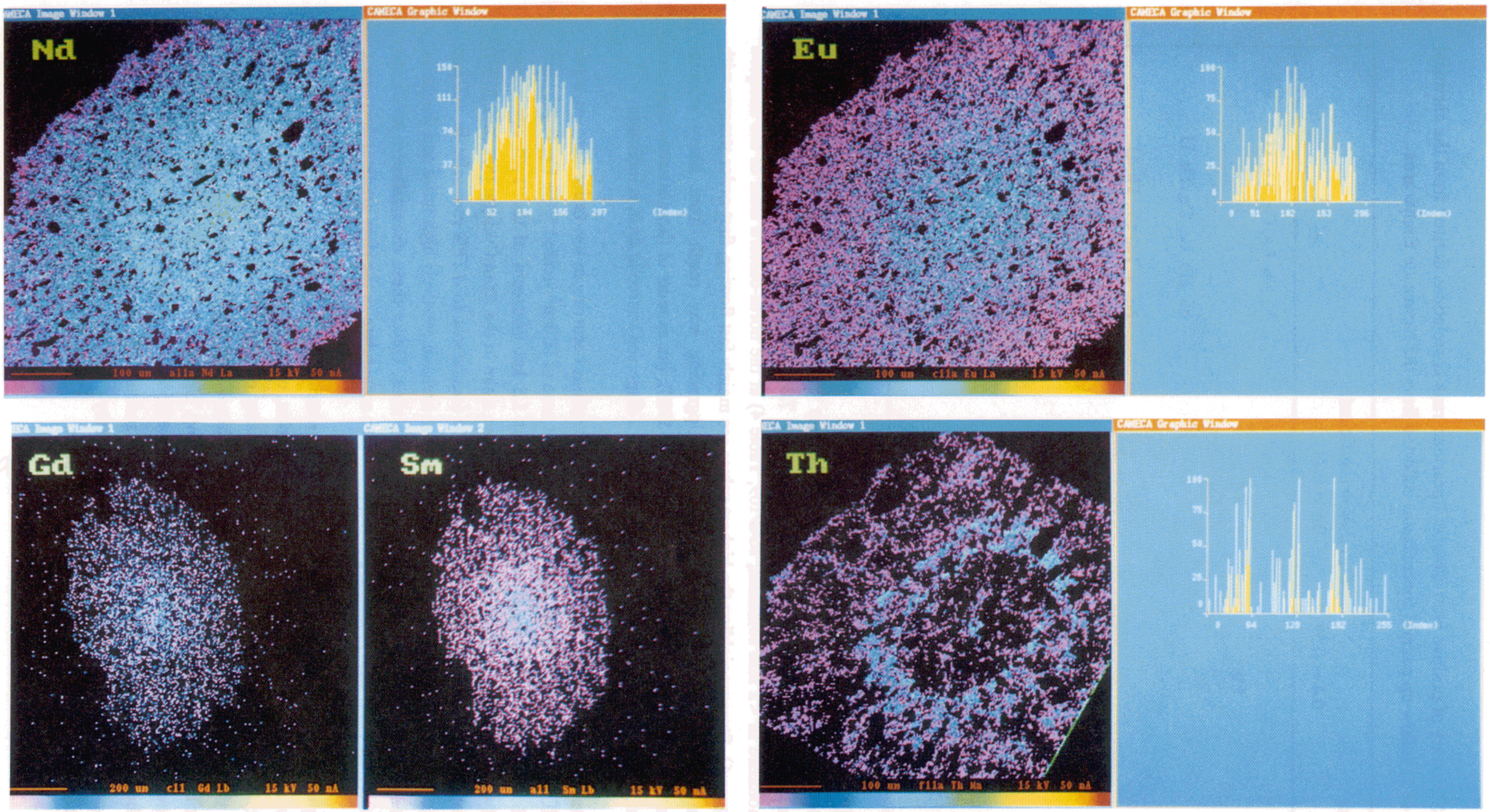

Plate 2 Microchemical maps and traverse plots showing the distribution of Nd, Sm, Eu, Gd and Th in a monazite nodule from sample RAR11 [SN 1994 2671]. The sections are through the centre on the short diameter.

Table 6 Summary of positive inter-element Spearman-rank correlations derived from the chemical analyses of 31 follow-up panned concentrates collected from the Newcastle Emlyn area

Element	Correlation coefficient		
	0.4 – 0.59	0.6 – 0.74	>0.75
Ni			Y, Nb, La, Ce, Th, U
Cu	Pb	Zn	
Zn		Cu	
Y			Ni, Nb, La, Ce, Th, U
Zr			
Nb			Ni, Y, La, Ce, Th, U
Mo			
Sn	Cu, Zn	Pb	
Ba			
La			Ni, Y, Nb, Ce, Th, U
Ce			Ni, Y, Nb, La, Th, U
Pb	Cu		
Th			Ni, Y, Nb, La, Ce, U
U			Ni, Y, Nb, La, Ce, Th

Afon Teifi catchment

An important feature of the new geochemical data for Ce is the presence of very high levels in some north bank tributaries of the Afon Teifi (up to 7.8% Ce at [SN 3746 4042], equivalent to 1.60% monazite in <2 mm sediment; RAP109, Table 4) at the north-eastern limit of the sampled area (Figure 6). Streams yielding the highest values are mainly fast flowing, first-order streams with small catchments (generally less than 5 km^2). Upgrading may result from heavy mineral accumulation at high-energy sites (Fletcher and Day, 1988), but as most of these streams contain a significant bedrock component, a local, as opposed to a dispersed source in drift, is indicated.

In contrast to the usual pattern of the highest concentrations occurring in low-order streams, a site (RAP120, Table 4) in the Afon Ceri with a catchment area of 60 km^2 yielded 5.1% Ce, (equivalent to 0.26% monazite in <2 mm sediment) at a point 1.5 km upstream of the Teifi confluence [SN 3093 4287] and, on the south side of the main river, a site in the Afon Cych (at [SN 2672 3787]) with a comparable drainage area contained 6.4% Ce (equivalent to 0.27% monazite in <2 mm sediment; RAP132, Table 4). Both streams originate in areas of relatively high relief and discharge into broad drift-filled valleys before entering the main river. Under these circumstances monazite, in common with other heavy mineral phases, is likely to accumulate as the river gradient decreases.

Six samples collected from the bed of the main river between Cardigan and the bridge at Pontalltycafan [SN 387 392] contain, with one exception, consistently high Ce values in the range 1.04–3.1% (Figure 6). These results display surprising consistency, especially when account is taken of the restricted access to favourable sample sites due to high flow and the inherent lack of reproducibility associated with heavy mineral sampling. Upstream of the bridge at Pontalltycafan, well sorted coarse-grained sediment from a bar-tail environment (sample RAP111 [SN 3895 3925]) yielded the lowest recorded value for active river-bed sediments in the entire catchment (0.24% Ce; Table 4). This probably reflects extreme local variability due to heavy mineral sorting rather than an upstream cutoff in the dispersion train of monazite.

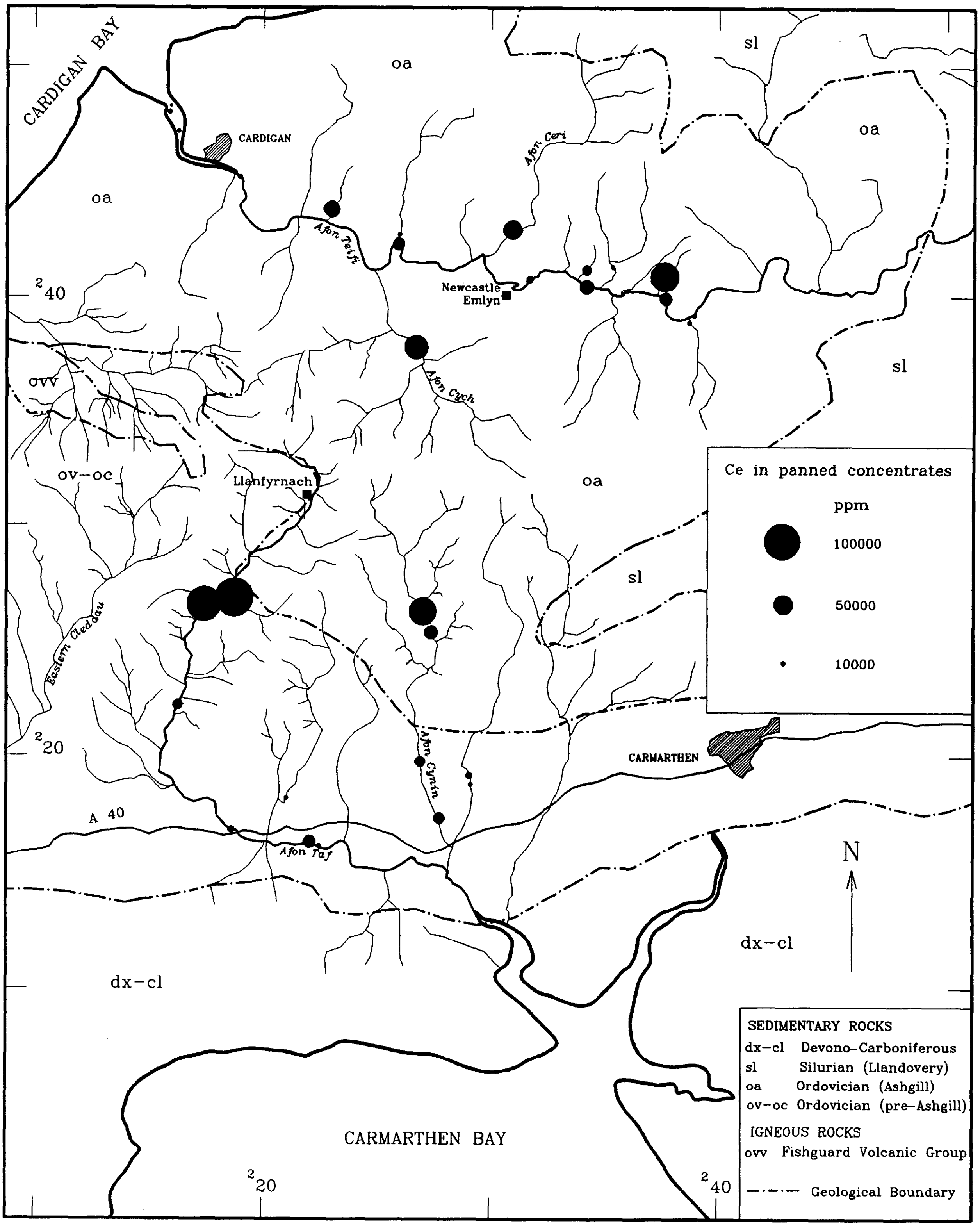

Figure 6 Geographical distribution of cerium in follow-up panned concentrates. The diameter of the circle denoting each sample point is proportional to the cerium content of the sample

Teifi estuary

Samples collected from the estuarine deposits downstream of the river bridge at Cardigan contain concentrations of Ce varying between 973 ppm and 1.09% (Figure 6). These levels, which are on average an order of magnitude lower than in river and stream sediments collected from the upper reaches of the catchment, most probably due to sorting and the presence of only the finest monazite nodules in the clay-rich estuarine deposits, are nevertheless highly anomalous relative to the background values normally associated with alluvial materials. Deep-water channel sediments likely to contain higher concentrations of heavy minerals were inaccessible, sampling being restricted to fine sand and silt-grade alluvium exposed at low tide.

At the seaward end of the estuary two samples, RAP125 and RAP126 contained 0.19% and 1.09% Ce respectively. At the first of these sites, located in an area of extensive tidal flats, the unprocessed sediment was entirely <2 mm in size (Table 4). Several profiles dug to about 1 m depth revealed no obvious colour banding indicative of heavy mineral layering. Samples were collected by bulking material from five pits randomly located within a radius of about 20 m to obtain a reliable estimate of average Ce content of the near-surface sand and silt. Despite the relatively low absolute abundance of Ce in RAP125, mineralogical inspection confirmed the presence of monazite at particle sizes estimated to be in the range 0.1–0.5 mm, considerably smaller than observed in immature river and stream sediments. Less than 200 m to the west, sample RAP126 with a significantly higher Ce content was collected from similar source material reworked by a small stream entering the estuary on the west bank of the Afon Teifi at [SN 157 483]. Since monazite was again present in the same distinctive fine particle size as in RAP125, rather than coarser grains typical of active stream sediments, recent fluvial reworking of the muddy estuarine deposits is the most likely cause of the increased Ce level.

The lowest Ce value (973 ppm) in the follow-up study was reported 250 m downstream of the river bridge in Cardigan, from a sample containing only a very small sand fraction, but rich in silt and clay-grade material. Much of this sediment had accumulated close to the channel margin (<100 m) by processes of vertical accretion involving a large component of fine-grained overbank material. Heavy mineral concentrations are more likely to be present in the less accessible channel lag deposits, where coarser sands result from the lateral erosion of bank material.

With the exception of monazite, zircon was the only heavy mineral noted in appreciable amounts in the estuarine samples. Unlike Ce, Zr reaches its maximum value of 1735 ppm in the fine-grained estuarine deposits, almost an order of magnitude higher than the average value in stream sediments from the Afon Teifi catchment. Zircon generally occurs at particle sizes <0.2 mm in the estuarine materials suggesting that primary grain size and the degree of sorting are the most important factors in determining the heavy mineral content of these estuarine deposits.

Afon Taf catchment

All samples from this catchment were derived from either the main river or its major tributaries. Much of the land occupied by the Afon Taf estuary was unsuitable for sampling because of the broad expanse of salt marsh or sampling was restricted by Ministry of Defence activities.

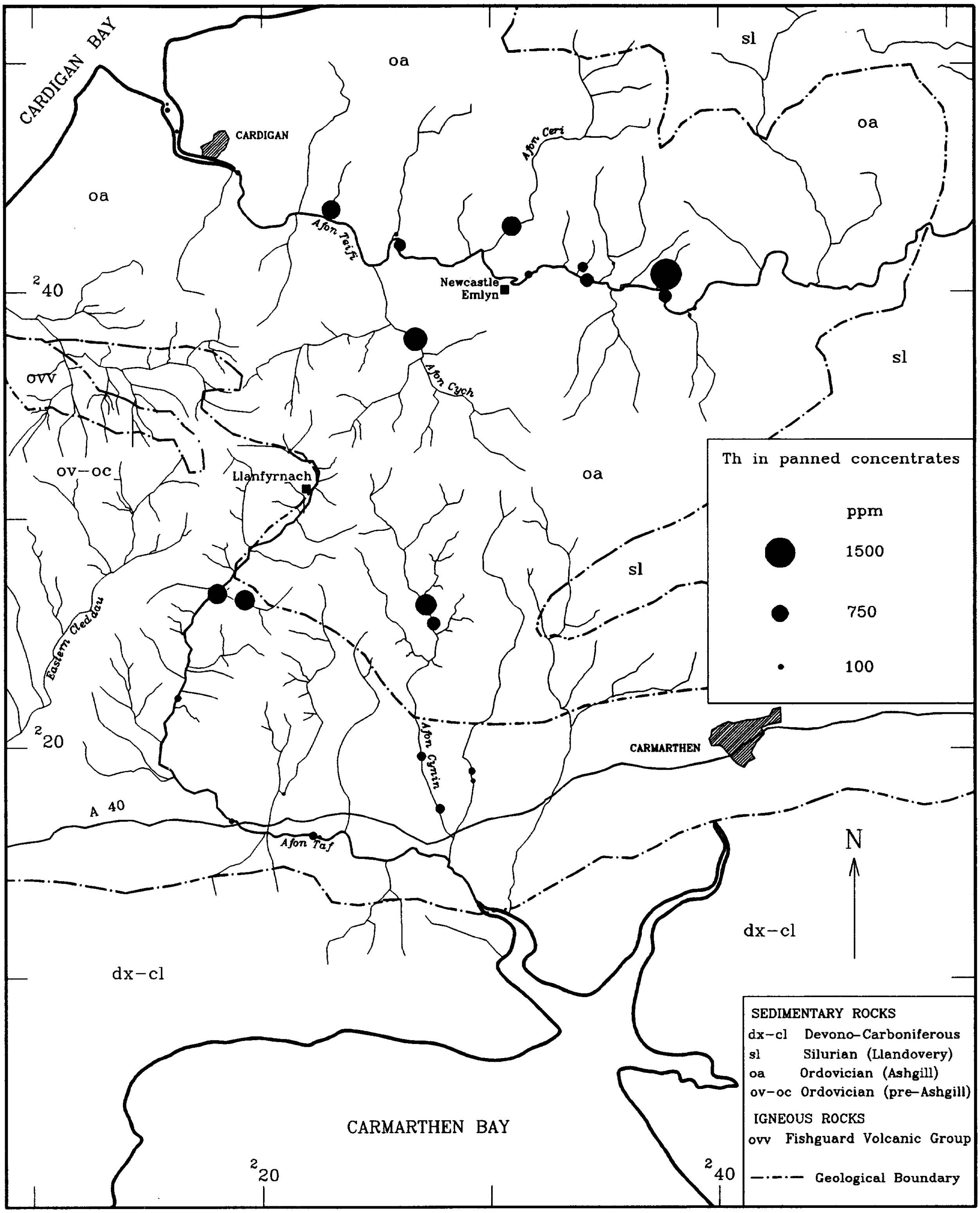

Figure 7 Geographical distribution of thorium in follow-up panned concentrates. The diameter of the circle denoting each sample point is proportional to the thorium content of the sample

Near the head of the Afon Taf, a sample from the Afon Tigen (RAP102 from [SN 1922 2645] containing 10.5% Ce, equivalent to 0.49% monazite in <2 mm sediment) confirmed the extremely high values from the earlier reconnaissance survey. A strong and persistent dispersion train can be traced into the main river approximately 200 m downstream of the confluence between the Afon Taf and the Afon Tigen (RAP101 from [SN 1802 2675] containing 9.5% Ce, equivalent to 1.65% monazite in <2 mm sediment; Table 4). Five kilometres downstream of this point a value of 2.6% Ce (RAP106, Table 4) suggests possible dilution from west bank tributaries which drain rocks of pre-Ashgill age. However, in the main river, percentage levels of Ce extend for at least a further 10 km downstream to the lowest sample site in the catchment between Whitland and St Clears. Here, a value of 3.1% Ce (RAP118; Table 4) from a bar-head site contrasts with a much reduced level of 0.17% (RAP119; Table 4) from sandy sediment at the bar-tail collected only 15 m downstream. This emphasises the high degree of within-site variation and the difficulty of confidently estimating monazite grades in well-sorted river alluvium from relatively small sample volumes. However, the dispersion pattern strongly suggests that nodular monazite is present in the estuarine deposits and that local accumulations may exist.

Thorium content of panned concentrates

High levels of Th are present in all of the Ce-rich follow-up samples (Figure 7), rising to a maximum concentration of 1608 ppm Th in a minor south-flowing tributary of the Afon Teifi (RAP109 [SN 3746 4042]). A high degree of correlation with Ce is observed (Table 6), principally due to the presence of both elements in monazite, but in several samples containing >7% Ce the relationship is less regular (Figure 5), Th tending to show more limited increase or even a decrease above this level of Ce. The reason for this behaviour is not clear, although it may reflect analytical constraints or regional variations in monazite composition, as the effect is most pronounced in samples from the headwaters of the Afon Taf, close to the Caradoc–Ashgill junction.

Based on an average Ce content of 30% in nodular monazite (Read, 1983) and the calculated median Ce/Th ratio of 55 in the panned concentrates, the estimated mean Th content of monazite from this area is about 0.5% (0.53% ThO_2), assuming insignificant amounts of Th and Ce in other heavy minerals. This suggests, and was confirmed later by the analysis of individual grains, that the nodular monazite from this area has the same low Th characteristics as nodular monazites from elsewhere (Donnot et al., 1973; Read, 1983; Milowdowski and Zalasiewicz, 1991), about an order of magnitude less than that of many igneous and metamorphic monazites (Overstreet, 1967).

REE content of panned concentrates

ICP-MS REE analyses of upgraded panned concentrates (containing c. 60% monazite) from four sites in the Afon Taf catchment (Appendix) have been recalculated to total REE = 100% and compared with other occurrences in Table 7. Shale-normalized patterns from the four sites are closely similar and characterised by extreme enrichment of the LREEs with respect to the NASC[1], with maximum enhancement at Sm, and uniformly low levels of the HREEs (Figure 8). Comparison with normalised REE data for panned concentrates from Central Wales (Read et al., 1987) and Brittany (Burnotte et al., 1989) reveals few significant differences, although Ce exhibits small negative anomalies in the project area (Figure 8), perhaps due to more strongly reducing conditions during the growth of monazite in this part of the Welsh Basin.

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[1] North American Shale Composite. Values from Taylor and McLennan (1985)

Table 7 The REE composition of nodular monazite from the Lower Palaeozoic of Wales and Belgium recalculated to 100% REE

	RA101	RA105	RA106	RA103	C. Wales[1]	Belgium[2]
La	22.510	18.729	20.098	17.357	20.90	21.10
Ce	38.340	38.810	45.188	42.82	45.80	46.40
Pr	6.826	6.930	5.577	6.391	6.20	5.30
Nd	25.996	27.984	23.827	26.278	20.80	20.98
Sm	4.589	5.702	3.950	5.353	3.30	3.60
Eu	0.810	0.928	0.626	0.918	0.66	0.60
Gd	N.A.	N.A.	N.A.	N.A.	1.59	1.90
Tb	0.232	0.237	0.177	0.227	N.A.	N.A.
Dy	0.606	0.590	0.487	0.581	0.49	0.25
Er	0.055	0.049	0.044	0.049	0.12	N.A.
Tm	0.005	0.004	0.003	0.003	N.A.	N.A.
Yb	0.026	0.025	0.021	0.018	0.03	0.0070
Lu	0.003	0.003	0.003	0.002	<0.01	0.0005

N.A.: Not analysed [1] : Read et al., 1987 [2] : Burnotte et al., 1989

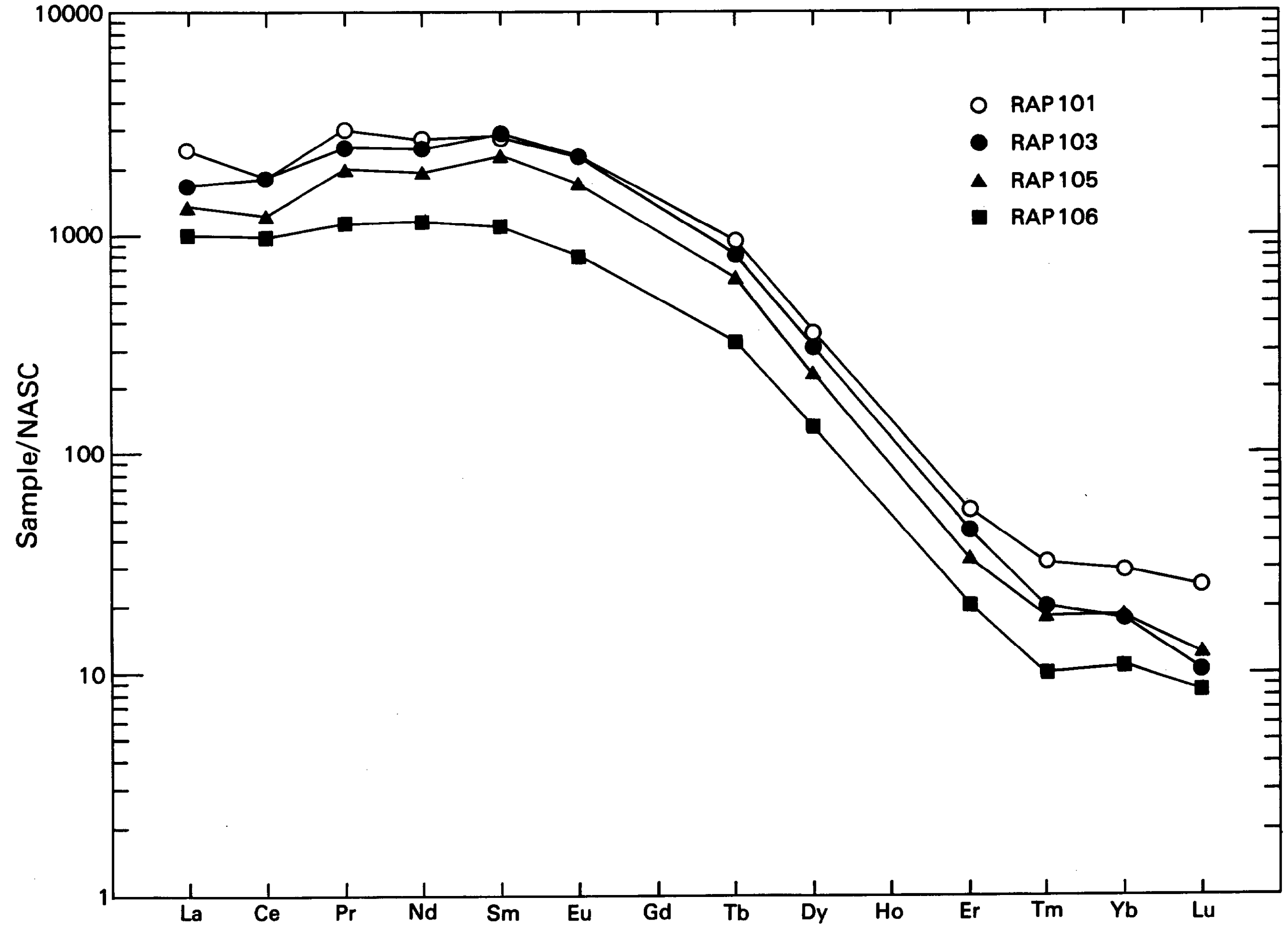

Figure 8 REE concentrations in four nodular monazite concentrates from the Newcastle Emlyn area normalised to the North American Shale Composite (data from Taylor and McLennan, 1985)

No anomalous behaviour is observed for Eu, which therefore apparently behaved as a trivalent REE ion during nodule formation. As a result Eu levels in nodular monazite are much higher than in monazites from igneous sources (Fleischer and Altschuler, 1969), a feature which reflects Eu depletion during igneous fractionation of plagioclase. Regional variation in the Eu and other MREE content of nodules is evident from the data presented in Table 7, the highest levels (up to 50% higher) occurring in the project area.

Implications for estuarine placer concentrations in Wales

The persistence of monazite concentrations downstream to or close to the estuaries of the Afon Teifi and Afon Taf suggests that concentrations of high-Eu, low-Th monazite are likely to be present in the estuaries of other river systems draining Ordovician and Silurian sedimentary rocks of the Welsh Basin. The sediments of the Afon Taf and Afon Teifi catchments are poor in other heavy resistate minerals, but the estuarine sediments derived from some other catchments are potential sources of additional heavy minerals, such as gold.

ROCK GEOCHEMISTRY AND MINERALOGY

Sampling and field observations

Monazite nodules are difficult to recognise in rocks unless the surfaces are fresh and there are well developed bedding or cleavage planes. Recognition of nodules in the project area was hampered by infrequent and poor exposure and weathering, particularly of the more fissile mudstones. These factors prevented any regional or local assessment of the precise distribution of nodules within the succession. A feature of the mudrocks examined throughout the survey area was the lack of well-defined hemipelagic mudstone horizons interbedded with turbiditic sandstones and mudstones. In the Upper Llandovery turbidites of Central Wales this hemipelagite-turbidite variation exerts a primary control on the distribution of monazite nodules (Milodowski and Zalasiewicz, 1991).

Afon Taf catchment

Guided by the distribution of Ce anomalies in panned concentrates, all readily accessible outcrops in the upper reaches of the Afon Taf, Afon Cynin and Afon Nyfer were inspected for nodular monazite. In total, nearly 200 km of minor roads were traversed and approximately sixty outcrops examined in an area of about 160 km^2. Nodular monazite was identified provisionally on rock surfaces at twelve locations and composite 1–2 kg samples of the predominant rock type, a medium to dark grey silty mudstone, were collected for analysis from twenty small roadside quarries or recent road and track excavations (Figure 9).

The rocks in which nodular monazite was provisionally identified ranged in age from Llandeilo to Ashgill. At six sites it was relatively abundant with a frequency of about 1 grain per 15 cm^2 on cleavage or bedding surfaces, whereas at the other six localities it was sparsely distributed at a frequency of about 1 grain per 50 cm^2. Semi-quantitative XRF analysis on hand specimens selected from the three best outcrops ([SN 1794 2671], [SN 2452 3503], and [SN 1649 3684]) subsequently confirmed the presence of nodules. They occur as small (0.2–1.0 mm), dark grey to black, ellipsoidal nodules protruding from cleavage surfaces. Compared with nodules from mid Wales, they have a smaller mean diameter, but are morphologically identical in other respects.

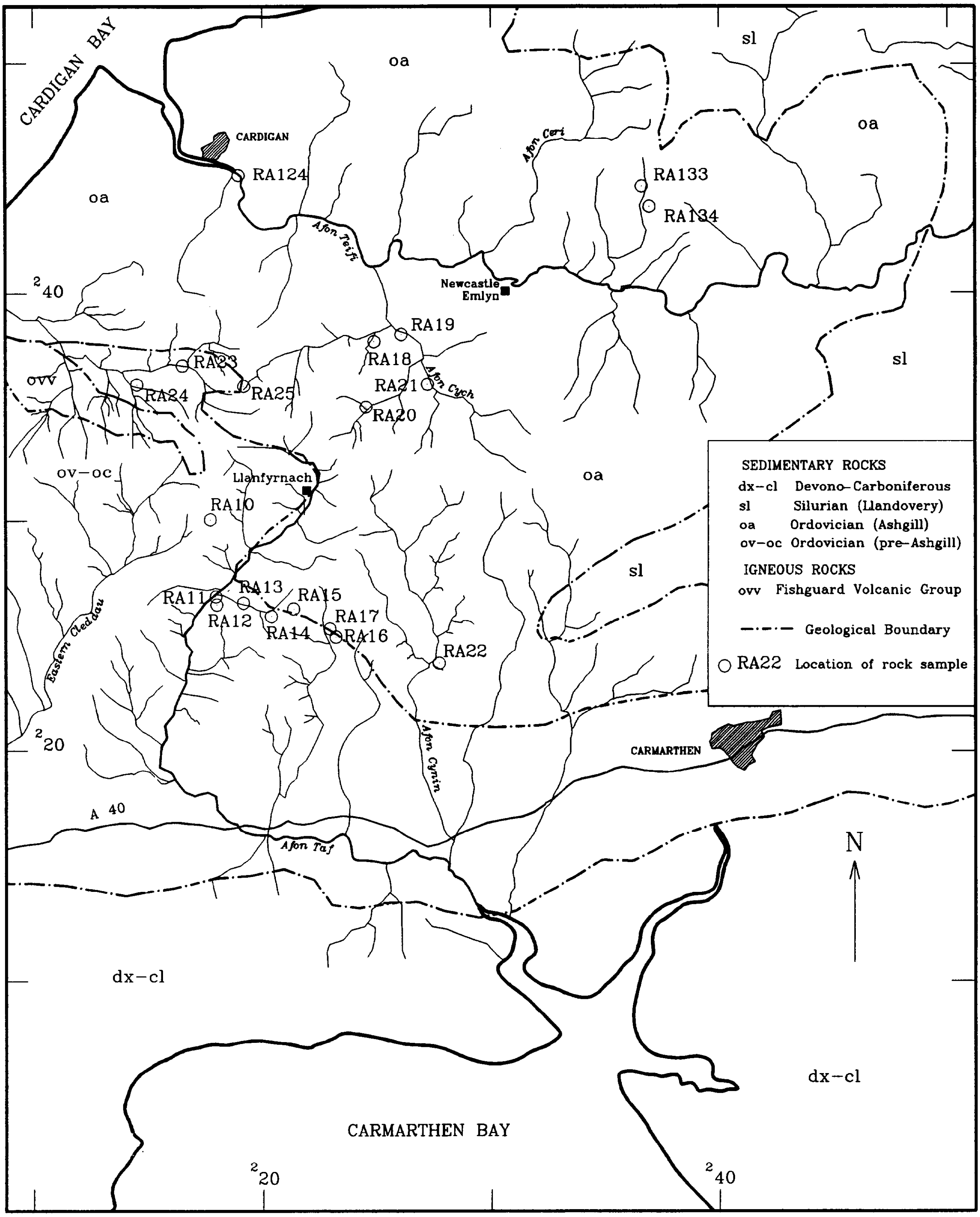

Figure 9 Location of rock sample sites

At the best of these localities, in a roadside cutting 100 m west of the river bridge at Llanglydwen [SN 1794 2671], the nodules can be found all along a recently exposed rock face (90 m long by 3–5 m high) dispersed through the well cleaved, uniform, dark grey mudstone sequence. Based on the close proximity (<100 m) of this occurrence to the conspicuous zone of highly anomalous Ce in panned concentrate results from the Afon Tigen and Afon Taf, it is inferred that many of the major drainage anomalies throughout the area are likely to have nearby sources in bedrock or locally derived superficial deposits.

Other nodular structures, shown by electron probe not to consist of monazite, are also common in these rocks. These tend to be larger than the monazite nodules and may be formed of a number of minerals including quartz. For example, two morphologically identical types of nodule were identified in the sample from [SN 1649 3684]. Smaller nodules in this rock, averaging about 0.3 mm, were confirmed to be monazite by XRF, but a few larger grains of about 1 mm contained neither phosphate nor REEs.

Afon Teifi catchment

A rapid reconnaissance of accessible outcrops in the Teifi valley revealed only three potential monazite occurrences, two near Llandyfriog ([SN 3661 4468] and [SN 3694 4379]) and a third, a short distance upstream of the river bridge at Cardigan [SN 1895 4516]. Subsequent laboratory studies failed, in each case, to identify either monazite or diagenetic phosphate nodules, which are known to be a common feature of Lower Palaeozoic sedimentary rocks in many parts of the Welsh Basin (Smith, 1987). Although the grains were morphologically indistinguishable from the monazite recorded in mudstones to the south, XRF and optical examination showed that they consisted of either quartz or, in two cases, albite. Although no other evidence for these pseudo-nodules was found in the Ordovician of this area, similar features were noted in Wenlock turbidites from mid-Wales by Dimberline and Woodcock (1987), who recorded nodules up to 1.5 mm in diameter formed from aggregates of fine sand, bound and rimmed by organic matter. The difficulty of distinguishing in the field between monazite and clastic grains of common rock-forming minerals may therefore have led to an overestimate in the number of nodular monazite occurrences where laboratory confirmation has not been undertaken.

The style and intensity of mudstone deformation, resulting in shiny, finely crenulated surfaces in many outcrops on the north side of the Teifi valley, contributed to the lack of positive monazite identifications in this catchment. North-easterly trending anastamosing fault structures on the north-west flanks of the Teifi–Llangeler anticline pass through this area (Anketell, 1987), and associated deformation may have been sufficient to obscure easy recognition of monazite over a wide area.

Composition and structure of the monazite nodules

Nodules from the suite of rock samples collected from the Taf catchment and one specimen from the type-locality in Central Wales [SN 8800 6894] described by Milodowski and Zalasiewicz (1991) were selected for mineralogical examination and electron microprobe analysis, to establish the characteristics of the nodules from this area and to compare them with those from Central Wales.

The nodules and their immediately surrounding matrix were cut from rock slabs, mounted in a resin block and polished to provide sections for electron microprobe study. Element distribution within the larger nodules was examined following the construction of microchemical maps using a Cameca SX50 electron microprobe.

In thin section the nodules are dark brown to opaque, exhibit incomplete extinction and contain an inclusion fabric of variably replaced and corroded low-grade metamorphic minerals identical to those of the host rock assemblage. Commonly the inclusions show parallel alignment to the direction of nodule elongation. Typical nodules, about 1 mm long, show distinctive zonation of light, intermediate and heavy REEs from core to rim (Plates 1 and 2). In the core, there are relatively high levels of MREEs (Eu–Sm), whilst towards the rim the LREEs show marked concentration, La increasing to a maximum in the outermost 20–30 μm, and Ce showing a more gradual increase from the centre towards the rim. In contrast, the MREEs and HREEs decrease sharply in the outer regions of the nodules. Element scans across the nodules give a symmetrical rim-to-rim pattern for each element examined. When other elements concentrated in the nodules are also taken into consideration, a pattern of complex zonation emerges. For example, in a single nodule up to seven distinctive concentric chemical zones between 10 and 100 μm wide were identified.

No significant difference in the distribution pattern of the REEs was discerned between nodules from this area and those from Central Wales (Milodowski and Zalasiewicz, 1991). The only element which exhibits markedly different behaviour is Th which, in Central Wales, shows erratic distribution but, in the nodule described above, is concentrated in the core (10 μm diameter) and, additionally, in two merging annular rings (c. 10 μm wide) about 100 μm from the nodule centre (Plate 2).

Lithogeochemistry

With respect to most major and trace elements, the mudstones of the project area are similar in composition (Table 8) to quoted averages for post-Archean shales from a variety of terrigenous sources (Taylor and McLennan, 1985). However, in common with fine-grained sedimentary rocks from elsewhere in the Welsh Basin (e.g. Ball et al., 1992), CaO, Sr and, to a lesser extent, MgO display some depletion, reflecting the lack of diagenetic and biogenic carbonate in Welsh Basin mudstones. K_2O, and several first row transition metals (Cr, Mn, Co and Ni) are also low, perhaps reflecting a low chlorite and illite content.

In contrast, the mean Ba value is exceptionally high. This is caused by the presence of six samples (RAR11–17) containing >1100 ppm Ba. Remaining samples contain Ba concentrations similar to those typical of mudstones, reflected in the median value of 541 ppm (Table 8), and similar to those reported from Central Wales (Ball et al., 1992). No baryte was noted in any of the rocks containing high Ba, but the sample with the highest Ba content (RAR13 from Pont Ty-coed [SN 1914 2664]) is a black pyritic mudstone also containing the highest levels of Mo and U reported. Some of the other Ba-rich samples also have high levels of these metals suggesting the possibility of a strata-controlled concentration. There is a positive correlation between Ba and Ce content (Table 9) but no obvious correlation with monazite nodules, some Ba-rich samples containing abundant nodules (e.g. RAR11) and others no visible nodules at all. The inter-element relationships and absence of high Ba levels in panned concentrates compared with sediments from the same sites in the area where the rock samples carrying anomalous Ba were collected (Figure 9), suggests that the presence of baryte is not responsible for the high levels of Ba.

Table 8 Summary statistics for the chemical analyses of 20 mudrock samples collected in the Newcastle Emlyn area

Element	Mean	Std. Dev.	Median	Minimum	Maximum	NE/CWM	NE/CWH
SiO_2	59.89	1.54	59.52	55.59	68.3	1.04	1.02
Al_2O_3	20.63	0.82	20.93	17.42	23.23	0.95	0.95
TiO_2	1.06	0.56	1.06	0.91	1.27	0.97	1.02
Fe_2O_3	7.37	1.12	7.65	2.42	9.63	0.88	1.05
MnO	0.07	0.03	0.05	0.01	0.18	0.46	0.65
MgO	1.70	0.20	1.69	0.97	2.32	0.81	0.81
CaO	0.11	0.05	0.11	0.03	0.35	0.73	0.91
Na_2O	1.00	0.20	0.96	0.44	1.73	0.87	0.88
K_2O	3.01	0.23	3.56	2.98	4.01	0.89	0.89
P_2O_5	0.12	0.02	0.10	0.05	0.25	2.40	2.40
V	142	17	146	109	178	1.01	0.99
Cr	86	9	87	72	106	0.91	0.88
Co	13	6	15	<1	23	0.65	0.48
Ni	32	13	34	10	75	0.83	0.88
Cu	25	12	25	10	59	1.60	0.94
Zn	91	20	94	50	125	0.84	1.10
Rb	145	14	147	122	172	0.96	0.81
Sr	122	28	115	67	192	0.90	0.89
Y	31	6	29	23	50	1.05	1.00
Zr	209	37	200	161	299	1.10	1.16
Nb	17	2.0	17	14	21	0.87	0.93
Mo	2.9	8.4	1	<1	44	-	-
Ba	1384	2460	541	388	11954	2.95	2.91
La	38	17	38	25	67	1.10	0.40
Ce	78	36	80	65	99	1.63	0.37
Pb	17	11	14	<3	48	1.07	0.34
Th	13	2.6	14	7	18	0.93	0.81
U	5.3	2.6	5	2	12	1.32	1.30

NE/CWM: average value for mudstones from the project area normalised to average Central Wales turbidite mudstone (Ball et al., 1992).

NE/CWH: average value for mudstones from the project area normalised to average Central Wales hemipelagite (Ball et al., 1992)

Despite the widespread development of phosphatic shales such as the Nod Glas Formation in the Caradoc (Cave, 1965) and of early diagenetic apatite nodules in the Llandovery sequence of Central Wales, P_2O_5 values are low compared with average post-Archean shales (0.16–0.22%; Taylor and McLennan, 1985). La and Ce levels are very similar to those quoted for average post-Archean shales (Taylor and McLennan, 1985) and considerably lower than in modern deep-sea clays (Chester and Aston, 1976). Y and Th levels are also similar to those of average post-Archean shales. Therefore, there is no indication from the overall composition of these mudstones of any unusual concentration of phosphate or REE which might indicate the presence of, or account for the development of, the monazite nodules. Neither was there any correlation evident between the frequency of nodules in the hand specimens and the REE or phosphate content.

Table 9 Summary of significant positive inter-element Spearman-rank correlations derived from the chemical analyses of 20 mudrock samples collected in the Newcastle Emlyn area

Element	Correlation coefficient		
	0.4 – 0.59	0.6 – 0.74	>0.75
Si	Zr		
Al	K, Mg, Fe, Zn, Rb, Sr, La, Ce	Ti, Cr, Nb	
Ti	Fe,Y, La, Ce	Cr, Sr	Al, Nb
Fe	Al, Ti, Mn, Co	Ni	Mg, Zn
Mn	Na, Fe, Zn	Co	Mg
Mg	Co, Ni		Mn, Fe, Zn
Ca	Fe, Zn		P
Na	Mn		
K	Al, V, Cr, Ba, Th, U		Rb
P	Y, Th		Ca
V	K, Ba	Rb	
Cr	La	Al, Ti, Sr, Nb, Ce	
Co	Mg, Fe	Mn, Ni, Cu, Zn	
Ni	Mg	Fe, Co, Zn	
Cu	Ni, Mo	Co	
Zn	Al, Ca, Mn	Co, Ni	Mg, Fe
Rb	Al, Cr, Ba, Th, U	V	K
Sr	Al, Nb, La	Ti, Cr, Ce	
Y	P, Ti, Cr, La, U	Nb, Ce, Th	Ba
Zr	Si		
Nb	Sr, La, Ce, Th	Al, Cr, Y	Ti
Mo	Cu, Pb		
Ba	K, V, Cr, Rb, Ce,	U, Th	Y
La	Al, Ti, Cr, Y, Nb	Ce	
Ce	Al, Ti, Nb, Ba, Th, U	La	
Pb	Mo		
Th	P, Cr, Rb, Nb, Ce	Ba, Y	U
U	K, Rb, Y, Ce	Ba	Th

Correlation coefficient at 99% confidence level = 0.50

Inter-element correlations (Table 9) can be related to (i) clay and chlorite content of the rocks, responsible for the large number of elements positively correlated with Al, notably Cr, Fe, K, Mg, Mn, Nb, Rb, Sr, Ti and Zn (e.g. Thomson et al., 1984); (ii) sandstone–mudstone variation, responsible for the Si-Zr correlation and probably caused by small amounts of zircon in the coarser units; (iii) elements commonly forming or co-precipitated with oxy-hydroxides, resulting in close correlations between Co, Fe, Mn and Zn; (iv) authigenic monazite, which generates Ce, La, Th, U, Y, and Nb positive correlations; (v) apatite, accounting for the very strong Ca-P association and weaker correlations with Th and Y; (vi) organic matter, which is considered responsible for positive Mo, Pb, and Cu correlations.

The strength of the Ca-P correlation suggests that a high proportion of P in the rocks is held in apatite rather than monazite. The relatively weak correlations between elements known to be concentrated in monazite probably reflects the presence of these elements in other phases, perhaps absorbed onto clays or in apatite. Their correlation with elements concentrated in clay minerals may reflect this behaviour or result from a concentration of nodules into the most argillaceous units. It also demonstrates the weak influence that the presence of monazite has on the whole-rock chemistry. There is no evidence for the strong correlation between monazite and whole rock K and Ba content noted in the Spanish occurrences by Windle and Nesbitt (1993) and related by them to the amount of arkosic detritus in the rock.

Comparison of rocks from the Newcastle Emlyn and Central Wales areas

Comparison of the composition of the rocks from this area with hemipelagite and turbidite mudstones from Central Wales (Ball et al., 1992) is expressed in Table 8 by the ratio of the means of the rock analyses for each group from the two areas. The ratios indicate the general similarity in composition of the mudstones from the survey area with those of both origins from Central Wales. Small but consistently lower mean concentrations of several major and trace elements (including Fe_2O_3, MgO, CaO, MnO, Co, Zn, and Ni) in rocks from the survey area are in part due to the slightly higher mean silica content of the Newcastle Emlyn rocks, but also probably reflect a low illite-chlorite and carbonate content (see above).

Outstanding chemical differences between the rocks from the Newcastle Emlyn area and both the turbiditic and hemipelagic mudstones from Central Wales are the much higher mean P_2O_5 and Ba and lower Mn and Co contents of the Newcastle Emlyn rocks (Table 8). As the P_2O_5 content of the Newcastle Emlyn rocks is lower than that given for average post-Archean shales, it demonstrates the very low P_2O_5 content of the Central Wales rocks, particularly when it is borne in mind that the hemipelagic mudstones (mean 0.04% P_2O_5) carry nodular monazite, which is related to an increase in REE content (Ball et al., 1992).

The other distinctive features are the high REE levels in the hemipelagic mudstones and the relatively low levels in the turbiditic mudstones of Central Wales (Table 8). Pb is also significantly higher in the Central Wales hemipelagites, a reflection of a high primary organic carbon content of these rocks (Ball et al., 1992). Average REE levels in the turbiditic mudstones are 35 ppm La and 48 ppm Ce, whilst for the laminated hemipelagites the values are 93 ppm La and 210 ppm Ce (Ball et al., 1992). The degree of REE enrichment in the hemipelagites, greatest for La–Eu, increases with either the proportion of turbidite units in the sequence or the thickness of the underlying turbidite unit (Milodowski and Zalasiewicz, 1991). Simple mass balance calculations based on the volume and Ce and La content of each major lithotype (hemipelagite, turbidite mudstone, and turbidite sandstone) given by Milodowski and Zalasiewicz (1991), yield bulk Ce and La values for the Central Wales succession of 85 and 40 ppm respectively, closely comparable to the median levels in the more uniform rocks of the Newcastle Emlyn area and average shale values. This suggests that LREE concentrations in the pre-diagenetic muddy sediments from different parts of the Welsh Basin in the Upper Ordovician and Lower Silurian were quite similar, and supports the model of REE redistribution within the sedimentary pile suggested by Milodowski and Zalasiewicz (1991).

The concentration of REEs into the Central Wales hemipelagites contrasts markedly with the behaviour of the other major component of monazite, P, which remains very low in these rocks. Of the other elements determined that might be concentrated into monazite (Y, Th, U), only Y shows any increase in the hemipelagites when compared with the levels in the turbiditic mudstones or the Newcastle Emlyn rocks. This strongly suggests that the mechanism of REE enrichment in the hemipelagites also affected Y but not P, Th or U.

Origin of nodular monazite in south-central Wales

From recent detailed studies (e.g. Read et al., 1987; Burnotte et al., 1989; Milodowski and Zalasiewicz, 1991; Windle and Nesbitt, 1993) it appears that nodular monazites in rocks from a variety of ages and locations have a number of features in common. These include size, shape, colour and texture, abundant inclusions identical to the host rock, a low thorium and high europium content compared with igneous monazite, a distinct chemical zonation with LREE-enriched rims, and occurrence in clastic sedimentary successions which have commonly been subject to low-grade metamorphism. Some differences between areas are apparent, as are differences between occurrences within the same basin, but the Newcastle Emlyn occurrences appear to be particularly similar to those in Ordovician black shales deposited in the distal (deeper) parts of an extensive Ordovician basin in Spain (Windle and Nesbitt, 1993). In both areas the nodules are apparently dispersed through mudstones which show no enrichment in REE or other bulk compositional features reflecting the presence of nodular monazite. In contrast, geochemical studies in the Lower Palaeozoic of Belgium (Burnotte et al., 1989) and the Llandovery rocks of Central Wales (Milodowski and Zalasiewicz, 1991; Ball et al., 1992) concluded that in these areas bulk rock REE composition was related to monazite content.

In spite of the contrasting distribution of nodules in the Central Wales and Newcastle Emlyn areas, the similarity of the nodules and the overall (turbidite plus hemipelagite) host rock composition suggests that nodules from both areas have a common origin. The differing distribution of nodules in the two areas can be reconciled by postulating that the mobilisation and concentration of REE into nodules is not restricted to the migrating pore-water model for turbidite–hemipelagite sedimentation proposed by Milodowski and Zalasiewicz (1991) for Central Wales, but occurs as a result of a similar process applicable more widely in mudrock sequences.

Based on analogy with modern deep-sea sediments, the muddy sediments in both areas probably contained the bulk of their REEs in relatively unstable phases such as iron-manganese oxides or adsorbed onto clays (German and Elderfield, 1989). Also it is probable that in these deep water conditions the seawater was at saturation with respect to rare earth phosphate coprecipitation (Byrne and Kim, 1993). If a high proportion of any REE mobilised during compactional dewatering of the sedimentary pile migrated upward in saturated pore-waters then, in the case of the alternating turbidite–hemipelagite lithologies, migration was effectively halted by precipitation, perhaps initially as rhabdophane, near the organic-rich base of the hemipelagite layers (Milodowski and Zalasiewicz, 1991). In the case of the mudrock-dominated succession of the Newcastle Emlyn area, relatively abundant finely dispersed phosphate-rich organic matter provided a larger number of more dispersed sites for reductive precipitation of REE phosphates.

The overall pattern of REE zonation in the nodular monazites can be ascribed to fractional precipitation resulting from the differential solubility of REE phosphates, or to an increasing

LREE/MREE ratio as pore-waters evolved during late diagenesis and authigenic growth (Read et al., 1987; Burnotte et al., 1989; Milodowski and Zalasiewicz, 1991). The complex compositional patterns reported here probably reflect these processes and, possibly, abrupt changes in physico-chemical conditions due to sediment movement related to deformation events.

The contrasting morphologies of nodules from the different areas also probably reflect local conditions. For example, the efficient removal of REE from the sedimentary pile at a large number of dispersed sites and early termination of nodule growth as the REE supply diminished, explains the characteristically smaller average grain size, more ragged form and the disseminated distribution of nodules in the Newcastle Emlyn area.

It is still not clear why monazite nodules form in some basinal sequences and not others, and any further study of the nodules should address this problem by examining the physico-chemical conditions under which nodule formation takes place and the role, if any, of the mineralogy of the sedimentary pile and source rocks.

ASSESSMENT

Until 1965 when bastnäsite deposits averaging 7% REO (rare earth oxide) commenced operation in the USA, monazite placers were the major world source of REE. In many commercial operations monazite, comprising less than 0.1% of the ore mined, was recovered from placer deposits containing 5–10% total heavy minerals. Monazite-bearing placers are widely reported in fluviatile, lacustrine and deltaic deposits, but beach and dune sands of Late Tertiary to Recent age are the most economically important. Current interest in placers has focused either on the richest deposits containing up to 5% monazite, especially those associated with higher-value heavy minerals such as gold, cassiterite, zircon, tantalite and ilmenite, or on very large tonnage, low-tenor deposits (Neary and Highley, 1984).

Economic potential of nodular monazite in the Welsh Basin

Composition

The results of electron microprobe studies on individual monazite grains confirmed the observation initially made by Read et al. (1987) that nodular monazites from Wales are characterised by high levels of europium and low thorium. The latter is an important consideration in reducing the amount of radioactive waste and by-products in any extractive operation and increases the economic potential of all Welsh monazite occurrences. Concentrations of europium in the monazite nodules of the Newcastle Emlyn area are at the upper limit of the concentration range reported by previous workers for monazites in the Welsh Basin and are at least five times the average abundance in igneous monazites. As a result, the concentration of europium in monazites from sediments in the Newcastle Emlyn area is much higher than the average for placer monazites (about 0.05% Eu_2O_3; Mariano, 1989) and well above the average for 'dark' (nodular) placer monazites (0.35% Eu_2O_3; Mariano, 1989).

Bedrock deposits

Estimates of nodule abundance from visual examination and X-ray radiography of cleavage rock surfaces in Central Wales suggested that at best, nodule frequency in the hemipelagite mudstone bands does not exceed $6/cm^3$ and is commonly in the order of $<1/cm^3$ (Milodowski and Zalasiewicz, 1991). Read (1983) conducted a more quantitative assessment in the same general area by separating the nodules from each of three 15 kg mudstone samples. An estimated 400–600 nodules, equivalent to 60–90 g of monazite per tonne of rock, were obtained from each sample.

Although the Newcastle Emlyn field survey was not exhaustive and was hampered by lack of outcrop, nodular monazite was identified sporadically in mudrocks covering a wide stratigraphic interval over a minimum area of 180 km^2. The nodules tend to be smaller and to be dispersed more uniformly through the sedimentary succession than those of Central Wales. Although variations in the concentration of nodules appears to exist in different mudstone units within this very large low-grade resource, the maximum observed nodule frequency was about one per 15 cm^2 on bedding or cleavage surfaces, and no evidence was found to suggest the presence of an economically viable stratabound monazite deposit.

In Central Wales the monazites are concentrated into hemipelagic mudstone units, but the concentrations of nodules in these units are too weak and the horizons too thin (normally 5–30 mm in thickness; Milodowski and Zalasiewicz, 1991) and infrequent to be of economic interest. The evidence available also suggests that it is unlikely that bedrock concentrations of economic interest exist elsewhere in the Welsh Basin. This conclusion might not apply if monazite-bearing horizons were to be found associated with some other strata-controlled metalliferous concentration.

Superficial deposits

The liberation of monazite from bedrock and its subsequent upgrading by fluvial processes has given rise to concentrations of nodular monazite in river and stream alluvium over a large area of south-central Wales. Locally, concentrations of over 1% monazite in the <2 mm (sand, silt and clay) fraction were recorded in this area (Table 4), suggesting that there is a possibility of discovering small high-grade eluvial placers close to a primary source in areas where the bedrock contains relatively high concentrations of nodular monazite, such as the Afon Tigen catchment at Llanglydwen.

More importantly, high concentrations of monazite have been detected over continuous tracts of the main river systems where fluvial deposits of considerable thickness and lateral extent may provide a large resource. A regular supply of monazite from the numerous fast-flowing tributary streams maintains the concentration over the entire length of the Afon Teifi and the upper 60% of the Afon Taf catchment, at levels well in excess of the threshold for mineable heavy mineral placers of fluvial origin where monazite is recovered as part of a heavy mineral suite (often including ilmenite, zircon and rutile). Monazite concentrations in the total sediment sample (<50 mm) vary widely between sites ranging from 0.002 to 0.37% (Table 4), and more rigorous sampling would be required to determine a reliable estimate for any of the individual deposits.

Transport energy loss at tributary confluences appears to be responsible for locally elevated levels and thus provides an ideal target for secondary upgrading. A characteristic of all these deposits, potentially beneficial for extraction purposes, is the high proportion of sand and gravel relative to clay and silt grade material.

Reconnaissance-scale MRP geochemical data indicates that similar concentrations are likely to exist in river catchments draining other parts of the Welsh Basin, notably in parts of Central Wales and marginal to the Harlech and Berwyn domes.

Significantly lower abundances ($<0.1\%$ estimated monazite content) characterise the clay-rich estuarine deposits at the mouth of the Afon Teifi, but no sampling was undertaken in the more favourable estuarine environments, such as the deep-water channel deposits, or in beach and dune sands which, by analogy with occurrences in other parts of the world (e.g. Overstreet, 1967), may contain thin but very high-tenor concentrations of monazite.

Qualitative examination of the panned concentrates supported by geochemical analysis revealed only minor amounts of other potentially valuable heavy minerals, such as zircon, in the sediments of the Taf and the Teifi. However, river sediments in other parts of Wales may contain significant quantities of other economic minerals besides monazite. Available information suggests that the most attractive in this respect is probably the Afon Mawddach and its estuary, which is known to contain nodular monazite, gold and, perhaps, Fe-Ti minerals, but the area is one of outstanding natural beauty and the opposition to any mineral working would be strong.

CONCLUSIONS AND RECOMMENDATIONS

1. All large ($> 1\%$) cerium anomalies in panned concentrates recorded by the MRP in Britain are caused by grey, nodular monazite. The largest area (>200 km^2) of these anomalies, unclosed to the east and north, is in the Newcastle Emlyn area of south-central Wales. Other areas of very high values are restricted to catchments draining Lower Palaeozoic rocks of the Welsh Basin and occur in Central Wales and marginal to the Berwyn and Harlech domes.

2. Many of the largest cerium anomalies in the Newcastle Emlyn area are in panned concentrates collected from streams underlain by mudrocks of Upper Ordovician age. Lesser anomalies are associated with sedimentary rocks of Lower Ordovician age, and only background levels are recorded from streams draining the Fishguard Volcanic Group.

3. Strong and persistent cerium anomalies extend from tributary drainage into the main river systems and, in the Afon Teifi, can be traced in fluvial sediments for tens of kilometres to the estuary west of Cardigan. Estuarine inter-tidal deposits comprising mainly silt and clay-grade material contain only small amounts of monazite, but larger amounts may be present in the more favourable but unsampled channel lag deposits.

4. Upgrading during fluvial transport and sorting has resulted in concentrations of low-thorium, high-europium monazite in sediment that are greater than the minimum exploitable grades in other parts of the world where monazite is recovered as part of a heavy mineral suite. Concentrations locally exceed 1% by weight of monazite in the <2 mm (sand, silt and clay) fraction, equivalent to 20 kg monazite/m^3 in tributary drainage. More typically, levels in the range 1–5 kg monazite/m^3 were recorded.

5. Several in-situ occurrences of nodular monazite dispersed in monotonous successions of dark silty mudstones were found in the Newcastle Emlyn area, but no discrete stratabound concentrations of monazite were discovered, and no examples were found of nodules concentrated

into distinct hemipelagic mudstone horizons between turbidite siltstone and sandstone units, as has been reported from Central Wales. These hemipelagites contain REE concentrations well below present economic grades, and it is unlikely that an economically viable bedrock source of monazite is present in the rocks of the Welsh Basin.

6. Mineralogical studies demonstrated that the monazites from the survey area are very similar in texture and composition to those described from Central Wales and elsewhere. However, they also have some distinctive properties: they appear to be smaller, more ragged in appearance and more depleted in thorium and enriched in europium than those from most other areas.

7. The common characteristics of the nodules from different basins and ages indicate a similar, pre-metamorphic, principally diagenetic, origin. It is believed that the nodular monazites formed by diagenetic growth under physico-chemical conditions that are poorly understood, but that involved local pore-water saturation of REEs with respect to REE phosphate co-precipitation. It is probable that, during anoxic dewatering, there was reductive release of REEs from iron-manganese oxides and other phases and subsequent fixation by phosphate released during decomposition of dispersed organic material. The source rocks (by their composition, mineralogy, transport and weathering) may also have played an important role by influencing the input of available REEs to the basin and sedimentary pile.

8. It is recommended that further work is undertaken to assess the potential for monazite placer deposits in river, estuarine, beach and dune-sand environments, both in the survey area and in other rivers and estuaries receiving sediment from Upper Ordovician and Lower Silurian sedimentary rocks of the Welsh Basin. The presence of other potentially economic minerals, such as gold, should also be evaluated during this exercise. Because of the limited grain-size variation exhibited by nodular monazite, predominantly coarse to fine sand fraction, beach and deep river channel deposits would be the preferred targets.

9. The results of this study make clear the importance of hydraulic processes in preferentially sorting and depositing monazite. Differences of up to an order of magnitude in cerium concentration were recorded between bar-head and bar-tail environments only a few metres apart in river bed sediments. Particular care must therefore be exercised in the choice of sample size, type and site when undertaking resource assessment exercises.

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APPENDIX 1: ICPMS Analysis of Nodular Monazite Concentrates

0.5 g of sample, previously ignited for 2 hours at 900° C, was mixed with 1.5 g of lithium tetraborate/metaborate flux (JM Spectroflux 100B) and 0.1 ml of holmium standard, in a platinum crucible. The sample was fused at 1000° C for two hours and the resulting bead dissolved in 1M nitric acid. The solution was transferred to a 250 ml plastic volumetric flask and made up to volume with 1M nitric acid.

Further dilution with 1M nitric acid by either x100 or x1000 was necessary because of exceptionally high REE concentrations. The samples were then analysed by inductively coupled plasma mass spectrometry (VG Plasmaquad 2+) calibrated with a diluted solution of Spex Plasma Solution Standard containing all the REEs at 10 μg/ml. Blanks and in-house reference materials were included in every batch of samples prepared, and the holmium concentration was monitored to ensure complete recovery through the whole procedure. The results were only accepted if the recoveries were between 90 and 110%.