

Natural Environment Research Council

Institute of Geological Sciences

Mineral Reconnaissance Programme Report

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No. 19

**A reconnaissance
geochemical drainage survey
of the Criffel-Dalbeattie
granodiorite complex and its
environs**

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**A reconnaissance geochemical
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Criffel-Dalbeattie granodiorite
complex and its environs**

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SUMMARY

Regional geochemical reconnaissance by stream sediments and panned concentrates was undertaken over an area of 850 km² of south-west Scotland. Rocks of Ordovician to Permian age are exposed within the area but the major part is occupied by the Criffel-Dalbeattie granodiorite complex.

Multi-element analysis of the samples collected demonstrates a number of patterns of trace element distribution related to the geology and mineralisation. Broad-scale patterns in the distribution of some elements reflect compositional variations in both the Lower Palaeozoic turbidite sequence and the Criffel-Dalbeattie granodiorite complex, both of which may be sub-divided into specific units on the basis of the geochemical data.

The follow-up of copper anomalies in drainage samples from the Black Stockarton Moor area led to the discovery of porphyry-style copper mineralisation within an arcuate belt at least 5 km by 1 km within the Black Stockarton Moor subvolcanic complex and of related disseminated copper mineralisation at Scree Burn. The area to the west of the Criffel-Dalbeattie plutonic complex is also characterised by relatively high boron levels in stream sediments reflecting the widespread occurrence of tourmaline both in association with and peripheral to the copper mineralisation. Vein mineralisation, usually containing baryte in addition to base metals, is also identifiable from the drainage survey at the eastern margin of the Criffel-Dalbeattie granodiorite; in association with the Lower Carboniferous rocks along the Solway coast; and within the Lower Palaeozoic turbidites in the west of the area.

INTRODUCTION

The drainage survey described in this report covered part of an area of south-west Scotland which was examined as part of the Mineral Reconnaissance Programme carried out on behalf of the Department of Industry and which for presentation purposes has been divided into three, based on each of the major granitoid complexes. Field sampling was first undertaken during 1970-1971 as part of a uranium reconnaissance programme sponsored by UKAEA and was continued from 1973 to 1975 under the broader based minerals programme.

The geochemical maps presented and interpreted cover an area of 850 km² within the Dumfries and Galloway Region and illustrate the distribution of a total of 30 elements in minus 100 (BSI) mesh (150 µm) stream sediments and panned heavy mineral concentrates from major streams and tributaries. Collection of the two sample types from the same sites increases the efficiency of detection of dispersions of elements of economic interest both in the detrital and hydromorphic forms (Leake and Smith, 1975). The sampling density for the reconnaissance survey was approximately one sample per 2 km² for stream sediments and one sample per 4 km² for panned concentrates but this was increased in areas of interest. Most of the survey area is included in the Kirkcudbright (5) Sheet of the one-inch geological map of Scotland with a part extending into the Annan (6) Sheet.

A series of single-element geochemical maps for stream sediments and panned concentrates is presented. The distribution pattern obtained for each of the elements is described in relation to the solid and drift geology, environmental effects and contamination. The project was undertaken primarily to locate areas of mineral potential and additionally to provide geochemical data of regional significance.

Geographical setting

The geology to a large extent controls the topography of the area, with high relief over the Criffel-Dalbeattie granodiorite complex and undulating terrain over the Lower Palaeozoic sediments. The highest peak is Criffel (569 m) in the south-east but the most rugged area is that around Screel Hill (343 m) within the aureole of the granodiorite.

The main rivers draining the area are the Dee, Urr and Nith which flow north-south into the Solway cross-cutting the structural grain of the Palaeozoic rocks.

The principal centres of population are Dumfries, Castle Douglas, Dalbeattie and Kirkcudbright (Fig. 1.) The main occupation of the area is farming, the land being given over to pasture and rough grazing. Recently forestry has become a major industry with large scale plantations occupying much of the higher ground.

GEOLOGY

General geology

The area surveyed lies within the Southern Uplands of Scotland, the geology of which is dominated by great thicknesses of Lower Palaeozoic turbidites and inliers of black shale, chert and volcanic rocks (Greig, et al. 1971). The Criffel-Dalbeattie plutonic complex (Phillips, 1956) and the Black Stockarton Moor subvolcanic complex (Leake et al., in prep.) are intrusive into turbidites of Silurian age. Grits, sandstones and basic volcanic rocks of Lower Carboniferous age are exposed along the Solway coast and rocks of Permian age cover a small area to the north-east around Dumfries.

Most of the Lower Palaeozoic sediments are graded turbidites and within the northern part of the Southern Uplands several different formations, which persist for long distances along strike and which are separated by major strike faults, have been recognised on the basis of mineral composition (Floyd, 1976). Recent work around the Fleet Granite (Leake et al., in press) indicates that similar divisions can be made of the Silurian turbidites within the southern part of the Southern Uplands. The south-eastern part of the Lower Palaeozoic outcrop, shown as Wenlockian in Figures 1 and 2, includes faulted inliers of shales, greywackes and conglomerates of Llandoveryian age with many carbonate nodules at some horizons. The rocks immediately to the north-west of the Wenlockian are of uncertain age but they may be Llandoveryian (Fig. 2) (Clarkson, Craig and Walton, 1975) or younger (Craig and Walton, 1959).

The Criffel-Dalbeattie plutonic complex has been divided into four components (Phillips, 1956) of which the Bengairn Quartz Diorite is considered to be the earliest. The Main Granodiorite, which was emplaced last, has a relatively basic margin and a more felsic core, mapped as the Porphyritic Granodiorite by Phillips (1956). Recent mapping of the area to the west of the Bengairn Quartz Diorite (Leake, Cooper and Brown, in preparation) has revealed a subvolcanic complex of minor intrusions comprising porphyrite and basic dykes, granodiorite sheet or cedar-tree laccolith complexes, small

granodioritic stocks and agglomerate vents. Three phases of igneous activity have been recognised within the complex, one of which predates all the plutonic activity to the east. The upper age limit of both igneous complexes is provided by the presence of detritus in the Upper Old Red Sandstone sediments of the Kirkbean area.

Fragments and boulders of most igneous rocks from both the plutonic and subvolcanic complexes are abundant in downfaulted Lower Carboniferous sediments exposed along the Solway Coast and which in the south-east overlie basal Carboniferous lavas contemporaneous with the Birrenswark lavas of the Langholm-Lockerbie area. The Dumfries basin to the north-east of the area is made up of breccias and sandstones of Permian age, the breccias being composed almost entirely of greywacke and porphyrite fragments.

Structure

The disposition of the Lower Palaeozoic sediments of the Southern Uplands is such that over most of the area younger beds occur towards the north-west. A series of large strike faults, trending north-eastwards, has, however, countered this effect so that the belts of rocks between them are successively younger towards the south-east. Recently the structure of the Southern Uplands has been interpreted by McKerrow et al. (1977) in terms of a dynamic model involving sequential accretion of an imbricating sedimentary wedge onto the margin of the North American continent. The model provides an explanation of the outcrop distribution within the Southern Uplands. The younging of successive wedges towards the ocean, coupled with the overall younging of the sequence within each wedge towards the continent, is diagnostic of modern accretionary prisms recognised in several parts of the world.

Drift geology

During the period of maximum glaciation the area described was completely covered by the advancing ice. Evidence of this is seen by the occurrence of erratics on the summit of Criffel (569 m). Striae on rock surfaces and the alignment of glacial deposits show evidence of ice movement from north to south radiating from a centre in the Loch Doon area of the Galloway Hills.

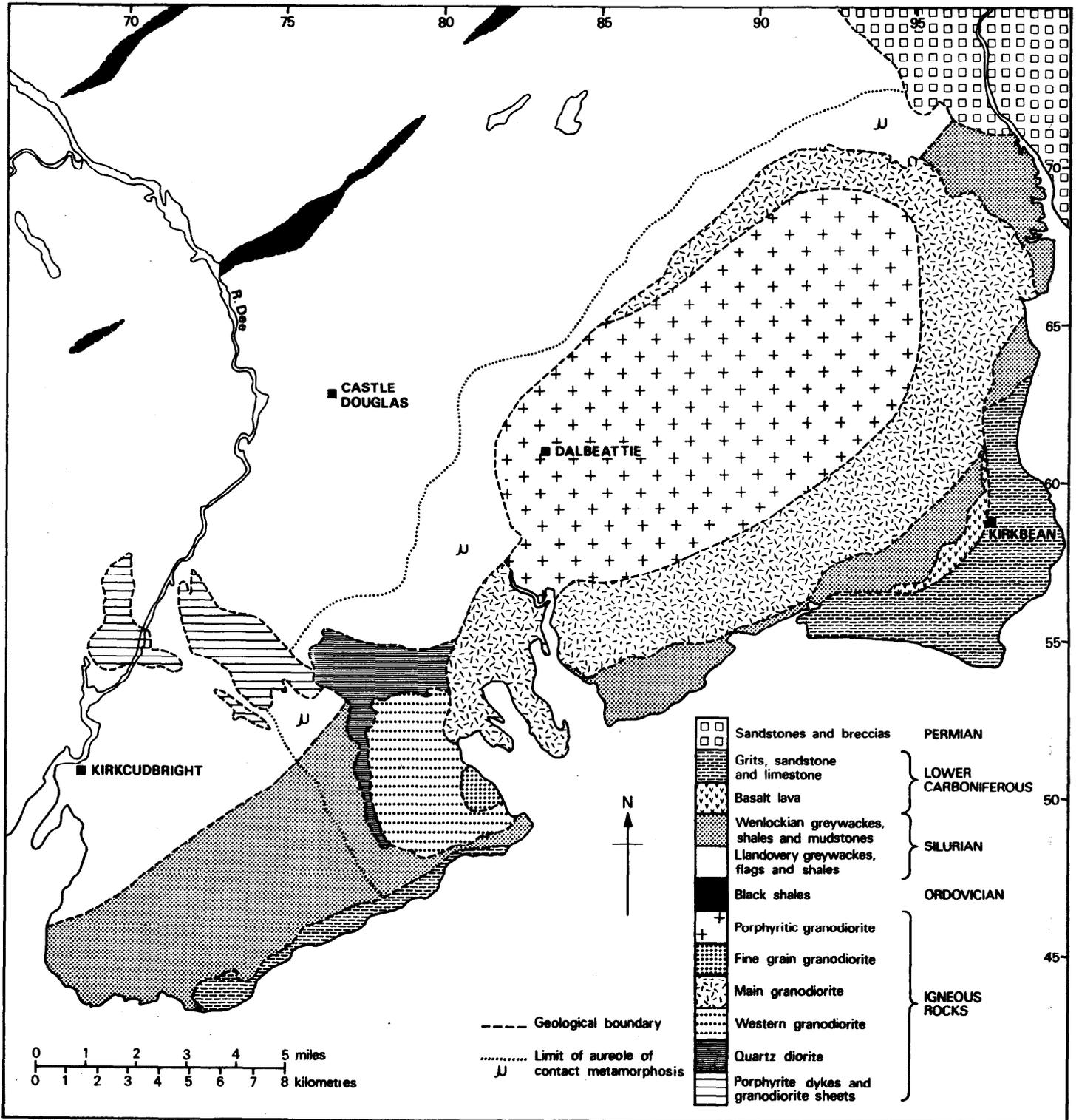


Fig. 2. Geology of area.

It was likely that the drainage system was established before the advance of the ice as the river valleys show thick accumulations of glacial till. Within the area glacial disintegration features in the form of drumlins are common, with their long axes indicating a north-south direction of ice movement.

Along the Solway coast there is abundant evidence of past changes in the relative position of land and sea as shown by raised beach deposits. Three terraces can be distinguished at the mouth of the Urr, at 7.5 m, 15 m, and 30 m levels respectively, consisting of sands, gravels and laminated clays.

Much of the higher ground over the Criffel-Dalbeattie granodiorite complex is covered by peat. Peaty soils also occur over the higher central area of the Black Stockarton Moor subvolcanic complex, in marked contrast to the well drained soils of the surrounding pasture land.

Previous mining activity

There has been no major mining activity in this area of south-west Scotland, the main sources worked being small localised veins often associated with faults.

Iron has been worked at Glenhead where hematite occurs in a west-north-west trending vein associated with a major fault. Hematite veins also occur within the aureole of the granodiorite. Copper minerals have been worked at Heston Island, Rascarrell, Colvend and Pipers Cove, commonly associated with quartz and barytes. A trial for copper was made within a fault zone at Billies, north of Black Stockarton Moor, but was not worked. Uranium mineralisation occurs in numerous small veins in a series of north-west tear faults (Miller and Taylor, 1966). Pitchblende is the dominant mineral, associated with hydrocarbon, chalcopyrite, native bismuth and hematite in a quartz-carbonate gangue.

DATA INTERPRETATION

Interpretative procedure

The method of class-interval, rather than continuous-function presentation has been adopted in order to give greater visual impact in delineating anomaly groups in the distribution of elements of economic interest.

Cumulative frequency diagrams were plotted on log probability paper for both sample types and the most obvious discontinuities used in the definition of class intervals. Where it was not possible to recognise breaks in slope on the cumulative frequency plot, class intervals were based on the mean plus one and two standard deviation levels of the log transformed data for elements showing a lognormal distribution. For elements, such as uranium in concentrates, where the detection limit is exceeded by only a small proportion of the population, class intervals were based on empirically selected values.

Inter-element correlation coefficients (Tables 1 and 2) were calculated from the log transformed data for both sample types as an aid to the interpretation of distribution patterns. In the course of follow-up investigations several sample types, comprising $-150 \mu\text{m}$ sieved sediment, panned concentrates, suspended fines (Leake & Smith 1975) or unsieved sediment samples were collected, providing information on the likely dispersion mechanisms and of the phases concentrating the anomalous metals.

Several concentrates were examined mineralogically after floating off the lighter fraction in tetrabromoethane and separating, using an "Eclipse" variable hand magnet, into fractions of different magnetic susceptibility. Optical identifications were confirmed in some cases by X-ray powder photograph and mineral compositions investigated by semi-quantitative XRF scanning.

Contamination

Human habitation, agricultural operations and road materials are the main sources of contamination in drainage samples. Streams were not sampled where contamination was obvious, but large amounts of metallic debris were found in streams flowing over low-lying farmland. Fragments of synthetic material have been found in many concentrate samples but in many cases the amount of base metal present in the debris is insignificant. The most common contaminant is ferromagnetic alloy in irregular fragments up to 4 mm long, but in most cases the levels of the elements of interest are low. Other materials identified included fragments of copper and alloy wire which gave high levels of copper and zinc, lead shot, flakes of rust and fragments of ceramic appearance. The analysed tin content of each sample type serves as a useful contamination monitor as the level of tin in rock forming minerals is generally low and tin mineralisation is unknown within the area investigated. Lead is most commonly found in association with tin at contaminated sites and rarely with copper and zinc except in highly polluted sites. Particular problems arise when detrital ore minerals occur within a contaminated sample as is the case with samples collected north of Black Stockarton Moor. In such cases the presence of an anomaly originating from hydrothermal mineralisation can be confirmed only by mineralogical examination of the concentrate.

In the first stage of follow-up investigations all concentrate samples with anomalous copper and zinc were examined for ore minerals, even when obviously contaminated, as were samples with significant baryte, pyrite or hematite/goethite content. Contaminated samples containing only tin and lead were usually rejected unless there was other evidence of mineralisation.

Comparison of sample types

Differences in the distribution patterns of the elements between the different sample types arise because of the ranges of particle size represented and because of the relative upgrading of heavy detrital minerals

in the concentrate sample. Particle size analysis of concentrates (Leake and Smith, 1975) reveals that only a small proportion (less than 5%) of the sample is finer than 150 μm (-100 BSI mesh) whereas the sieved sediment contains material ranging in size from 150 μm to less than 2 μm .

In general there is good agreement between the two sample types, particularly in the case of elements contained in heavier minerals resistant to chemical breakdown, eg Ti and Zr. Concentration of minerals by panning can result in improved geochemical contrast between different rock types. The distribution of elements which occur in significant quantities in readily decomposed rock forming minerals are only detected in the stream sediment. Variations in the distribution patterns for Fe and Mn can be attributed to secondary precipitation of the oxides, particularly in areas of impeded drainage. Elements such as Zn and Co which are co-precipitated with manganese oxide from stream waters may display distribution patterns unrelated to the underlying rock geochemistry.

Comparing the distribution of elements in both sample types, it is clear that dispersion from metalliferous mineralisation is predominantly in the detrital phase. Results from stream sediments show that the dispersion of Pb, Zn, Ba and U is influenced by secondary environmental factors. However panned concentrate results show, by virtue of the relatively coarse mineral fragments and the lack of chemical breakdown, significant dispersion patterns and are therefore more efficient in locating areas of potential hydrothermal mineralisation. Only in the case of Cu in stream sediments is hydromorphic dispersion evident, possibly derived from pyritiferous mineralisation southwest of the Bengairn quartz diorite. A comparison of metal levels in the different sample types is an effective means of evaluating drainage anomalies and of determining the predominant mechanism of dispersion. Sites shown to be anomalous by two or more sample types indicate dispersion over a relatively

broad particle size range and may reflect a larger source of mineralisation than indicated by a single sample type.

Compositional variations between the two sample types are also reflected in their correlation matrices (Tables 1 and 2). The presence of Ca and Ba in the feldspar fraction is shown by their significant positive correlation with K, Ga, Rb, Sr and Pb in the sieved sediments. The existence of detrital hosts such as sphene for several minor elements is shown by the inter-correlations of Ca, Ti, Nb, Sn, Ce, Th and U in the concentrate sample but is obscured in the stream sediment by other variations

Geological interpretation

The distribution of elements in alluvial samples provides a useful aid in the elucidation of macro-geological features. However, such factors as the secondary environmental enrichment of certain elements in sieved sediments, the artificial concentration of the heavy minerals in panned concentrates and the tendency of some streams to follow mineralised faults must be taken into account when interpreting the data. This type of reconnaissance survey has been particularly useful in the Southern Uplands of Scotland where geological knowledge is limited. Several conclusions of geological significance can be drawn from the present survey.

Geochemical differences between the components of the Criffel-Dalbeattie complex are clearly apparent from the drainage samples. A marked distinction exists between the Main Granodiorite and the Western Granodiorite/Bengairn Quartz Diorite. The Main Granodiorite is the most variable in composition, with a margin as mafic as the Bengairn quartz diorite and a central core richer in granitophile elements than the Western Granodiorite. Additionally the Main Granodiorite appears to be significantly enriched in Li, Be, Mn, Y, Nb, Mo, Sn, Ce, Th and U and poor in Ni, Cu and Zn when compared with the Western Granodiorite. It is suggested that this compositional variation of the three rock types indicates two separate magmas, the earlier giving rise to the

Bengairn Quartz Diorite from which the Western Granodiorite evolved followed by a later separate igneous event from which the Main Granodiorite evolved. The chemical compositions of drainage samples from the Black Stockarton Moor subvolcanic complex show a similar geochemistry when compared to the Bengairn Quartz Diorite and the Western Granodiorite.

The Main Granodiorite was recognised by Phillips (1956) to comprise a marginal basic facies passing gradationally into a central more felsic porphyritic facies. The results of the reconnaissance drainage survey confirm these relationships within the Main Granodiorite. The most mafic part of the intrusion is shown by the enrichment of drainage samples in Mg, Ca, Ti, Mn, Ni and Zn in the extreme south-east in the vicinity of the summit of Criffel. A similar but rather less mafic facies occurs in the south-western part of the intrusion, separated from the mafic variety around Criffel by a zone of more siliceous granodiorite. The most highly differentiated part of the Main Granodiorite is shown by a grouping of drainage samples highly enriched in Ga and Rb and depleted in Ca, Sr and Zr occupying an elongate zone parallel to the long axis of the intrusion but displaced from the centre towards the northern contact. The asymmetry of the intrusion shown by the mapping of Phillips (op.cit.) is therefore confirmed, with relatively mafic rocks absent from the northern margin of the intrusion. The occurrence of a group of drainage samples in the extreme north-east of the Main Granodiorite which are relatively depleted in Li, Be, K and Rb may indicate the presence of a separate intrusion to the north of New Abbey Pow.

Comparison of the composition of drainage samples derived from the igneous rocks and the Lower Palaeozoic rocks indicates significant geochemical differences. Compared with the adjacent sediments the intrusive rocks are enriched in Li, Be, K, Ca, Ga, Rb, Sr, Y, Ce, Pb, Th and U and depleted in B. Though much of the plutonic rock is thought to have been derived from remobilised and ingested sedimentary material (Phillips, 1956), the relative

TABLE 1. Correlation matrix for stream sediments

Correlation coefficients significant at > 99.95% confidence level							
Element	0.20-0.30	0.30-0.40	0.40-0.50	0.50-0.60	0.60-0.70	0.70-0.80	0.80-0.90
Li	-B Mn Fe-Ni		Ba Pb	Be	Ca-Cr Ga Sr U	K Rb	
Be	-B Zr	Ca-Cr-Ni Ga Pb U	Rb Sr	Li K			
B	-Li-K-Ca Zn-Rb-Mo	Mg Cr V-Sr Y	Ti-U	Ni Cu			
Mg	Ca Cr Fe Co Zn-Rb-U	B Y	Cu	V		Ti Ni	
K	-B Mn	Ni	Pb	Be Ca Ba	-Cr Ga Sr U	Li Rb	
Ca	-B Mg Mn Fe	Be Zr	Ga Rb Pb	K-Cr Ba U	Li		Sr
Ti	-Rb Zr-Mo-Pb	Cr Y-U	B V Cu		Ni	Mg	
V	Zn-Rb	B	Ti Co Cu Y	Mg	Fe Ni		
Cr	Y-Mo	-Be B Ti-Mn-Fe-Ba	Ni	-Ca-Rb-Sr-Pb	-Li-K-Ga-U		
Mn	Li K Ca Rb Sr U	-Cr Ga Ba Pb	Fe Co Zn		Vi Co		
Fe	Li Mg Ca Cu Ba U	-Cr Ni Ga	Mn Zn Mo	Pb	Fe		
Co	Mg Cu Ba	Ga	V Mn Ni Mg Pb	Zn	Ti V	Mg	
Ni	-Li	-Be-K Fe Zn-Sr Y	Cr Co-Rb U	B Ca			
Cu	Fe Co Y	Zn-U	Mg Ti V	B Ni			
Zn	B Mo V-Zr Ba	Ni Cu Pb	Mn Fe	Co			
Ga		Be Mn Fe Co Ba	Ca Sr U	Rb Pb	Li K-Cr		
Rb	-B-Mg-Ti-V Mn-Y	Ba Pb	Be Ca-Ni	-Cr Ga Sr U		Li K	
Sr	Mn-Y	-B-Ni Zr	Be Ga Rb	-Cr Rb U	Li K Ba		Ca
Y	Cr Cu-Rb-Sr Zr	B Mg Ti Ni	V				
Zr	Be Ti-Zn Y U	Ca Sr					
Mo	-B-Ti-Cr	Pb U	Fe Co				
Sn							
Ba	Fe Co Zn	-Cr Mn Ga Rb U	Li Pb	K Ca	Sr		
Pb	-Ti	Ba Mn Zr Rb Mo	Li K Ca Co Sr Ba U	-Cr Fe Ga			
U	-Mg Mn Fe Zr	Be-Ti Cu Mo Ba	-B-Ni Ga Pb	Ca B Rb Sr	Li K Cr		

TABLE 2. Correlation matrix for panned concentrates

Element	Correlation coefficients significant at > 99.95% confidence level					
	0.25 - 0.30	0.30 - 0.40	0.40 - 0.50	0.50 - 0.60	0.60 - 0.70	0.70
Ca		Ti Mn Y Nb Ce Th				
Ti	Zn Pb	Ca Zr	Mn Y Sn Ce U	Nb Th		Fe
Mn	Zr U	Ca Ni Y Th	Ti Zn Nb	Fe		
Fe	Sn Ce	Cu Y Nb Pb Th U		Mn	Ni Zn	Ti
Ni		Mn Cu			Fe	Zn
Cu		Fe Ni		Zn		
Zn	Ti Ba Pb		Mn	Cu	Fe	Ni
Y	U	Ca Mn Fe	Ti Nb Th			Zr
Zr	Mn	Ti U		Nb Th		Y
Nb		Ca Fe	Mn	Ti Y Zr	Th	U
Sn	Fe	Pb	Ti			
Sb						
Ba	Zn					
Ce	Fe Th	Ca	Ti			
Pb	Ti Zn	Fe Sn				
Th	Ce	Ca Mn Fe		Ti Y Zr	U	Nb
U	Mn Y	Fe Zr	Ti		Nb Th	

enrichment of the above elements indicates a significant magmatic component which originated at greater depth, carrying upwards concentrations of the alkalis and other elements. Evidence for the existence of ghost stratigraphy in the Main Granodiorite is provided by the presence of relatively high levels of chromium (an element not normally enriched in the more siliceous igneous rocks) in drainage derived both from the north-western part of the intrusion to the east of Kirkgunzeon and from the adjacent sedimentary rocks. Chromium levels are similar to those in samples derived from turbidite units rich in chrome spinel near Crossmichael and elsewhere in the Southern Uplands (Leake et al., in preparation, Dawson et al., 1977). In view of the extremely refractory nature of chrome spinel, original detrital grains may have remained inert during magmagenesis.

Within the Lower Palaeozoic turbidite outcrop three greywacke compositional types can be recognised from the geographical distribution of elements in drainage samples. One type which occurs only in the north-west of the area is characterised by relative K, Mn, Co, Ga, Rb, Sr, Y, Mo, Ce, Pb and U enrichment and probably contains a relatively high proportion of minerals and fragments derived from rocks of granitic composition. Chromium enrichment is the main feature distinguishing the second greywacke type from the third greywacke type.

Metalliferous and radioactive mineralisation

Several types of previously unrecognised mineralisation have been located by the reconnaissance geochemical drainage survey. The drainage response from each of the main types of mineralisation known to occur, either as a result of follow-up work carried out during this survey or from previous published work, is discussed below.

Porphyry-style copper mineralisation

Follow up of copper anomalies in both sample types from streams to the north of Black Stockarton Moor led initially to the discovery of structure-controlled vein mineralisation containing chalcopyrite or malachite with calcite, baryte and traces of lead and zinc minerals. Subsequently, further follow-up investigations proved porphyry-style copper mineralisation at Black Stockarton Moor in an arcuate zone at least 5 km long and up to 1 km wide. This mineralisation is described in detail in a further report (Brown et al., in preparation). Evaluation of the copper distribution in drainage samples from the area indicates that copper dispersion from this mineralisation in the few minor streams which drain it is very limited. Pyrite-rich concentrate samples were obtained downstream of the pyrite halo which occurs to the west of the copper mineralisation but these contained only background levels of copper. The anomalously high boron content of all stream sediments collected downstream of the mineralised area is considered to be due to tourmaline which is known to occur in thin veinlets within the propylitic alteration envelope. The relatively high levels of Ga and Rb in the same sediment samples are thought to be also derived from the propylitic alteration zone. The weak Cu anomalies and relatively high B, Ga and Rb levels of samples from the area to the south of Black Stockarton Moor are probably derived from similar porphyry style mineralisation. The anomalous levels of Cu in sieved sediment samples from the area south-east of Barcloy Hill may also be derived from related mineralisation as concentrations of pyrite in both igneous and sedimentary rocks occur in this area.

Copper anomalies from north of the Bengairn Quartz Diorite are derived from both vein or fault-controlled and disseminated mineralisation. The mineralisation at Screel Burn and nearby areas which forms the subject of a separate report (Leake et al., in preparation) is complex as there appear to be several phases. The earliest phase consists principally of finely disseminated sulphide, chiefly bornite, pyrite and arsenopyrite, within hornfelsed turbidites and is probably related to the porphyry-style copper mineralisation at Black Stockarton Moor. There is also disseminated pyrite and vein mineralisation with minor chalcopyrite and galena, mostly to the south of the stream, which is probably derived from late-stage fluids associated with the Bengairn Quartz Diorite. Several later east-west breccias and brecciated porphyrite dykes also cut the area and usually contain vein quartz, dolomite, hematite, minor chalcopyrite and, in places, manganese. Tourmaline is also of widespread occurrence north-west of the Bengairn Quartz Diorite, eg near Nick of the Tun (GR NX 758 556). The copper anomalies reflect minor structure-controlled mineralisation with either malachite in calcite veins or massive sulphide segregations containing pyrite, arsenopyrite, chalcopyrite and chalcocite. Chalcopyrite, sphalerite and baryte which occur in alluvial sediment west of White Hill are probably derived from vein mineralisation but there is also evidence of disseminated pyrite-rich mineralisation (Leake et al., in preparation) which is probably a component of the Black Stockarton Moor porphyry-style mineralisation complex. Drainage barium anomalies to the east of Kirkcudbright reflect vein baryte mineralisation which is widespread between Kirkcudbright and Black Stockarton Moor.

Mineralisation associated with major linear structures

A prominent mineralised structure extends at least 14 km north-north-west from Kirkbean parallel to the margin of the Permian Dumfries basin. Vein baryte, hematite and quartz breccia have been observed in stream sections within the zone, but drainage samples provide evidence for the additional presence of pyrite, sphalerite and secondary lead and copper minerals. The pattern of drainage anomalies indicates that the mineralisation is controlled to a large extent by the nature of the adjacent rocks. Copper is most conspicuous where faulting brings the Lower Carboniferous basic lavas or the Lower Palaeozoic sediments against the south-eastern edge of the Main Granodiorite. Sphalerite and baryte are also more abundant where the structure cuts sedimentary rocks but are less abundant within the granodiorite. Copper and lead reappear in drainage samples derived from the continuation of the zone to the north of the intrusion. A conspicuous mineralised fault zone parallel to the regional trend of the Lower Palaeozoic rocks is followed by the stream east of Loch Mannoeh which provides the source of the copper, zinc, lead and barium anomalies. Anomalies to the south-south-east of Loch Mannoeh are also probably derived from similar fault-controlled mineralisation.

Baryte mineralisation along the Solway coast

Vein baryte mineralisation occurs frequently within the Lower Carboniferous rocks to the east of Dundrennan together with minor amounts of copper. Similar mineralisation is indicated further to the west by the anomalous barium, lead and copper content of stream sediments from south-east of Dundrennan.

Uranium mineralisation

Stream sediment anomalies from east of Dundrennan suggest that uranium mineralisation of the type described by Miller and Taylor (1966) also occurs in the aureole of the Western Granodiorite adjacent to the Lower Carboniferous outcrop.

CONCLUSIONS

The drainage survey has identified new areas of metalliferous mineralisation of potential economic interest, and provided additional information on the composition of the major rock units. Regional geochemical maps, compiled from multi-element analysis of stream sediments and panned concentrates, show a number of patterns of element distribution related to the geology and the mineralisation. The distribution of each element may be modified to varying degrees by the effects of contamination and the influence of the secondary environment. The main conclusions drawn from the survey are as follows:-

1. Broad-scale patterns in the distribution of some elements reflect compositional variation both in the Lower Palaeozoic turbidite sequence and in the Criffel-Dalbeattie granodiorite complex. Considering the geochemical evidence, the turbidite sequence may be divided into three units based on composition. A change in the drainage sample geochemistry along the strike of the Lower Palaeozoic rocks suggests the existence of a major counter-Caledonide fault. This is substantiated by the recognition from Landsat imagery of a major north-north-west lineament passing through Woodhall Loch. The data also confirm the division of the main granodiorite, suggested by Phillips (1956), into a marginal basic facies passing into a more felsic porphyritic central zone.
2. Copper anomalies in stream sediments and panned concentrates within the Black Stockarton Moor sub-volcanic complex are related to fault-controlled vein mineralisation in Milnthird burn and/or to porphyry style mineralisation within an arcuate belt some 5 km by 1 km in surface extent (Brown et al., in preparation).

3. Anomalous boron in a zone around the subvolcanic complex and bordering on the Bengairn quartz diorite may be due to tourmaline of hydrothermal origin, associated with the porphyry style mineralisation. High boron to the south-east and east of the subvolcanic complex may reflect the occurrence of similar porphyry style mineralisation.
4. Other copper anomalies can be attributed to structurally controlled mineralisation at Screel Burn, Nick of the Tun, Barcloy Hill and White Hill. It is suggested that the mineralisation is genetically related to the porphyry style mineralisation at Black Stockarton Moor because of similar geochemistry and mineralogy.
5. Anomalous levels of copper, lead, zinc and baryte in drainage samples locate mineralised fractures, the most notable being a structure extending at least 14 km north-north-west from Kirkbean. The drainage samples also reflect the baryte, copper and lead veins abundant in the Lower Carboniferous rocks, some of which have been worked in the past.
6. Uranium anomalies in stream sediments show an enrichment of uranium in the granodiorite in the vicinity of Kirkgunzeon. Anomalies east of Dundrennan suggest similar mineralisation to that already known within the granodiorite aureole around Sandyhills Bay.

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Methods of sample collection and chemical analysis

Sample collection of stream sediments

Stream sediment samples were obtained from major streams and tributaries at natural sediment traps, beneath large boulders, at the upstream end of riffles and the base of waterfalls. The material was collected by wet-screening through nylon-mesh sieves to minus 0.25 cm as described by Plant (1971). The sediment was then oven dried and sieved to give a minus 100 BSI mesh ($<150 \mu\text{m}$) fraction for analysis as this has been shown by Plant (op. cit.) to be the optimum size fraction for regional geochemical reconnaissance within upland environments in Scotland.

Chemical analysis of stream sediments

With the exception of Mo and Sn (determined by optical emission spectrography with plate evaluation by visual comparison, after Nichol and Henderson-Hamilton, 1964), Zn (determined by atomic absorption spectrophotometry with nitric acid sample attack) and U (determined by the delayed neutron method, Ostle et al., 1972) analytical data presented for stream sediment samples was obtained by D-C arc direct-reading optical emission spectrometry using a technique developed by the Analytical and Ceramics Unit, Geochemical Division, for the analysis of a wide range of geological materials.

The analytical method is based on a Jarrell-Ash 1.5 m Atomcounter, covering the wavelength range 250.0 to 850.0nm at a reciprocal dispersion of 0.56nm/mm, and incorporating 40 channels (see Table 3) with sequential data output. The spectrometer is 'on-line' to an IBM 1130 Computer via an interface (Westinghouse Brake and Signal Ltd.) used to convert output signals to a computer compatible form. The interface also relays control

TABLE 3. Instrumental parameters for the Jarrell-Ash 1.5m Atomcounter

EXIT SLIT NO.	ELEMENT	WAVE-LENGTH (nm) & ORDER	EXIT SLIT WIDTH (um)	REFRA-CTOR PLATE	SECON-DARY OPTICS	DETEC-TOR TYPE	CHANNEL NO.	NOTES
1	Si*	251.61	75	Q		R212	9	
2	Ge*	265.12	75	Q	MIRROR	R212	21	
3	Pt	270.24	75	Q		R212	3	INTERNAL STANDARD NO
4	Pb	283.31	75	Q		R212	33	
5	Sn*	286.33	10	Q	MIRROR	R212	29	
6	Ga	294.36	75	Q		R212	20	
7	BKGD-1	304.00	75	Q		R212	37	BACKGROUND MONITOR NO
8	Mo*	317.04	75	Q		R212	27	
9	Zr	339.20	75	G		R212	25	
10	Co	345.35	75	G	MIRROR	R212	17	
11	BKGD-2	371.00	75	G		R212	38	BACKGROUND MONITOR NO
12	Al*	394.40	75	G	MIRROR	R212	8	
13	W*	400.88	10	G		R212	32	
14	In	410.18	75	G		R212	1	INTERNAL STANDARD NO
15	Cr	425.44	75	G		R212	14	
16	La*	433.37	75	G		R212	31	
17	Ca	445.48	75	G		R212	11	
18	Ba	455.40	75	G		R212	30	
19	Sr	460.73	75	G	MIRROR	R212	23	
20	Eu	462.72	75	G	MIRROR	R212	2	INTERNAL STANDARD NO
21	Be	234.86 II	75	C	MIRROR	R106	5	
22	B	249.77 II	35	C		R106	6	
23	Mn	257.61 II	75	C	MIRROR	R212	15	
24	Fe	260.71 II	75	C		R212	16	
25	Hg	546.07	25	G		R212		OPTICAL MONITOR
26	BKGD-3	572.60	75	G		R212	39	BACKGROUND MONITOR NO
27	Mn-2	293.93 II	75	C		R212	36	MANGANESE HIGH LEVEL
28	Li-2	610.36	75	G	MIRROR	R212	35	LITHIUM HIGH LEVEL
29	Bi*	306.77 II	75	C		R212	34	
30	Nb*	316.34 II	75	C	MIRROR	R212	26	
31	V	318.40 II	75	C		R212	13	
32	Ti	324.20 II	75	C	MIRROR	R212	12	
33	Cu	327.40 II	75	C		R212	19	
34	Li	670.78	75	G		R212	4	
35	Ag*	338.29 II	75	C		R212	28	
36	Ni	341.48 II	75	C		R212	18	
37	Y	371.03 II	75	C		R212	24	
38	Mg	382.94 II	75	C		R212	7	
39	Rb	780.02	75	Y	FIBRE	FW130	22	THERMOELECTRIC COOLING
40	K	404.41 II	75	G		R212	10	

Q = Quartz
G = Glass
C = Corex blue glass
Y = Yellow glass

* = Not utilised

data, including sample identification, to and from a Friden Flexowriter 2305. The latter, with a 24" carriage width, is the primary output device for 'hard copy', providing sample identification and computed data for the 39 analytical channels on one line. Other options for data output include the IBM 1130 card punch, paper tape punch, and lineprinter.

The minus 100 mesh (150 μm) fraction of the stream sediment was ground in agate to pass 300 mesh (50 μm) using a Fritsch Pulverisette 5. A portion of the ground material was ignited at 450°C for two hours, and a 100 mg sub-sample mixed with an equal weight of spectroscopic buffer, a 1:1 mixture of NaF (Koch Light Chemicals, high purity) and pelletable graphite (Johnson Matthey Chemicals 'Specpure') containing In, Eu and Pt as internal standards.

A 30 mg pellet of the buffered sample mixture was arced (99 sec at 13A, anode excitation) in a flow of argon/oxygen (75% / 25%) used to control arc wandering and limit interference from CN emission.

The accumulated counts for 39 channels were recorded by the IBM 1130 Computer. Calibration was performed by carrying out polynomial regression, to the third order if necessary (Coats, 1974), on data obtained for a series of synthetic reference materials prepared by a co-precipitated gel technique (Date, 1977) and arced in the same way. The selection of internal and background correction channel for each analytical element was made using correlation data for a wide series of synthetic matrix reference materials, and by consideration of results obtained for international standard rocks and geochemical prospecting samples.

The computed values of concentration for trace, minor and several major elements were output on the Flexowriter and in the form of punch cards. Several trace elements were corrected for major element interferences

Sample collection of panned concentrates

Heavy mineral concentrates were obtained by panning 2-3 kg of sediment screened through a 0.25 cm nylon sieve by the classical gold panning technique to constant volume as described by Leake and Aucott (1973), to provide 25 - 30 g of concentrate. Samples were then oven dried and subsampled by riffing to provide 12 g portions for analysis. The remainder was retained for mineralogical examination.

Chemical analysis of panned concentrates

The 12 gram subsamples were ground at 960 rev min^{-1} with 3 grams of Elvacite 2013 (Dupont and Co's low molecular weight poly methyl n-butyl methacrylate) for five minutes in a 100 ml tungsten carbide vibratory disc mill. The resultant minus 200 BSI mesh powder was pressed at 25 tons load in a 40 mm diameter pellet die to form relatively robust discs with a flat, smooth surface. Comminution of both concentrate and polymer, within which no inorganic impurities have been detected, and their mutual homogenisation took place during grinding (Smith, 1971).

The determinations were made with a Philips PW1220C automatic X-ray fluorescence spectrometer fitted with a tungsten anode tube. $K \alpha$ lines were used except for thorium and uranium ($L \alpha$) and lead ($L \beta$), and counting times ranged from 2 to 200 seconds per element. Further details of instrumental conditions are given in Smith and Hertroys (in preparation). Calibration standards were prepared by addition of pure compounds to a matrix of varying proportions of ferric oxide, calcium carbonate and silica.

A monitor standard was used for external ratio at the wavelength of the analytical line for each element. For most elements a further internal (inverse) ratio was made at a suitable continuum wavelength such that

$$R_i = \frac{I_i^x}{I_i^s} \cdot \frac{I_{scatter}^s}{I_{scatter}^x}$$

where x = unknown sample
s = monitor standard
i = analyte
R = external/internal ratio
I = intensity already corrected for background and line overlap

This provided a correction for mass absorption variations between differing matrices (Smith and Hertroys, op. cit.). The external/internal ratios were then fitted by least squares regression to the equation

$$C_i = (m_i + m_i^* C_i) R_i + C_i^*$$

where c = concentration
c* = intercept on concentration axis
m = slope
m* = slope correction

in order to obtain the calibration constants.

The concentrate samples collected during the earlier part of the survey (approximately 40% of the total) were analysed with the same spectrometer and conditions and a similar monitor but with a different method of calibration and mass absorption (see Leake and Aucott, 1973). Linear regressions of 40 selected samples analysed by both methods enabled adjustments to be made where necessary to the results to make them compatible with previous results.

Analytical precision

Stream sediments

Table 4 shows estimates of analytical precision for elements determined in sieved sediments both in the form of coefficients of variation and a logarithmic analytical variance parameter derived from the comparison of duplicate samples. Estimates of the relative standard deviation are derived from a total of 164 determinations of 5 in house standard sediment samples.

Estimates of analytical variance, including the subsampling of the sieved and ground sample, calculated for comparison with the total sampling plus analytical variance estimates, are based on the analyses of 42 duplicate stream sediment samples using the formula of Garrett (1973) -

$$S_A = \frac{1}{2N} \sum_{i=1}^N (x_{1i} - x_{2i})^2$$

where S_A = analytical variance
 N = number of replicates
 x_{1i} x_{2i} = log (10) of concentrations of an element in the two replicates

No meaningful estimates of S_A can be obtained for elements where the majority of samples contain levels below the detection limit of the analytical method as is the case for Mo and Sn. Estimates of the relative standard deviation fall between 4% and 25% except in the case of zirconium where the poor analytical precision probably results from the refractory properties of zircon in the emission arc.

Panned concentrates

Table 5 shows estimates of analytical precision for elements determined in panned concentrates, derived by the same methods as for sieved sediments. Because of lack of sufficient data, analytical precision estimates for Y, Zr, Nb, Th, and U were calculated from the consideration of counting statistics at levels corresponding to the mean concentration of these elements in the total population of panned concentrates. Estimates of the relative standard deviation of analytical precision fall between 1% and 3% for elements where concentrations are generally well above the detection limit of the analytical method, but as the average concentration of an element approaches the detection limit the estimates rise markedly.

TABLE 4. Analytical precision for stream sediments.

Element	Method	Coefficient of variance %		Average level of 164 determinates of 5 standard samples in ppm	Analytical Variance log 10
Li	D.R.	4.9	A	93.1	0.0005
Be	D.R.	22.1	A	7.2	0.0085
B	D.R.	15.9	A	148.8	0.0055
MgO	D.R.	7.2	A	2.1	0.0045
K ₂ O	D.R.	20.0	A	6.3	0.0050
CaO	D.R.	3.9	A	0.7	0.0020
TiO ₂	D.R.	8.2	A	1.1	0.0025
V	D.R.	14.7	A	173.6	0.0065
Cr	D.R.	14.6	A	96.5	0.0045
Mn	D.R.	15.4	A	0.29%	0.0120
Fe ₂ O ₃	D.R.	14.4	A	7.34	0.0050
Co	D.R.	12.4	A	60.9	0.0065
Ni	D.R.	15.6	A	201.8	0.0085
Cu	D.R.	6.4	A	274.3	0.0075
Zn	A.A.S.	7.4	B	107.2	0.0050
Ga	D.R.	10.6	A	24.3	0.0015
Rb	D.R.	9.0	A	188.1	0.0010
Sr	D.R.	14.7	A	160.3	0.0075
Y	D.R.	12.1	A	33.6	0.0045
Zr	D.R.	57.0	A	563.0	0.0515
Mo	O.E.S.	10-15%	C	-	-
Sn	O.E.S.	10-15%	C	-	-
Ba	D.R.	10.5	A	677.0	0.0020
Pb	D.R.	24.8	A	341.7	0.0075
U	D.N.A.	3.0	D	-	-

NOTES

- A - Mean of coefficient of variation of 164 determinations of 5 standard sediments
- B - Coefficient of variation of 296 determinations of 1 standard sediment
- C - Estimated at the 50 ppm level
- D - From Ostle et al., (1972).

TABLE 5. Analytical precision for panned concentrates.

Element	Method	Coefficient of variance %	Average level of 183 determinations of 9 samples	Analytical variance \log_{10}
Ca	XRF	2.9	0.87%	0.00015
Ti	"	1.1	0.49%	0.00009
Mn	"	1.9	938 ppm	0.00009
Fe	"	1.5	5.06%	0.00005
Ni	"	4.4	33.3ppm	0.00140
Cu	"	12.1	44.5ppm	0.00174
Zn	"	2.4	110.0ppm	0.00054
Y	"	15.0	-	-
Zr	"	1.1	-	-
Nb	"	9.0	-	-
Ba	"	1.8	604.0ppm	0.00017
Ce	"	17.4	50.3ppm	0.04850
Pb	"	18.2	52.3ppm	0.00435
Th	"	40.0	-	-
U	"	55.0	-	-

A - Estimated from counting statistics at log mean total population level

Comparability of analytical methods

The comparability of results obtained by the XRF and D-C arc direct-reading optical emission spectrometry methods of analysis is assessed by analysis of the same samples by both methods. Fig. 3 compares determinations of Ca, Ti, Mn, Fe, Cu, Ba and Pb in 15 stream sediments. Relative agreement between the two methods is good with the exception of Fe and Pb. A similar degree of scatter to that exhibited in Fig. 3 is shown by a comparison of AAS and XRF lead results in Leake and Smith (1975) over a similar compositional range but over a wider range of lead contents agreement between the two methods is better (Leake and Aucott, 1973). Linear regression between 448 DR stream sediment lead determinations and the same number of AAS determinations after digestion of the sample in a $\text{HNO}_3 - \text{HClO}_4$ mixture also shows close relative agreement over a wide compositional range (correlation coefficient 0.96) but a significant positive bias and intercept in favour of the Direct Reader results (regression coefficient 1.55 or intercept 11.3 ppm). The high degree of correlation shown between XRF and AAS zinc determinations is illustrated in Leake and Aucott (op. cit.) and Leake and Smith (op. cit.). Both XRF (Leake and Aucott, (op. cit.)) and direct reader nickel determinations compare favourably with AAS results for 376 stream sediment samples the correlation coefficient for nickel between DR and AAS results being 0.88 and the regression coefficient 1.01).

Sampling precision

Estimates of sampling precision have been made by the resampling and analysis of sediments and concentrates from 47 sites within south-west Scotland. These sites were selected to represent a range of rock and mineralisation sources. Resampling was carried out by collecting a duplicate at the original site after the lapse of at least one year. This procedure was adopted to provide an estimate of sampling precision over a long period of time, a factor not taken into account by the simultaneous collection of

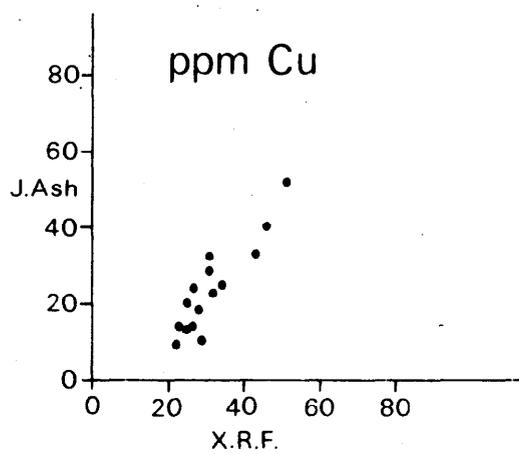
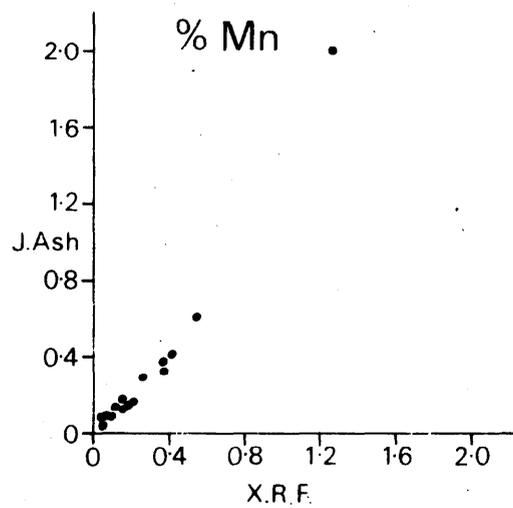
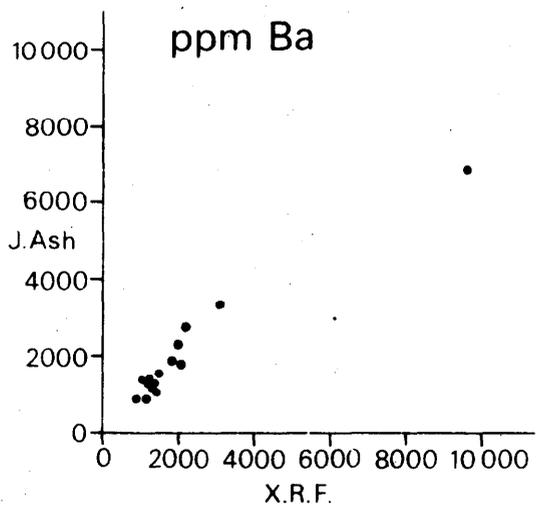
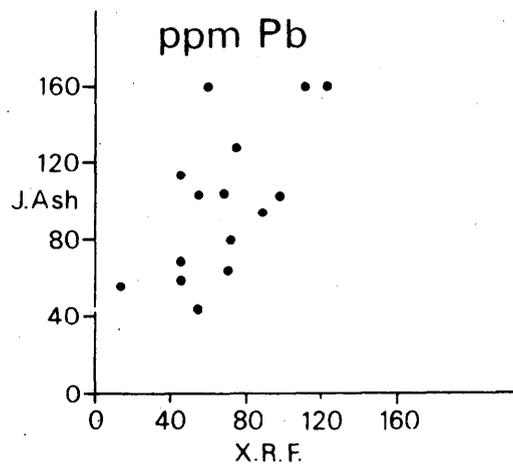
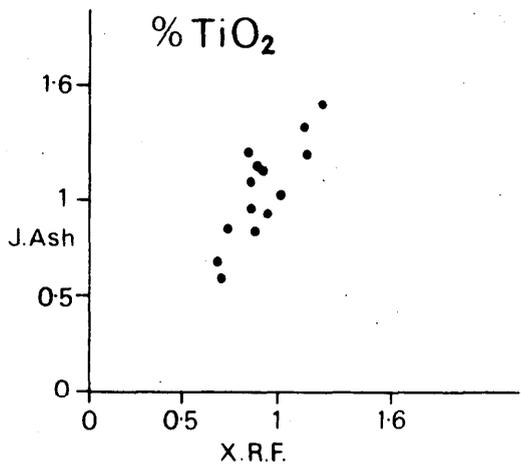
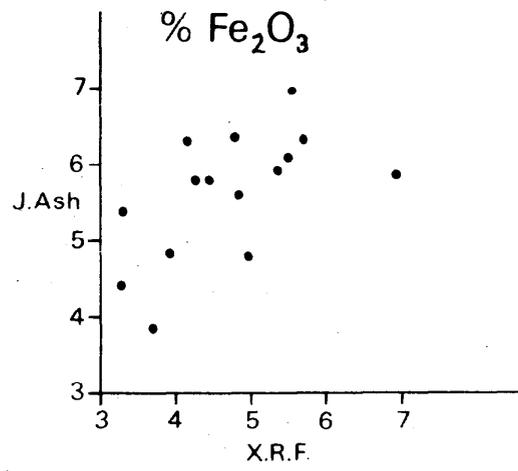
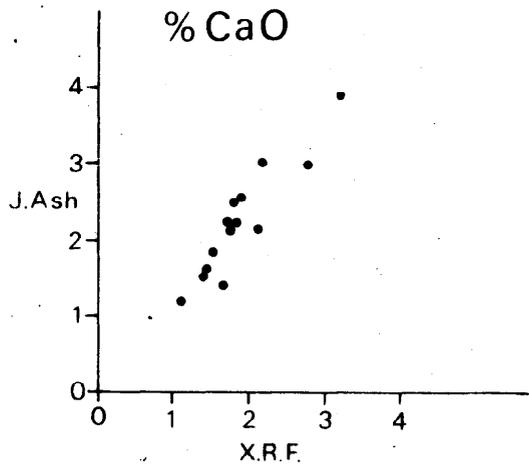


Fig. 3. Comparison of analytical methods.

replicate samples. The total sampling plus analytical variance for each element in both sample types was estimated using the method of Garrett (1973) and compared (Tables 6 and 7) with the corresponding analytical variance estimates to give a measure of the sampling variance by difference.

Fig. 4 and 5 compare the variances for the sieved sediments and concentrates respectively, the difference being a measure of the sampling plus preparation sub-sampling variance for the sieved sediments and the sampling plus sub-sampling variance for the concentrates. No precision estimates have been made for molybdenum and tin in stream sediments or tin and antimony in concentrates because of the small number of samples containing detectable quantities of these elements.

Comparison of the analytical and total variance estimates for each element reveal substantial variations in sampling precision which to a large extent can be related to the mode of occurrence in the stream sediment. The elements with the highest sampling precision are Ti, Mg and Cr, which occur predominantly in common relatively-resistant detrital minerals, and those which occur in common rock forming silicates or their weathering products, such as K, Sr, Li, Ca, Rb and Be. The lowest sampling precision is shown by Mn, which occurs frequently in the form of secondary oxide precipitates, formed in oxygenated streams draining boggy areas. Similar behaviour is shown by elements which are often absorbed onto these precipitates or onto the finest clay and organic components of the stream sediment such as Co, Zn, U and Pb. Fe, V, Cu and Ba, which may be variably partitioned between detrital, precipitate or absorbed phases (Gibbs, 1973; Levinson, 1974) display an intermediate sampling precision.

Several factors may account for the relatively low sampling precision of elements associated with secondary oxide or clay grade fractions of stream sediments. The amount of rainfall and run-off immediately prior to

sampling probably influences both the quantities of elements adsorbed on clay grade material and the proportion of this fraction within the stream sediment. Thus elements like uranium which are widely dispersed in the Main Granodiorite and released into solution by rock weathering will not only be removed rapidly by high run-off but will also tend to accumulate in the adsorbed form during periods of low rainfall.

Sampling tends to account for a higher proportion of the total variance of elements in concentrates than sieved sediments, except in the case of Mn, Fe, Zn and Ba. Concentrate sampling error for elements occurring predominantly in common rock-forming minerals is lower than for elements present mostly in the heavier accessory minerals, such as Y, Zr and Ce. Sampling variance for Mn appears anomalously high, probably as a result of the influence of grain coatings in some samples. For elements present in minerals derived from hydrothermal mineralisation, sampling precision is partially related to the mode of occurrence of the mineral. The survey provides evidence that where concentrate samples are collected downstream of mineralised structures perpendicular to the stream, or where ore minerals occur as minor relatively coarse grains, the sampling precision is poor. Where samples are derived from larger mineralised sources or from structures sub-parallel to the stream there is a marked improvement of the sampling precision.

TABLE 6. Sampling and regional variance for stream sediments.

Element	Analytical variance (log 10)	Total sampling + analytical variance (log 10)	Regional variance (log 10)	F ratio
Li	0.0005	0.0035	0.024	6.9
Be	0.0085	0.0110	0.021	1.9
B	0.0055	0.0156	0.038	2.4
MgO	0.0045	0.0101	0.046	4.6
K2O	0.0050	0.0048	0.055	11.5
CaO	0.0020	0.0069	0.093	13.5
TlO2	0.0025	0.0064	0.013	2.0
V	0.0065	0.0147	0.024	1.6
Cr	0.0045	0.0095	0.065	6.8
Mn	0.0120	0.0580	0.200	3.4
Fe2O3	0.0050	0.0210	0.031	1.5
Co	0.0065	0.0395	0.065	1.6
Ni	0.0085	0.0200	0.034	1.7
Cu	0.0075	0.0264	0.060	2.3
Zn	0.0050	0.0365	0.081	2.2
Ga	0.0015	0.0100	0.016	1.6
Rb	0.0010	0.0060	0.065	10.8
Sr	0.0075	0.0070	0.106	15.1
Y	0.0045	0.0017	0.013	0.8
Zr	0.0515	0.1275	0.112	0.9
Ba	0.0020	0.0205	0.056	2.7
La	0.0055	0.0470	0.070	1.5
Pb	0.0075	0.0310	0.093	2.4
U				

TABLE 7. Sampling and regional variance for panned concentrates

Element	Analytical variance (log)	Total sampling + analytical variance	Regional variance (log)	F ratio
Ca	0.00015	0.0158	0.164	10.4
Ti	0.00009	0.0240	0.087	3.6
Mn	0.00009	0.0425	0.093	1.9
Fe	0.00005	0.0158	0.112	7.1
Ni	0.00140	0.0200	0.070	3.5
Cu	0.00174	0.0470	0.522	11.0
Zn	0.00054	0.0070	0.060	8.6
Y	-	0.1060	0.275	2.6
Zr	-	0.1345	0.025	6.1
Nb	-	0.1365	0.450	3.3
Ba	0.00017	0.0095	0.314	4.2
Ce	0.04850	0.0425	0.341	7.0
Pb	0.00435	0.0750	0.189	2.5
Th	-	0.1955	0.449	2.3
U	-	0.0295	0.310	3.5

PRECISION FOR STREAM SEDIMENTS

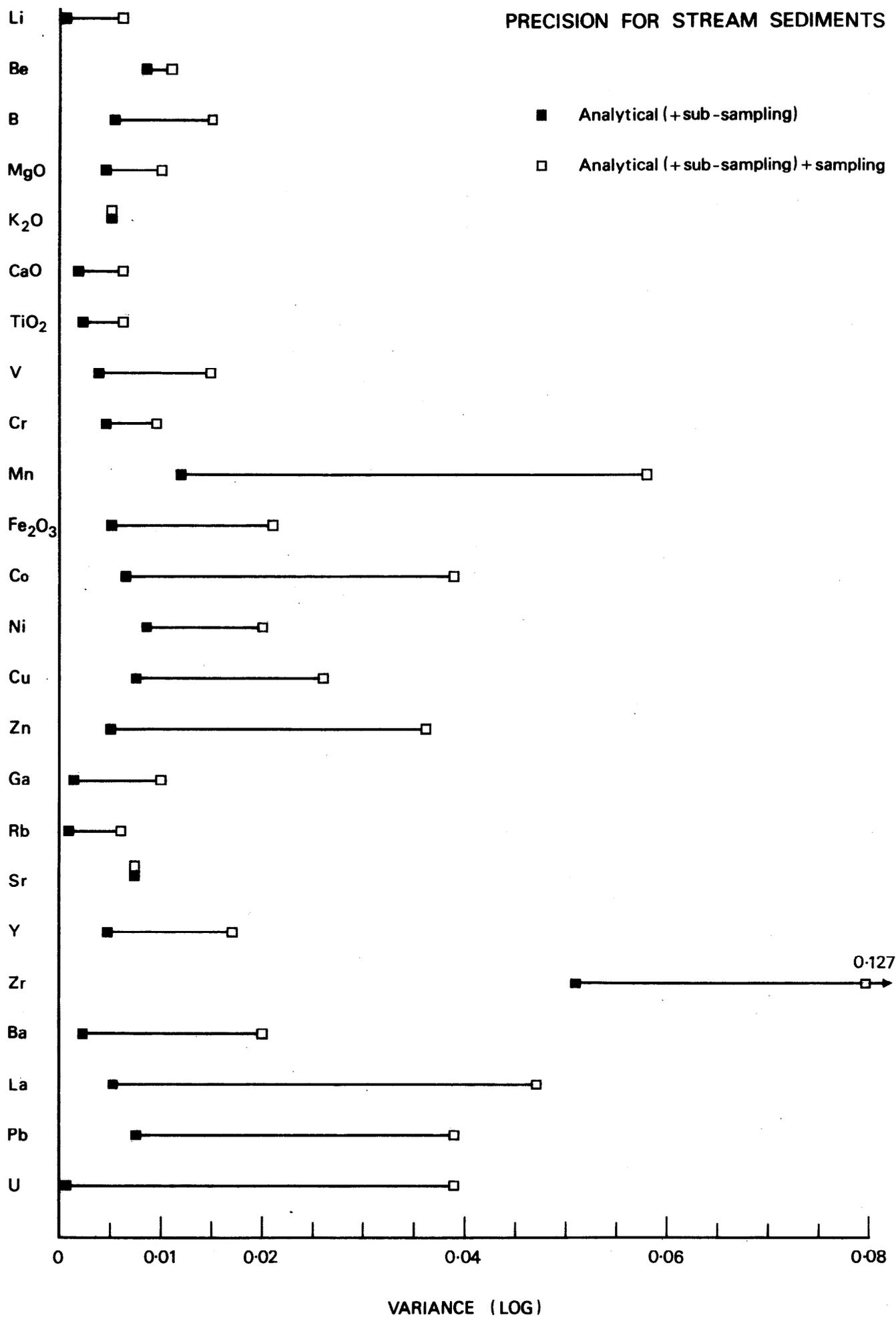


Fig. 4.

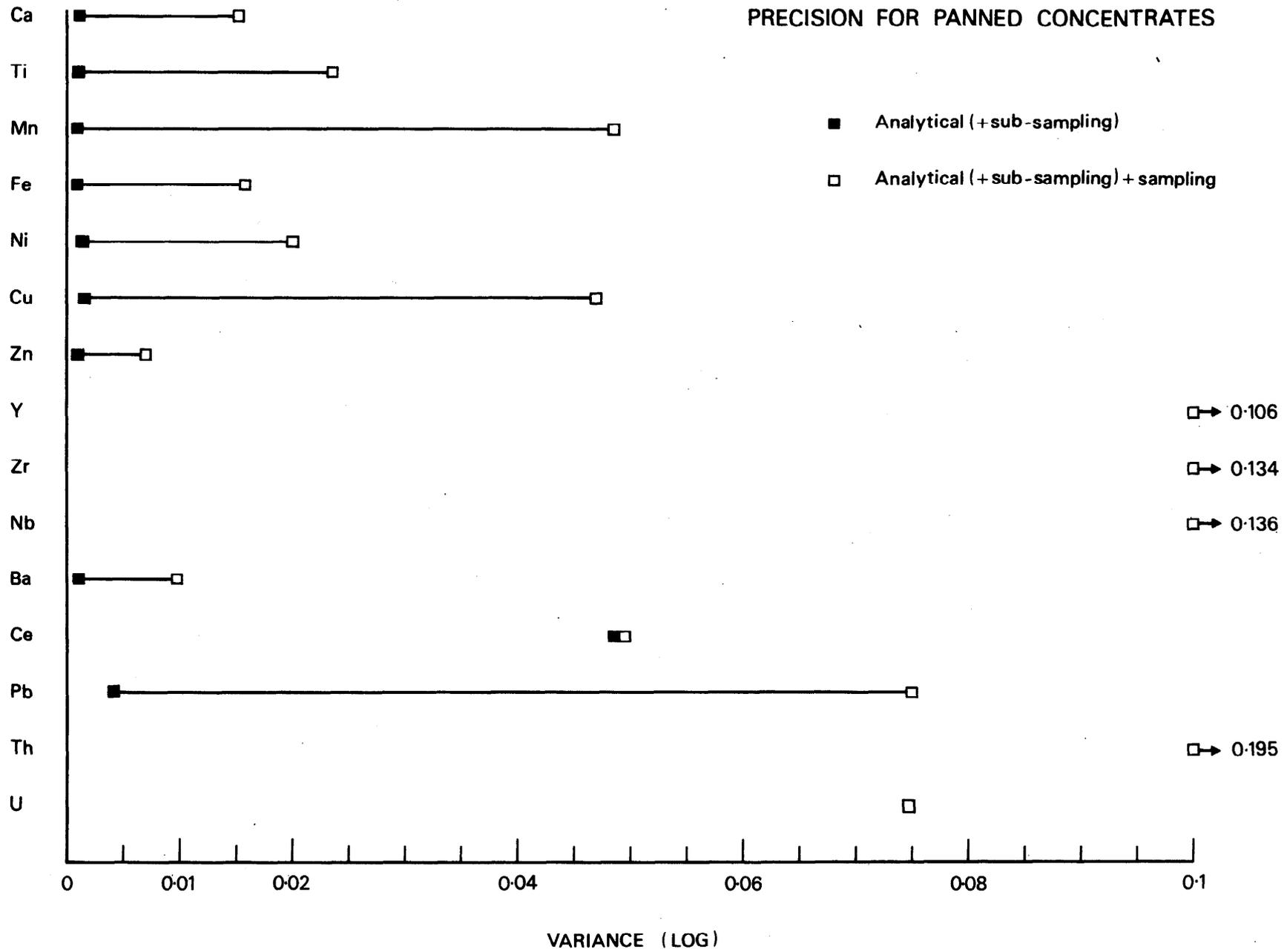


Fig. 5

APPENDIX II GEOCHEMICAL MAPS AND DESCRIPTION OF ELEMENT DISTRIBUTION

Introduction

Lithium	sediment
Beryllium	sediment
Boron	sediment
Magnesium oxide	sediment
Potassium oxide	sediment
Calcium oxide	sediment
Calcium	concentrate
Titanium oxide	sediment
Titanium	concentrate
Vanadium	sediment
Chromium	sediment
Manganese	sediment
Manganese	concentrate
Iron oxide	sediment
Iron	concentrate
Cobalt	sediment
Nickel	sediment
Nickel	concentrate
Copper	sediment ;
Copper	concentrate
Zinc	sediment
Zinc	concentrate
Gallium	sediment
Rubidium	sediment
Strontium	sediment
Yttrium	concentrate
Zirconium	sediment
Zirconium	concentrate
Niobium	concentrate
Molybdenum	sediment
Tin	sediment
Tin	concentrate
Antimony	concentrate
Barium	sediment
Barium	concentrate
Cerium	concentrate
Lead	sediment
Lead	concentrate
Thorium	concentrate
Uranium	sediment
Uranium	concentrate

Introduction

Class intervals plotted for the distribution of Fe, Co, Cu, Zn, Sr, Zr, Ba, Pb and U in sieved sediment and Ca, Ti, Mn, Fe, Zr, Sn, Ba, Ce, Pb and Th in panned concentrates are based on the changes in slope on the cumulative frequency diagrams. The geochemical maps showing the distribution of Be, B, Mg, Ca, Ti, Mn and Rb in sieved sediments and Cu, Zn and Nb in panned concentrates are plotted in terms of class intervals based both on a break in slope on the cumulative frequency plot and on the log mean plus one and two standard deviation levels of the upper population. Class intervals for Li, K, Cr, Ni and Ga in sieved sediment and Ni and Y in panned concentrate which show a close to lognormal distribution are based on the log mean plus one and two standard deviation levels for the total population. Class intervals used in the plotting of Mo and Sn in sieved sediments and Sb and U in panned concentrates are based on an estimate of the analytical detection limit together with breaks of slope or arbitrary limits.

Lithium (sediment)

Relative lithium enrichment is confined to samples derived from the plutonic igneous rocks or their immediate contact zones. The greatest lithium contents occur in samples derived from the central part of the Main Granodiorite to the south of New Abbey Pow. As other samples derived from the central more siliceous porphyritic phase of intrusion contain relatively low levels of lithium, it is concluded that lithium distribution is not related simply to the degree of magmatic differentiation of the Main Granodiorite. The relatively low positive correlation between lithium and manganese and iron, together with the lack of lithium enrichment in the relatively clay-rich grab samples, which were collected simultaneously with the sieved sediments from a few sites within the Main Granodiorite,

also suggest that lithium distribution is not significantly influenced by secondary environmental factors. Compared with the Main Granodiorite the lithium content of samples derived from the Western Granodiorite and the Bengairn Quartz Diorite, except for its northern margin, are relatively low.

Beryllium (sediment)

Beryllium is relatively enriched in samples derived from the Main Granodiorite, particularly from the west-central part of the intrusion. Comparison of beryllium contents of clay-rich grab samples collected simultaneously with the sieved sediments at a few sites within the Main Granodiorite suggest a positive correlation between beryllium levels and the amount of clay derived from the weathering of the granodiorite within the stream sediments. Both the geographical distribution of relatively beryllium-rich samples and the high positive correlation between beryllium and potassium and rubidium (Table 1) indicate a tendency for beryllium to be concentrated in the central most differentiated porphyritic facies of the Main Granodiorite. No obvious distribution patterns are discernable within samples derived from the Lower Palaeozoic turbidites.

Boron (sediment)

Samples in the lowest class are almost all confined to the outcrops of the Main and Western Granodiorite and there is a tendency for the lowest levels to occur in samples derived from the central most-differentiated part of the intrusion. According to Harder (1976) the boron in most granitoid rocks is largely contained in sericite derived from plagioclase, and the boron content increases with anorthite content. Such a source would account for the greater boron contents in the peripheral more basic facies of the intrusion.

Samples derived from the Lower Palaeozoic turbidites clearly contain more boron than those from the granitic rocks. Though tourmaline has been identified in the heavy mineral fraction of greywackes from the Southern Uplands, chemical analysis of Silurian greywackes from Lesmahagow (Walton, 1963) showed the boron to be associated in particular with the illite clay fraction.

Samples with the highest boron contents are concentrated in two areas where hydrothermal mineralisation is known to occur. In the extreme east of the area boron is derived from a prominent north-north-west trending mineralised fracture zone where it cuts the sedimentary rocks adjacent to the Main granodiorite. No boron enrichment is associated with the structure as it cuts the intrusion. Between Bengairn and the River Dee there are two main areas of boron enrichment, one marginal to the Bengairn quartz diorite and the other in an arcuate zone adjacent to the River Dee.

Tourmaline is a conspicuous component of both disseminated and vein copper-bearing mineralisation at Screel Burn (Leake et al., in preparation) and has also been observed in igneous rocks around Bentudor and Barcloy Hill.

The Screel Burn mineralisation appears to lie within the pyrite halo which surrounds the Black Stockarton Moor porphyry-style mineralisation complex (Brown et al., in preparation) and studies of American porphyry coppers (Chaffee, 1976) indicate that boron is often relatively enriched within the cores of these deposits. The presence of tourmaline also probably accounts for the boron anomalies adjacent to the River Dee as minor amounts of the mineral have been observed in rocks showing propylitic alteration outside the pyrite halo of the Black Stockarton Moor mineralised complex. Tourmaline has also been recorded in the peripheral alteration zones of some American porphyry coppers (Lowell and Gilbert, 1970). Boron-

rich samples from south of Black Stockarton Moor and from west of White Hill are also thought to reflect porphyry-style copper mineralisation belonging to the same mineralisation complex.

Magnesium oxide (sediment)

The majority of the samples in the lowest class are derived from the central part of the Main Granodiorite, coinciding approximately with the more acid porphyritic facies. The marginal parts of this intrusion are characterised by a higher magnesium content with a distinct area in the south-east particularly rich in the element. Hornblende together with biotite and some epidote have been identified in panned stream sediments as the main magnesium hosts in this area. The Western Granodiorite is more magnesium-rich than the central more acidic part of the Main Granodiorite. The most magnesium-rich samples, with up to 10.3% MgO, are derived from the Bengairn quartz diorite where clinopyroxene in addition to amphibole and biotite are the main host minerals. Relatively magnesium-rich samples are derived from the separate granodioritic/dioritic sheet intrusions of Bentudor and to a lesser extent those associated with the Black Stockarton Moor sub-volcanic complex (Leake et al., in preparation).

Potassium oxide (sediment)

Relatively high potassium concentrations are clearly associated with the Main and the Western Granodiorite but there is a considerable range of values and no clearly discernible pattern. Stream sediments derived from parts of the contact zone of the Criffel-Dalbeattie complex are also relatively potassium rich, particularly in the south-eastern part. A group of samples in the north-west of the area, to the west of Woodhall Loch, contain more potassium than others derived from the Lower Palaeozoic turbidites. Samples from this area in addition contain higher levels of other elements which tend to concentrate in granitic rocks. In view of the lack of evidence of any suboutcropping granite in the area these samples are thought to have

been derived from a greywacke unit containing a significant proportion of granitic detritus.

Calcium oxide (sediment)

There is little variation in the calcium contents of samples derived from the Lower Palaeozoic turbidites but there is considerable contrast between different parts of the Criffel-Dalbeattie complex. The central and northern parts of the Main Granodiorite are characterised by samples with low calcium but are surrounded to the north-east and south by areas richer in calcium. High calcium concentrations are evident towards the south-east of the intrusion, an area also characterised by magnesium enrichment, with stream sediments containing more calcium than those derived from the Western Granodiorite and most parts of the Bengairn quartz diorite.

Calcium (concentrate)

There is close agreement between the concentrate and the corresponding sieved sediment map, but there is rather more scatter in the former, explained by the lower total sampling plus analytical precision and only slightly greater regional contrast of the concentrates.

Hornblende has been identified as the main calcium-rich mineral in concentrates derived from the igneous rocks, together with leucoxene, sphene and epidote, but samples originating from areas of sedimentary rocks can also contain a significant amount of apatite and augite.

Titanium oxide (sediment)

There is no obvious pattern of titanium distribution over the Lower Palaeozoic turbidite sequence. The majority of samples derived from the Main Granodiorite are relatively depleted in titanium but two areas, in the south-west and the south-east, are relatively titanium-rich, as are samples from the northern contact zone. Evidence from the examination of concentrate samples from the Main Granodiorite suggests that the titanium occurs mostly as sphene, a prominent constituent of the granodiorite. The stream sediments

demonstrate that the Bengairn quartz diorite and possibly the northern part of the Western Granodiorite are also relatively rich in titanium and mineralogical evidence indicates that the titanium is mainly contained in oxide minerals rather than sphene. The area dominated by the Black Stockarton Moor subvolcanic complex is also characterised by samples with relatively high titanium concentrations. The basic Birrenswark lavas at the base of the Carboniferous probably account for some titanium-rich samples in the extreme south-east of the area.

Titanium (concentrates)

There are significant differences between the two titanium maps. The Main Granodiorite shows a much larger area of relative titanium enrichment and a greater scatter of values for concentrates than sediments, which in part can be accounted for in terms of the significantly poorer overall sampling and analytical precision shown by the concentrates. Anatase and sphene have been identified in concentrates derived from the central part of the granodiorite. The concentrate map shows little titanium enrichment associated with the Bengairn Quartz Diorite or the Porphyrite complex unlike the sediment map. This divergence is difficult to explain unless the titanium-bearing minerals are relatively fine grained and therefore poorly sampled by panning. Though there is agreement between the two sample types in the predominantly low levels of titanium associated with the Lower Palaeozoic sediments there is little correlation between those samples of each type containing higher levels. The moderately titanium-rich samples in the extreme south-east of the area are partly derived from the Birrenswark lavas at the base of the Lower Carboniferous sequence.

Vanadium (sediment)

Vanadium distribution patterns are relatively subdued but three modes of enrichment in stream sediments can be distinguished. The relatively vanadium-rich samples which are grouped over the outcrop of the Bengairn Quartz Diorite and to a lesser extent the Black Stockarton Moor

subvolcanic complex can be explained by the greater proportion of iron oxides associated with these intrusive rocks compared with the Main Granodiorite and the surrounding sedimentary rocks. Magnetite, which in igneous rocks is frequently relatively vanadium-rich (Goldschmidt, 1959), is probably the main host mineral in these samples. For the majority of samples belonging to the upper concentration class the vanadium enrichment is probably of secondary origin as at these sites there is a relatively high proportion of environmentally precipitated iron oxide. Some indication of an association of vanadium with hydrothermal mineralisation is shown by the occurrence of vanadium-rich samples from Screel Burn, Troadale Burn and along the eastern margin of the Main Granodiorite where vein mineralisation is known to occur. In these areas hematite is the only mineral of significance that acts as a host, though analysis of separated minerals (Evans and Landergren, 1974) indicates that the vanadium content of most hydrothermal iron oxides appears to be relatively low. West of Kirkbean relatively vanadium-rich samples could reflect the outcrop of the basic basal Carboniferous Birrenswark lavas.

Chromium (sediment)

In general samples derived from the sedimentary rocks are much richer in chromium than those originating from the igneous rocks. Enrichment in chromium is not universal within the sediments but can be correlated with certain units within the turbidite sequence, the most obvious of which follows the regional strike to the south of the black shale belt near Crossmichael. Chromian spinel has been identified as the main chromium-bearing mineral in concentrate samples from this area. A further chromium-rich turbidite unit appears to follow the northern margin of the Criffel-Dalbeattie plutonic complex. Several samples derived from the Main Granodiorite adjacent to this belt also contain similar levels of chromium.

As chromium shows no significant correlation with elements which vary according to the degree of differentiation within the granodiorite it is suggested that these high chromium values might be due to the incorporation of chromium-rich turbidites into the igneous rock and the preservation of the chromian spinel in spite of magmagenesis, because of its refractory nature (Goldschmidt, 1954).

Manganese (sediment)

Manganese shows a greater range, from 200 ppm to 17.9%, than any other element in the stream sediments but shows very poor total sampling and analytical precision. Both of these features of the data are the result of the major environmental influence on the pattern of manganese distribution which also makes variations in concentration related to geological differences difficult to detect. In most cases samples derived from the Lower Palaeozoic sedimentary rocks contain less manganese than those derived from the igneous rocks, particularly the Bengairn Quartz Diorite. There also appears to be a significant increase in manganese contents to the west of the counter-Caledonoid fault passing through Woodhall Loch which may represent compositional differences in the greywackes on either side of the fault.

Samples derived from the Main Granodiorite show a much greater range in manganese contents than those from other rocks but this is largely due to environmental enhancement of manganese in boggy upland terrain by precipitation in the relatively oxidising stream course. Only one manganese-rich sediment sample, from Screel Burn, can be considered with confidence to reflect the presence of manganese of hydrothermal origin. The manganese is in an oxide form in a gossan developed within brecciated altered porphyrite and greywacke also containing vein quartz, hematite and secondary iron oxides and some secondary copper minerals. There is possibly some manganese derived from the mineralised structure in stream sediments collected south of Loch Kindar.

Manganese (concentrate)

The enrichment of manganese on grain surfaces due to co-precipitation of hydrous manganese oxide may account for the relatively poor sampling precision when compared with other elements in panned concentrates. This effect is more serious for stream sediment samples, where meaningful geological patterns may be obscured. A relatively high manganese concentration is a feature of samples from the south-east, south-west and north of the main granodiorite. This distribution pattern is similar to that of titanium oxide in sieved sediments and reflects the more mafic parts of the intrusion. The few manganese-rich samples from the central porphyritic zone may be due to secondary enrichment. The concentrates show no evidence of relative manganese enrichment in the western granodiorite or the Bengairn Quartz Diorite. Within the outcrop of the Lower Palaeozoic sediments manganese levels are generally low except in the vicinity of the Black Shale belt near Crossmichael and west of the counter-Caledonide Fault passing through Woodhall Loch. Manganese enrichment associated with hydrothermal mineralisation is detectable in samples from Screel Burn and in others derived from the north-north-west trending fault system east of Criffel and its probable northern extension.

Iron oxide (sediment)

Distribution patterns are indistinct and only partially related to known or presumed geological variations. In general samples from the Lower Palaeozoic rocks have a relatively low iron content. Samples from the south of the Main Granodiorite have a higher iron content than those from the north, reflecting the more basic nature of the granodiorite in the south. Samples collected over more felsic parts of the granodiorite which show high iron can in most cases be explained by iron enrichment in streams within poorly drained ground. Samples derived from the Bengairn Quartz Diorite are relatively rich in iron, reflecting its basic nature and also the presence of hematite-bearing structures.

Iron (concentrate)

Both the total sampling plus analytical precision and regional variance are greater for iron in concentrates than in sieved sediment samples. Because of secondary environmental influences on iron concentrations in sieved sediments, agreement between the two sample types in many areas is poor. The concentrate samples reflect differences in iron oxide and silicate content related to host rock composition but are more influenced by the presence of hematite mineralisation and concentrations of pyrite. Within the granodiorite complex there is a tendency for the samples with the lowest iron concentrations to be derived from the central porphyritic granodiorite and those with rather higher concentrations to be derived either from the south-eastern part of the Main Granodiorite or from the Bengairn Quartz Diorite. Samples from the Main Granodiorite exhibit a particularly high range of iron concentrations but in some cases those within the upper two classes are known to be derived in part from hematite-bearing structures, e.g. in the north-north-west trending fracture system east of Criffel, or the granodiorite margin in the vicinity of Kirkgunzeon. Hematite mineralisation is also the major source of high iron levels in Screel Burn and the areas to the west and south-west around the Bengairn Quartz Diorite. Iron-rich samples from the area of the Black Stockarton Moor subvolcanic complex reflect the presence of hematite veins and disseminated pyrite or iron oxide mineralisation associated with porphyry-style copper mineralisation in the area.

Cobalt (sediment)

Sampling precision is relatively poor because of the close association of cobalt with environmentally influenced secondary manganese precipitation. This process tends to dominate the distribution of cobalt, particularly in the Main Granodiorite, as most samples within the upper two concentration classes

are associated with high manganese levels. Exceptions are provided by those samples derived from the north-north-west trending fracture system where the cobalt is probably of hydrothermal origin. The cobalt concentration of samples derived from the sedimentary rocks generally falls within the lowest class except in the extreme north west and around Woodhall Loch but even in these areas manganese levels tend to be relatively high. There is a tendency for samples from the Bengairn Quartz Diorite and the granodiorite sheet intrusions around Barcloy Hill to show slight relative cobalt enrichment which is probably related to the more mafic nature of these rocks compared with other members of the igneous complex.

Nickel (sediment)

The nickel contents of samples derived from the Lower Palaeozoic sediments are relatively low except for two from the Black Shale Belt near Crossmichael. The Bengairn Quartz Diorite is the only member of the Criffel-Dalbeattie complex from which samples with relatively high nickel contents are derived, and this reflects its relatively basic composition. Several nickel-rich samples are also associated with the subvolcanic complex centred on Black Stockarton Moor, particularly the granodiorite sheets around Barcloy Hill. Some nickel is also associated with the hematite-rich mineralised structure in Screel Burn and its continuation to the west. Nickel concentrations are also relatively high in samples derived from the mineralised fracture system to the east of Criffel but as the Birrenswark basic lavas outcrop at the base of the Carboniferous in this area some of the nickel could be derived from these rocks.

Nickel (concentrate)

Nickel-rich samples are concentrated in the area of the mineralised fracture system at the margin of the granodiorite to the east of Criffel, the nickel probably being accommodated largely in iron oxides derived partly from the mineralised structure or partly from the Birrenswark lavas which outcrop against the fault system. There is little evidence of mafic

silicates except for chlorite (which could also accommodate nickel) in concentrates downstream of the lava outcrop. The only two nickel-rich samples derived entirely from the Main Granodiorite occur within the most basic part in the extreme south-east. Unlike the stream sediments, concentrates derived from the Bengairn quartz diorite are not anomalously rich in nickel. Nickel-rich concentrates are derived from the iron-rich mineralised structures in Screel Burn but the source of a similar anomalous group of samples in the nearby streams to the north is not known. The nickel within the two anomalous samples from north of Black Stockarton Moor may be associated with iron-rich alloy fragments identified as contaminants in the samples in addition to being accommodated in iron oxide minerals.

Copper (sediment)

Copper is clearly most abundant in stream sediments from within and around the Bengairn Quartz Diorite intrusion and in the northern and southern parts of the area underlain by the subvolcanic complex. The porphyry style copper mineralisation at Black Stockarton Moor (Brown et al., in preparation) contains disseminations and veinlets of chalcopyrite, bornite, chalcocite, covellite and trace tetrahedrite/tennantite on the eastern side of the arcuate pyrite zone. Little if any of this mineralisation appears to have been detected directly by the stream sediment samples. Chalcopyrite-bearing carbonate and baryte veins peripheral to the pyrite halo have been observed north of Black Stockarton Moor and are probably responsible for the copper anomalies in stream sediments. In Screel Burn the copper anomalies are accounted for by the presence of copper carbonate as a minor component of hematite, quartz, dolomite veins and breccias and also disseminated bornite, joint coatings of copper carbonate/arsenate and veinlets with chalcopyrite in hornfelsed turbidites. The detailed sources of anomalies to the south-west of Barcloy Hill are not known but observation suggests some similarity in veining and hydrothermal alteration to that occurring at Screel Burn. A weak

dissemination of chalcopyrite is considered to be the source of low amplitude anomalies within the outcrop of the Bengairn Quartz Diorite. Baryte veins carrying small amounts of chalcopyrite and malachite account for the anomalous samples from the outcrop of Lower Carboniferous rocks to the south-east of Dundrennan. The copper anomaly from east of White Hill may be due to contamination from metallic rubbish as it is conspicuous at the site. Two samples with anomalous copper concentrations are associated with the north-north-west trending mineralised fracture system both north and south of the granodiorite outcrop but no explanation has been found as to the source of the anomaly near the granodiorite contact to the south-west of Kirkbean. The source of the isolated copper anomalies within the area of Lower Palaeozoic rocks is unknown although pyrite is conspicuous in some parts of the Black Shale belt to the east of Crossmichael.

Copper (concentrate)

The estimate of sampling precision for copper in concentrates is relatively low but this is greatly influenced by two sites where coarse grained chalcopyrite is intermittently associated with vein baryte. There is moderate agreement between the distribution pattern of copper in concentrates and that in sediments, except in an area within and to the south-west of the Bengairn Quartz Diorite where there is a lack of concentrate anomalies. Other sites with highly anomalous levels of copper in the sieved sediment, such as the one west of Kirkbean and another near Crossmichael, contain very little copper in the concentrate and possibly reflect hydromorphic dispersion from, in the case of the site near Crossmichael, a fine grained dilute source such as a black shale horizon. Examples of sites where only the concentrate sample contains an anomalous level of copper can be related to detrital dispersion of relatively coarse minerals as in the stream west of White Hill. In concentrates that have been examined microscopically copper occurs usually as chalcopyrite or

within pyrite or martite but chrysocolla has also been observed in one sample. Contamination is conspicuous at the two sites south-east of Loch Mannoich but vein mineralisation is also suspected in the area. The copper anomaly in the sample from east of Loch Mannoich is derived from a mineralised structure followed by the stream. The source of the three anomalies within the Main Granodiorite has not been located although the samples are also iron rich.

Zinc (sediment)

Zinc is greatly influenced by secondary precipitation of hydrous manganese oxide in boggy environments, as shown by its greater correlation with manganese and cobalt than with other elements. Thus distribution patterns tend to be complex and sampling precision low. In general the samples derived from the Main and Western Granodiorites contain relatively little zinc, though there is a tendency for higher levels to occur along the southern edge of the intrusion where the granodiorite is considered more basic. The zinc-rich samples from within the Main Granodiorite are all from sites where there is a high concentration of secondary manganese. Samples derived from the Bengairn Quartz Diorite are conspicuously more zinc-rich than those from elsewhere within the complex but as no evidence of zinc mineralisation has been found other than as a minor constituent of veins and breccias near Screel Burn it is concluded that the zinc is derived from rock-forming silicates and oxides. The zinc content of samples derived from the sedimentary rocks is generally low, but is higher in the vicinity of the Black Shale Belt at Crossmichael and west of the fault through Woodhall Loch. Zinc occurs as a minor component of baryte-rich vein mineralisation and can be detected by anomalous levels of zinc in some samples, i.e. the fault zone east of Griffel and near the Solway Coast to the east of Dundrennan. There is also mineralogical evidence that zinc anomalies to the north of Black Stockarton Moor and possibly to the south-east of Barcloy Hill are derived from minor veins containing some zinc mineralisation.

Zinc (concentrate)

Sampling precision is relatively high compared with stream sediments because of the small proportion of secondary grain coatings in concentrates and because of the significant zinc content of several common rock forming minerals. Samples within the lowest concentration class are most frequent within the central part of Main Granodiorite and also the Western Granodiorite but higher zinc concentrations occur in the south-eastern and northern parts of the Main intrusion reflecting the greater mafic silicate concentrations in these rocks. In at least two samples from the central part of the Main Granodiorite zinc-rich manganese grain coatings account for the slightly higher zinc content compared with surrounding samples. Both the Bengairn quartz diorite and the subvolcanic complex appear relatively zinc-rich compared with the Main Granodiorite. Samples within the second concentration class predominate over the Lower Palaeozoic rocks and chromian spinel has been identified as a significant zinc host mineral in some of these samples east of the fault running through Woodhall Loch. The presence of sphalerite which has been identified in some samples, probably accounts for the majority of anomalies in samples from the structure east of Griffel, from west of White Hill, from north of Black Stockarton Moor and from the vicinity of Loch Mannoeh. Contamination possibly accounts for the anomaly east of White Hill and the zinc-rich sample near Dundrennan, as fragments of alloy and wire containing significant amounts of zinc have been observed.

Gallium (sediment)

The stream sediment samples clearly indicate that gallium is generally more enriched in igneous than sedimentary rocks, which probably reflects differences in feldspar content. Within the outcrop of Lower Palaeozoic sedimentary rocks samples from south-west of Woodhall Loch and others derived from the Black Shale Belt near Crossmichael stand out as relatively gallium-rich. The highest levels of gallium occur in samples derived from the porphyritic facies of the Main Granodiorite and comparison of sieved and grab samples from this area indicate that the element is associated to a large extent with the clay fraction. Within the Main Granodiorite outcrop, samples with relatively low gallium concentrations are prominent in the south-west and north-west. Higher concentrations are evident in the south-east which on the basis of the distribution of other elements appears to be the most basic part of the intrusion.

Rubidium (sediment)

There is a sharp contrast between rubidium concentrations of samples derived from the Main Granodiorite and those from the surrounding sediments, with the highest rubidium levels concentrated over the central, most differentiated, part of the intrusion. Stream sediments from the extreme north-east of the Main Granodiorite contain relatively little rubidium and may indicate the presence of an intrusive phase of different composition in this area. Several relatively rubidium-rich stream sediments are associated with the peripheral parts of the Black Stockarton Moor subvolcanic complex. Within the outcrop of Lower Palaeozoic rocks, relative rubidium enrichment is associated with stream sediments from the Black Shale belt near Crossmichael and with those from west of the Woodhall Loch fault, which probably reflects a greater alkali feldspar content of the greywackes in this area.

Strontium (sediment)

Samples within the lower two concentration classes predominate over the outcrop of Lower Palaeozoic rocks, though there appears to be a slight increase in concentration in the north-west of the area. Appreciably higher strontium levels are clearly characteristic of samples derived from the igneous rocks, including parts of the Black Stockarton Moor subvolcanic complex. Strontium concentrations are generally lower in samples derived from the porphyritic facies of the Main Granodiorite than from peripheral parts of the intrusion, particularly to the south. This relationship, together with the high correlation between strontium and calcium, indicates that most of the strontium is accommodated in plagioclase, which is more calcic in the marginal basic parts of the intrusion (Phillips, 1956). The significant strontium content of baryte accounts for the relatively high strontium levels in samples from the vicinity of the Solway Coast south-east of Dundrennan and possibly others from north of Black Stockarton Moor.

Yttrium (concentrate)

The analysis of yttrium in stream sediments was undertaken but the results are not presented in map form as no meaningful patterns emerged, due to the relatively low regional variance. Yttrium in concentrates shows more contrast but distribution patterns are relatively diffuse. In general, samples with high yttrium values are derived from the marginal parts of the Main Granodiorite. There is also a suggestion of slight relative yttrium enrichment to the west and south-west of Woodhall Loch which may reflect differences in greywacke composition on either side of the counter-Caledonide fault. As no rare-earth minerals have been identified in concentrate samples from the area it is probable that most of the yttrium is accommodated in zircon or sphene because of the relatively high positive correlation between yttrium, zirconium and titanium (Table 2).

Zirconium (sediment)

Analytical precision is much worse for zirconium than other elements determined in sieved sediments, so distribution patterns tend to be relatively diffuse. Within the Main Granodiorite, zirconium-poor samples are concentrated in the central part while relatively high zirconium levels are characteristic of samples from a narrow marginal zone along the northern contact and a larger area to the south. Thus within the Main Granodiorite zirconium appears to have been depleted by differentiation. The Bengairn Quartz Diorite is less zirconium-rich than either the Western Granodiorite or the more basic marginal parts of the Main Granodiorite. There is considerable scatter in the zirconium content of samples derived from the Lower Palaeozoic sediments but there is a tendency for zirconium to be enriched in the Black Shale belt near Crossmichael.

Zirconium (concentrates)

Sampling precision for zirconium in concentrates is relatively poor, possibly because of the fine grain size of much zircon which, in spite of the high density of the mineral, tends to be lost during the process of panning. Nevertheless there is general agreement between the distribution of zirconium in both sample types within the Main Granodiorite, with a clear distinction between the central zirconium-poor porphyritic zone and the more enriched mafic marginal facies. The separation of two zirconium-rich areas in the southern part of the Main Granodiorite by a zone of low zircon corresponds to the distribution of the most basic sectors of the intrusion as deduced from the distribution of other elements. The predominance of relatively zirconium-poor concentrates derived from the Western Granodiorite and the Bengairn Quartz Diorite indicates a geochemical difference between these two intrusions and the Main Granodiorite. There is a considerable variation in the zirconium contents of samples derived from the Lower Palaeozoic rocks but no clearly defined pattern can be discerned.

Niobium (concentrates)

Niobium-rich samples are confined, with few exceptions, to the outcrop of the Main Granodiorite but the distribution within the intrusion is irregular. The very high positive correlation between niobium and titanium levels indicates that niobium is largely accommodated in sphene, which is the most abundant titanium mineral in the intrusion.

Molybdenum (sediment)

Some environmental influence on molybdenum distribution is indicated by its significant correlation with iron, cobalt and manganese levels in the stream sediments, similar to that noted in the Shin area, northern Scotland (Leake and Smith, 1975). The highest molybdenum concentrations occur in sediment samples from two areas within the Main Granodiorite, in the north and west respectively. This distribution pattern is not related to the magmatic differentiation of the complex as revealed by variations in stream sediment contents of many other elements and therefore probably reflects superimposed hydrothermal mineralisation. Molybdenum is detectable in some samples derived from the Bengairn Quartz Diorite but not in samples derived from the Black Stockarton Moor subvolcanic complex where molybdenite occurs as a minor constituent of porphyry-style copper mineralisation. Except in the extreme north-west and in the manganese-rich sample from south-west of Woodhall Loch detectable molybdenum is not found in samples derived from the Lower Palaeozoic rocks.

Tin (sediment)

The geographical distribution of tin is irregular, particularly over the Lower Palaeozoic rocks, this being due to tin occurring as a contaminant. Although attempts were made to avoid obviously contaminated sites, metallic rubbish is widespread in streams near human habitation and at the sides of roads and is not always visible. Table 1 shows that no elements have a significant correlation with tin at the 99.95% confidence limit, but at the

99.5% confidence limit there is a significant positive correlation between lead and tin. The correlation with lead reflects an association of the two elements in dumped debris in streams, e.g. solder from tin cans. The grouping of several sites over the Main Granodiorite with detectable tin probably reflects its distribution in rock, as contaminants are not usually present in the upland area of Criffel.

Tin (concentrate)

Tin mineralisation is unknown in the area, though a trace of very fine cassiterite has been identified from two samples from north of Black Stockarton Moor. Concentrate samples tend to be more sensitive than sieved sediments in detecting metallic contamination because of the high density and relatively coarse grain size of much of this material. Thus more concentrates than sediments contain anomalous levels of tin, particularly in the areas underlain by Lower Palaeozoic rocks where relief is subdued and farming widespread. Concentrate samples also contain detectable tin levels at most of the sites where it is found in the sieved sediment. There are exceptions where anomalously high tin levels in sediment are not present in the concentrates, particularly over the Main Granodiorite, but the explanation of this is not known. In addition to a positive correlation of tin and lead, a more significant positive correlation with titanium indicates that some tin is accommodated in sphene or other titanium minerals derived from the Main Granodiorite.

Antimony (concentrate)

Detectable levels of antimony occur in very few concentrates, and are invariably derived from hydrothermal mineralisation. In samples from Screel Burn antimony is associated with the fractions of the concentrates which are rich in hematite and secondary iron oxide, but the most likely hosts are sulphosalt minerals which occur as minor components of small scale veins in the area. Antimony occurs also as a minor component of the porphyry style copper mineralisation at Black Stockarton Moor; tennantite has been identified

at this locality but it has not been detected in any of the concentrate samples. In addition to other samples from around the Bengairn Quartz Diorite, antimony is detectable in one baryte-rich sample from near the Solway coast and in three samples from the vicinity of the fracture zone running north-north-west by the east side of the Main Granodiorite.

Barium (sediment)

Samples with barium contents within the lowest concentration class are confined to the area underlain by Lower Palaeozoic rocks, particularly south of the Black Shale belt near Crossmichael. Stream sediments derived from the Main Granodiorite fall predominantly within the second concentration range, except in the more mafic south-western and south-eastern parts where levels are higher. This distribution pattern is compatible with the tendency for the barium content of feldspars to decrease with differentiation. Barium also decreases in the marginal facies where there is an increase in biotite. Most of the samples with relatively high barium contents from the central part of the Main Granodiorite are also very rich in secondary manganese oxides. A similar tendency for barium to be absorbed on secondary manganese precipitates has been observed in finer sediment samples from the Shin area, northern Scotland (Leake and Smith, 1975). Outside the outcrop of the granodiorite complex, samples within the upper two concentration classes contain a significant amount of detrital baryte.

Barium (concentrate)

The marked change in slope of the cumulative frequency diagram at the 650 ppm level coincides, from evidence of mineralogical work, with the appearance of baryte in the concentrate samples. Baryte occurs most abundantly in the southern part of the north-north-west trending fracture zone to the east of Criffel, in structures along the Solway Coast and in parts of the Black Stockarton Moor subvolcanic complex. Baryte also occurs to the west of Loch Mannoich in a prominent west-south-west trending lineament but is rare over most of the outcrop of Lower Palaeozoic rocks.

Cerium (concentrate)

The majority of cerium-rich samples are derived from the Criffel-Dalbeattie igneous complex, with higher levels in the Main Granodiorite than the other components of the complex. Within the Main Granodiorite cerium is concentrated in samples derived from the margin of the intrusion near Kirkgunzeon but elsewhere there is a considerable scatter of levels giving no clear distribution pattern. Cerium shows strong positive correlations with yttrium and titanium, which suggests that much of the rare-earth element content of the samples is accommodated in sphene. Within the outcrop of the Lower Palaeozoic rocks some cerium enrichment occurs in samples derived from the vicinity of the Black Shale belt near Crossmichael and in those derived from the turbidites to the west of Woodhall Loch.

Lead (sediment)

Most of the samples relatively rich in lead are derived from the igneous rocks and in particular the Main Granodiorite. There is a highly significant positive correlation between lead and iron, cobalt, potassium, barium, gallium and lithium. A comparison of wet-seived and relatively clay-rich grab samples derived from the Main Granodiorite indicates that lead accumulates in the decomposition products of feldspar and is absorbed on secondary oxide precipitates, particularly that of iron. Within the Main Granodiorite, samples with relatively high lead contents are predominantly derived from the more acidic parts of the intrusion. The lead in samples from the south-eastern part of the intrusion may ultimately be derived from plagioclase, as potassium concentrations in the stream sediments are relatively low. The stream sediments demonstrate some lead enrichment associated with the north-north-west trending structure to the east of Criffel and possibly with structures along the Solway coast but in general there is little evidence from the data to suggest significant lead mineralisation within the area. The lead content of the sample from east of White Hill is probably derived from metallic contamination as this is particularly conspicuous at the site.

Lead (concentrate)

The distribution patterns of lead in concentrates are particularly difficult to interpret as the sample is sensitive in detecting both detrital lead minerals and metallic contamination. Several samples, such as those from north of Black Stockarton Moor, contain both metallic rubbish and a suite of minerals derived from hydrothermal mineralisation, the mode of lead occurrence being ascertained by careful mineralogical examination and X.R.F. scanning of individual components. Concentrates with high lead contents in which all the lead is probably contained in contaminants were collected near Dundrennan and east of White Hill. Samples containing a significant amount of lead of hydrothermal origin in the form of white secondary minerals but sometimes mixed with contaminants are associated with the major structure in the east of the area, with the west-south-west trending lineament to the east of Loch Mannoeh and with the region to the north of Black Stockarton Moor. Concentrates containing intermediate levels of lead are most frequent within the Main Granodiorite outcrop with a prominent grouping near Kirkgunzeon. There is generally a positive correlation between lead, rare earths, titanium and to some extent zirconium at these sites, which suggests that the lead is accommodated in heavy accessory minerals such as sphene and zircon. The lead contents of samples derived from the Lower Palaeozoic rocks are very low although some lead enrichment is associated with the Black Shale belt near Crossmichael.

Thorium (concentrate)

With one exception all the thorium-rich samples are derived from the Main Granodiorite with a prominent grouping near Kirkgunzeon. The distribution within the Main Granodiorite bears little relation to the pattern of magmatic differentiation revealed by variation in many elements in both sample types. Thorium shows the highest positive correlations with yttrium, titanium, and niobium, zirconium and uranium, particularly in samples derived from the central part of the intrusion. This suggests that most of the thorium is accommodated in sphene and zircon.

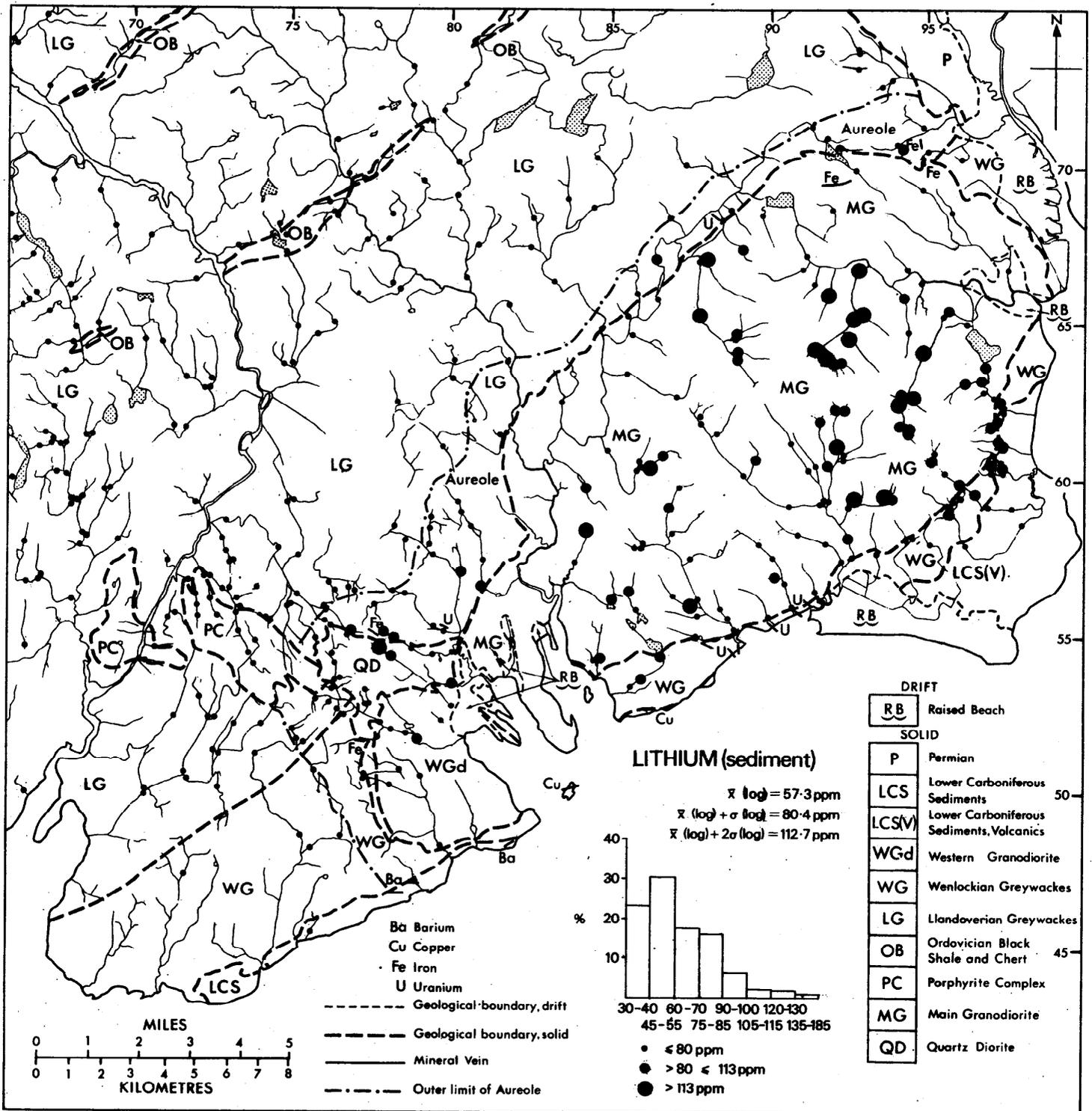
Uranium (sediment)

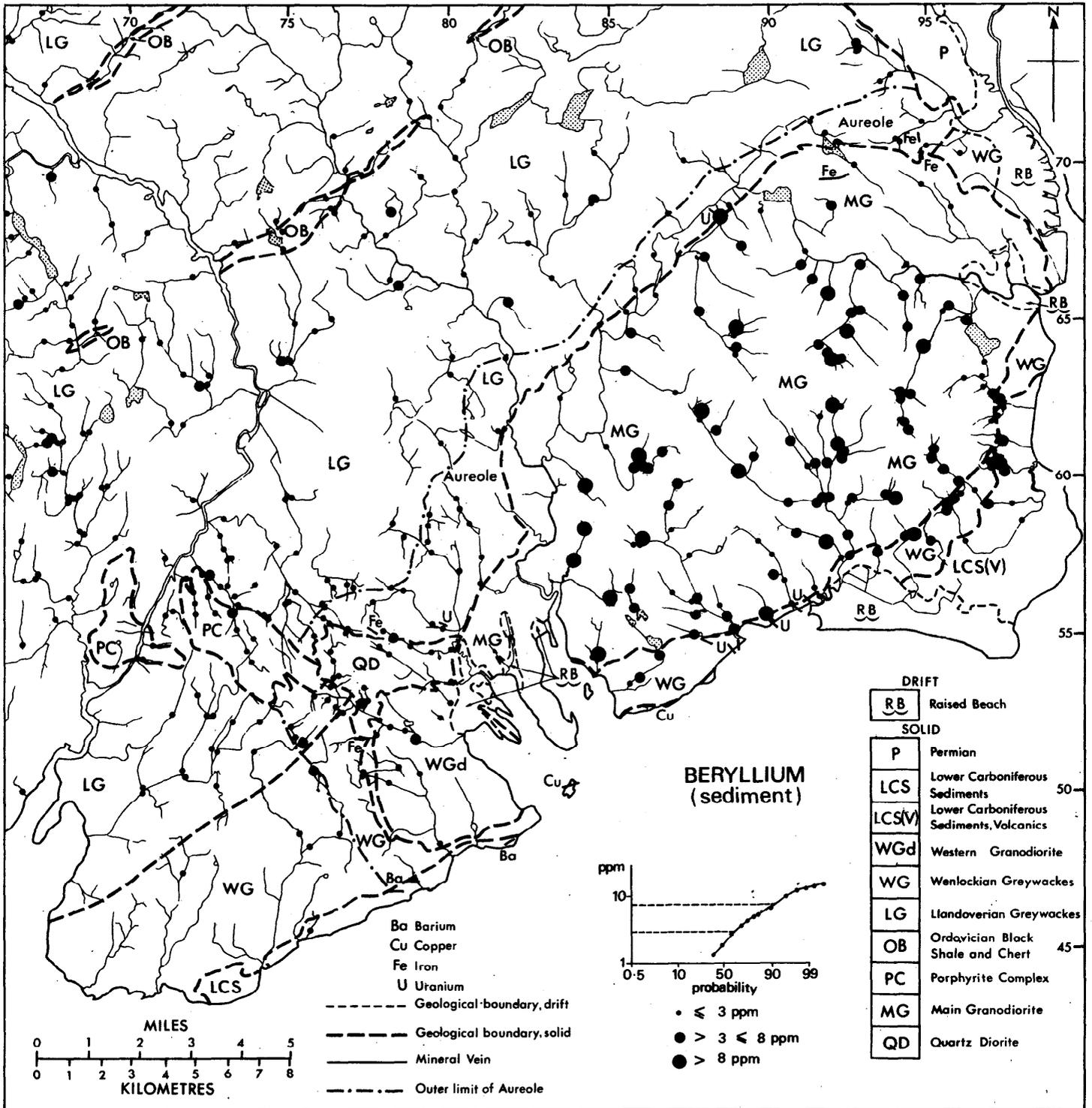
The estimate of sampling precision for uranium in sediments gives a poor value because of a strong environmental influence on the distribution, particularly in upland boggy areas within the Main Granodiorite. Both chemical analysis of various size fractions of a bulk sediment sample (Gallagher et al., 1971) and comparisons of the uranium contents of sieved sediments, grab sediments and water suspended material collected simultaneously from sites within the Main Granodiorite indicate that uranium is predominantly associated with the finest grain-size fraction. This association is also suggested by the lack of correlation between uranium in sediment and concentrate samples over most parts of the granodiorite. As uranium shows higher correlations with potassium, gallium, rubidium and strontium than with manganese it is concluded that most of the uranium in stream sediments derived from the Main Granodiorite is adsorbed onto clay minerals formed mostly from the decomposition of feldspars. Much of the uranium content of the source rock is thought to be closely associated with feldspar minerals as thin coatings appear in cracks and on grain boundaries. Samples with the highest uranium concentrations are clearly associated with the Main Granodiorite and its immediate aureole and particularly with an area to the east of Dalbeattie where boggy terrain predominates. Elsewhere within the central part of the intrusion samples are relatively low in uranium, which suggests depletion in the most highly differentiated part of the intrusion. Samples from the extreme north-eastern part of the intrusion are also relatively uranium poor which supports the conclusion from other element distributions of geochemical differences between this and the rest of the Main Granodiorite. Compared with the Main Granodiorite the Western Granodiorite and Bengairn Quartz Diorite appear relatively uranium poor but significantly more uraniferous than the surrounding Lower Palaeozoic rocks. There appears to be little relation between the uranium content of stream sediments and the distribution of known uranium mineralisation around the Criffell-Dalbeattie

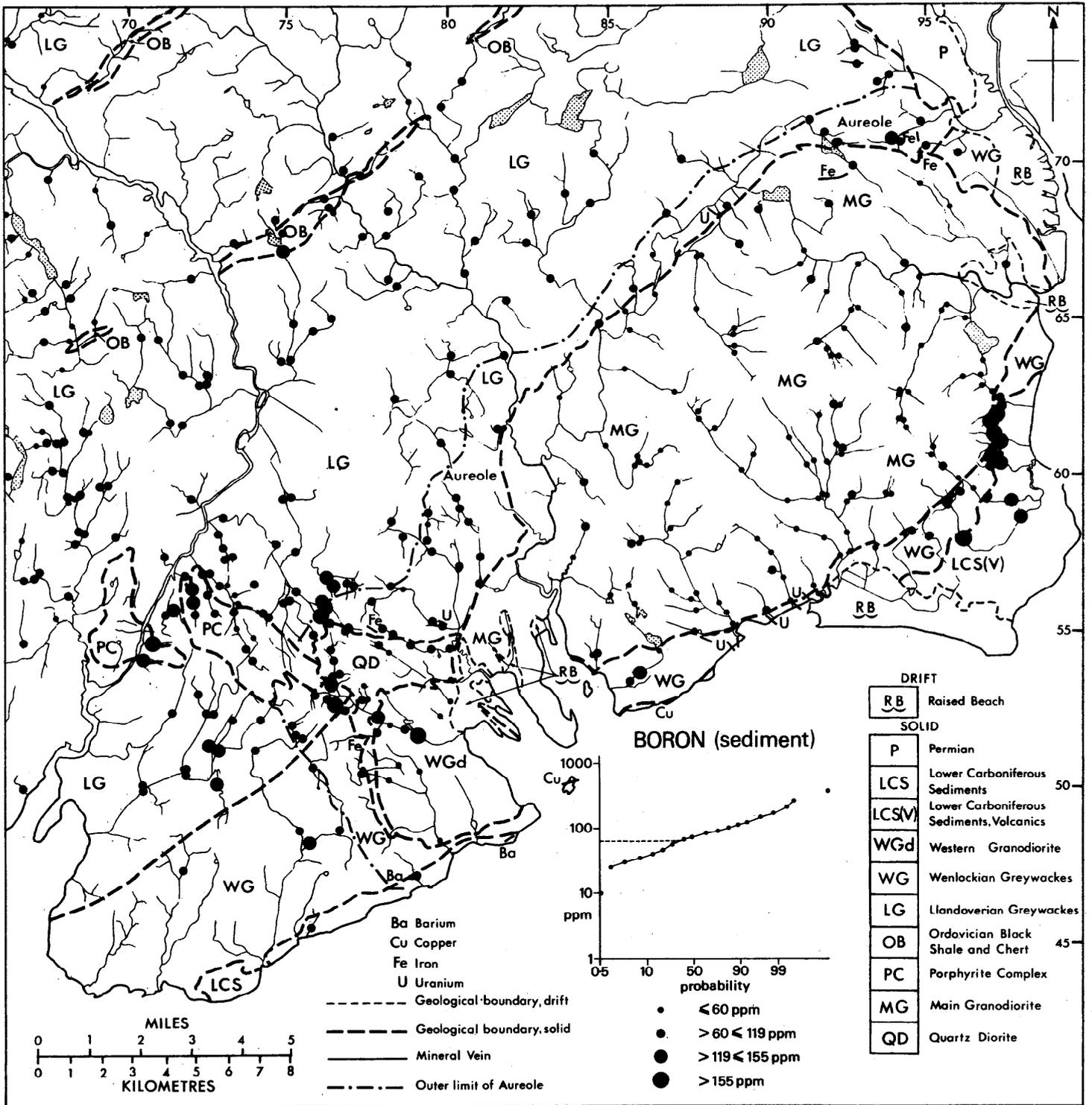
complex (Gallagher et al., 1971; Miller and Taylor, 1966) but the two uranium rich samples from the southern aureole of the Western Granodiorite are anomalous compared with samples derived entirely from the igneous body and may therefore represent dispersion from discrete uranium-bearing structures in the area. In view of the discovery of a radioactive granite boulder (Gallagher et al., op.cit.) it is possible that dispersion from discrete uranium mineralisation also accounts for the particularly high uranium levels in sediment from east of Dalbeattie.

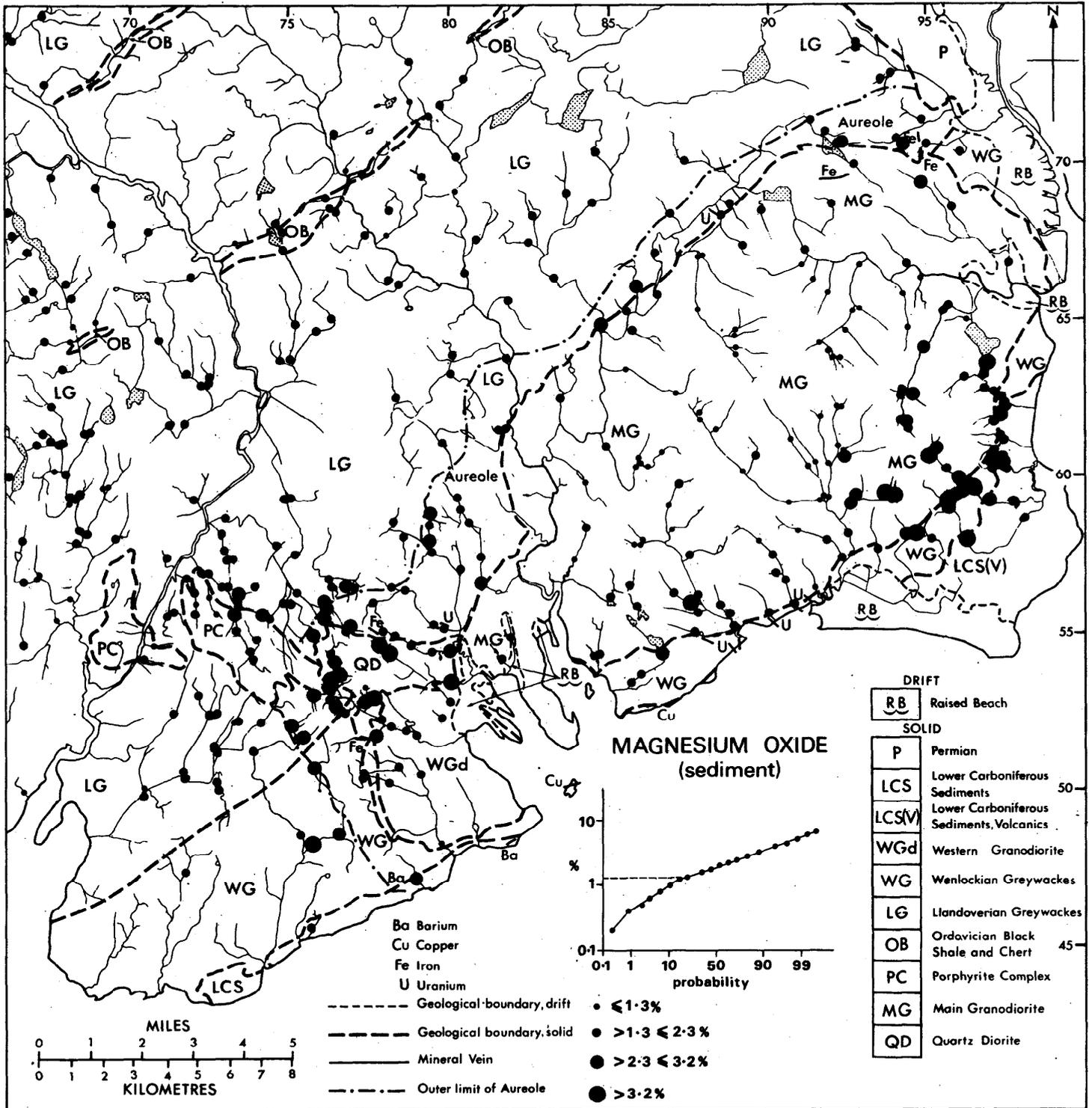
Uranium (concentrate)

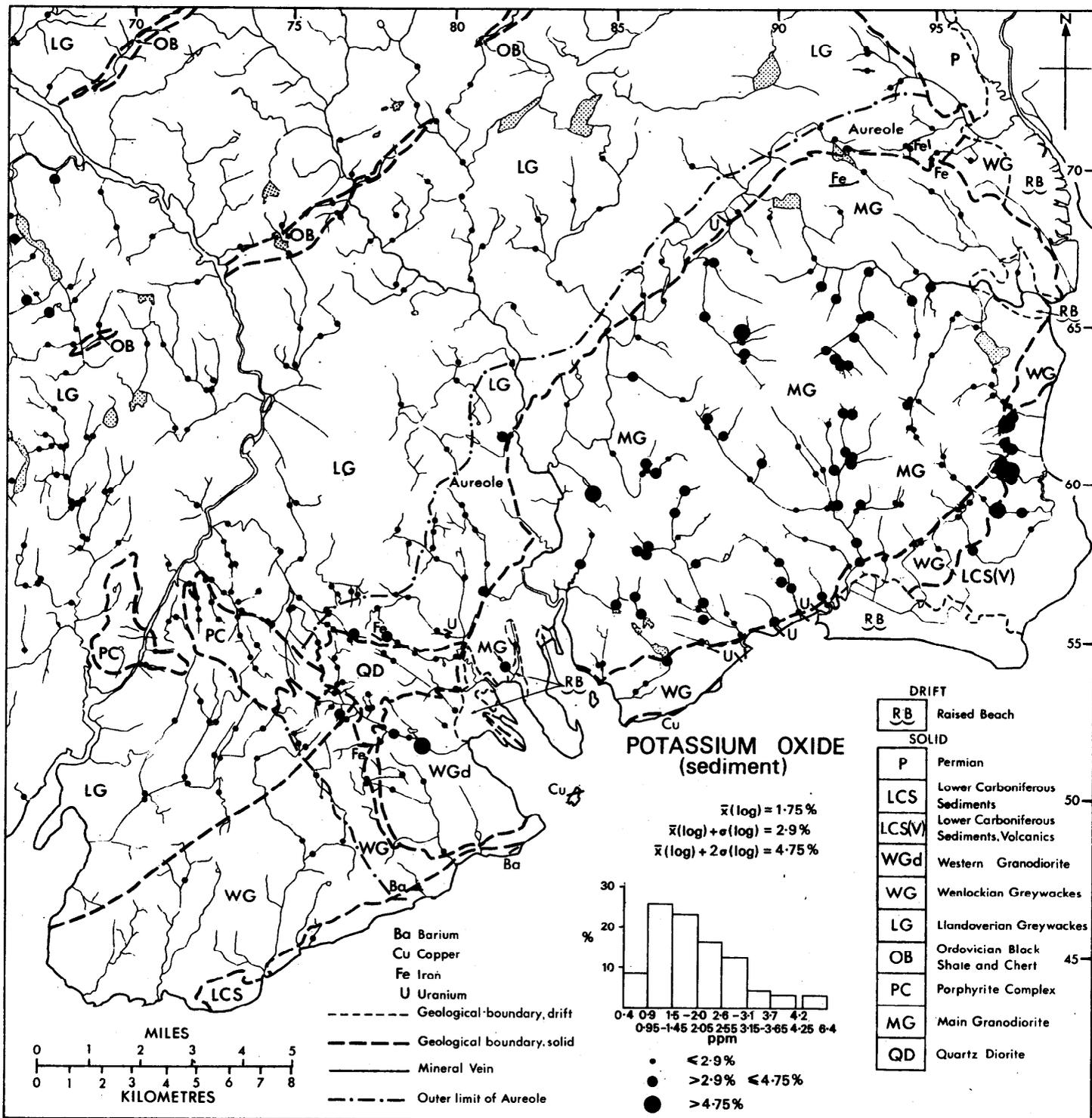
All samples containing detectable uranium are derived from the Main Granodiorite or its immediate aureole, but the distribution is unrelated either to that of uranium in stream sediments or to the pattern of magmatic differentiation of the body. Uranium in concentrates shows the highest positive correlations with thorium, niobium, titanium and zirconium, which suggests that the main uranium host minerals are sphene and zircon. Enrichment in heavy accessory minerals in the Main Granodiorite to the east of Kirkgunzeon is indicated by the conspicuous grouping of uranium, thorium and rare-earth rich concentrates in the area. As several uranium-bearing structures have been found in the hornfels adjacent to the granodiorite in this area (Gallagher et al., 1971) it is possible that this mineralisation is derived by redistribution from an originally uranium-rich part of the intrusion. This mineralisation would therefore be distinct from that occurring to the south of the igneous complex where boundary faulting parallel to the Solway Coast is considered to exercise some degree of control.

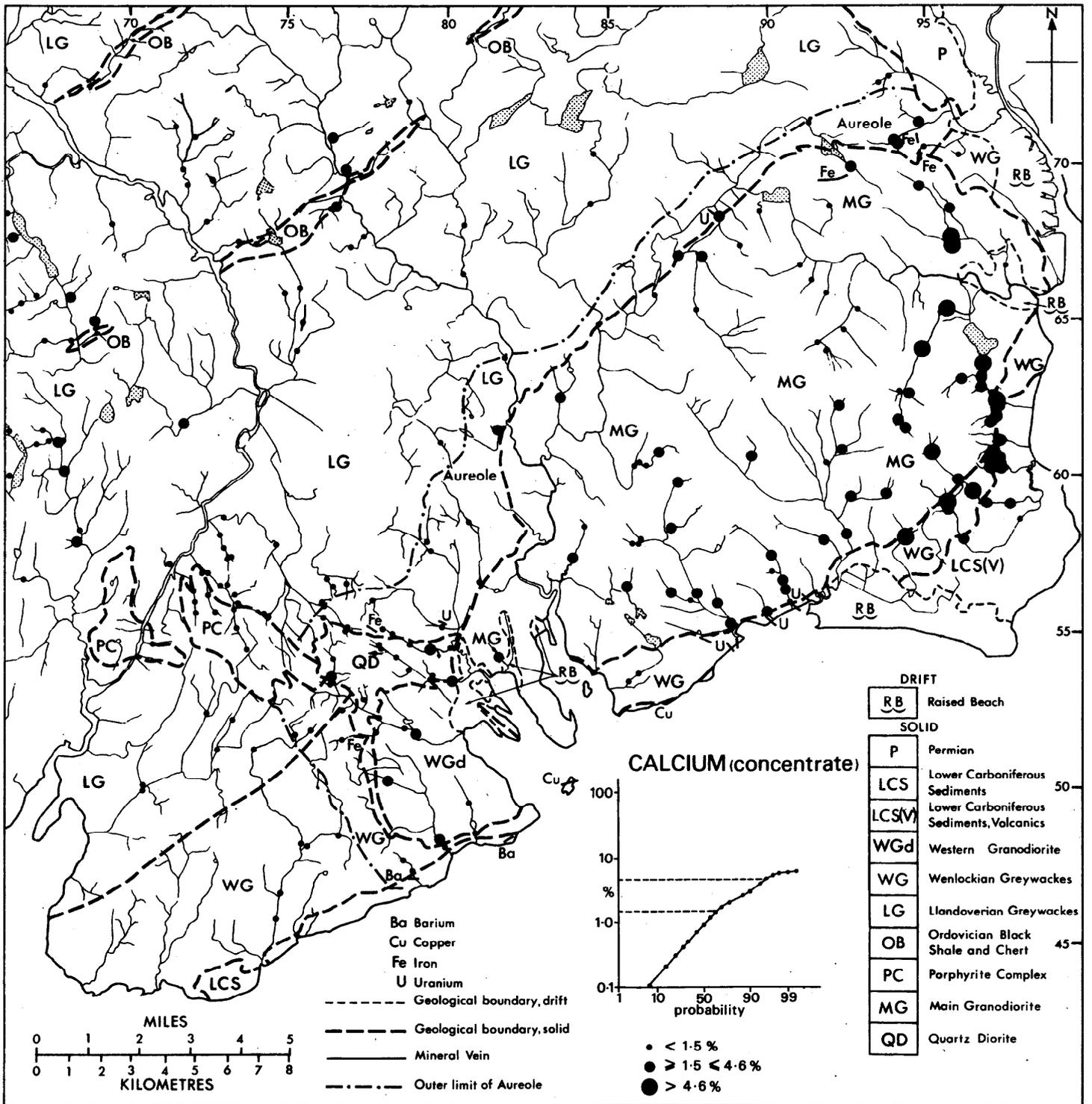


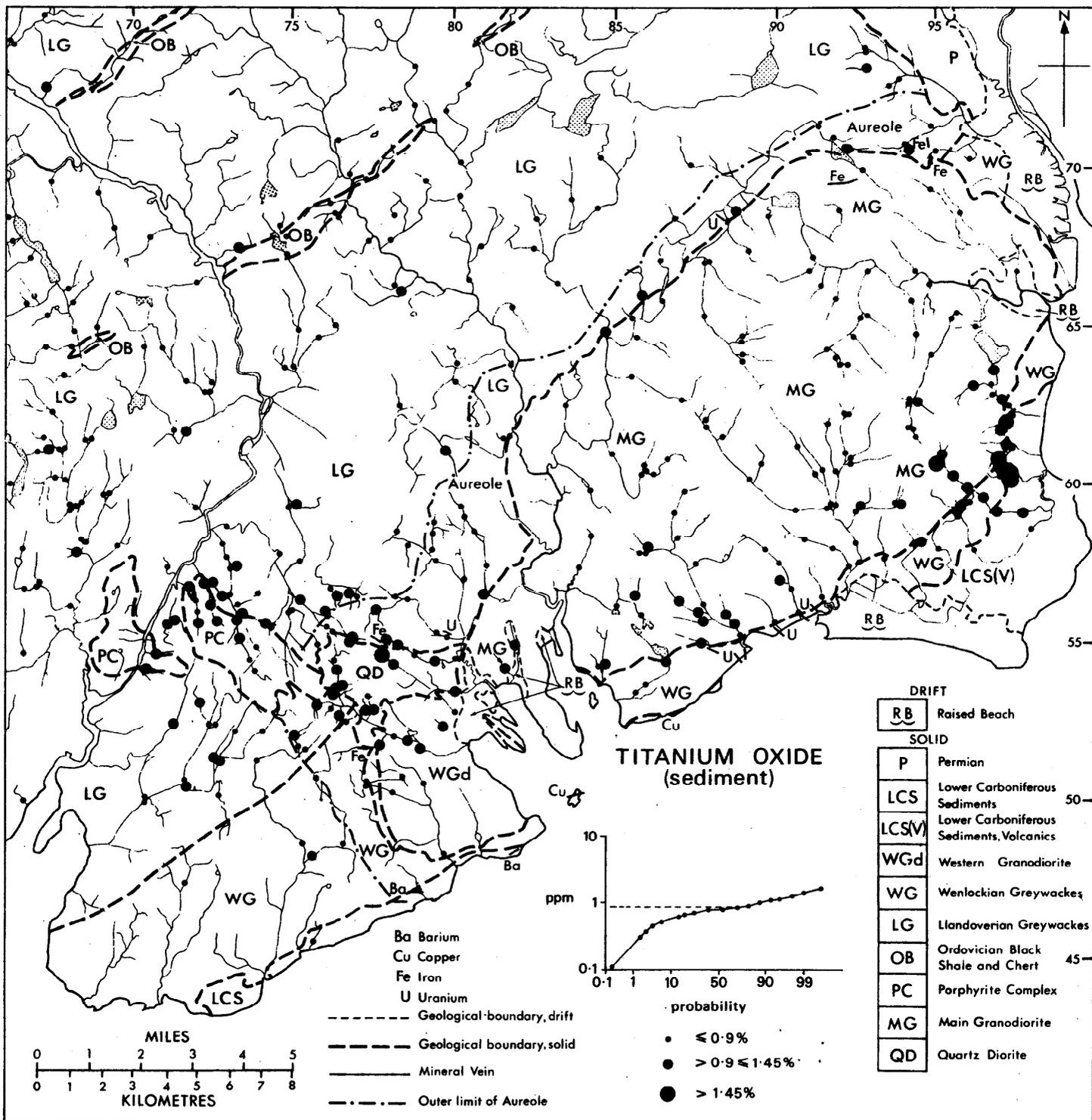


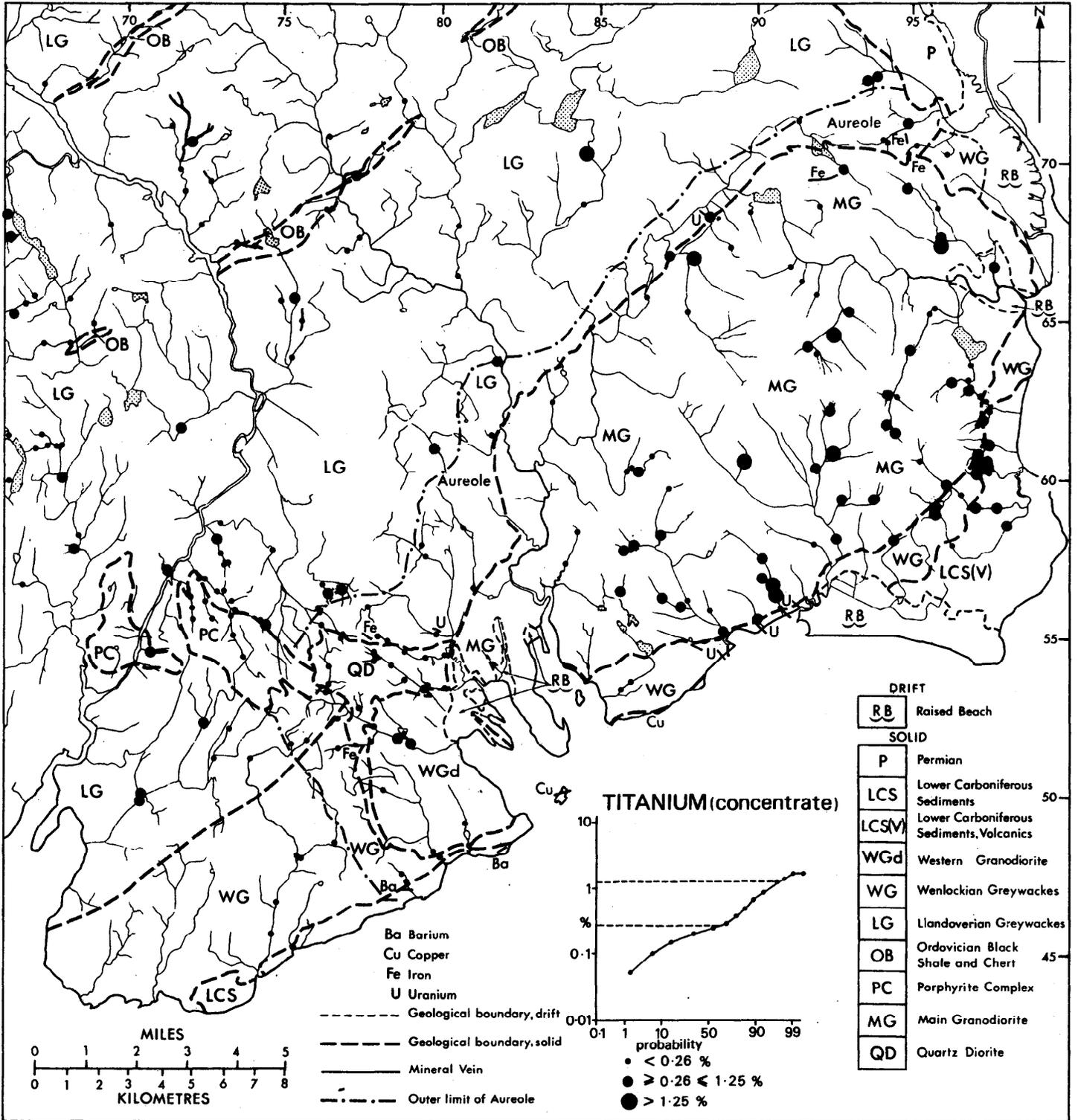


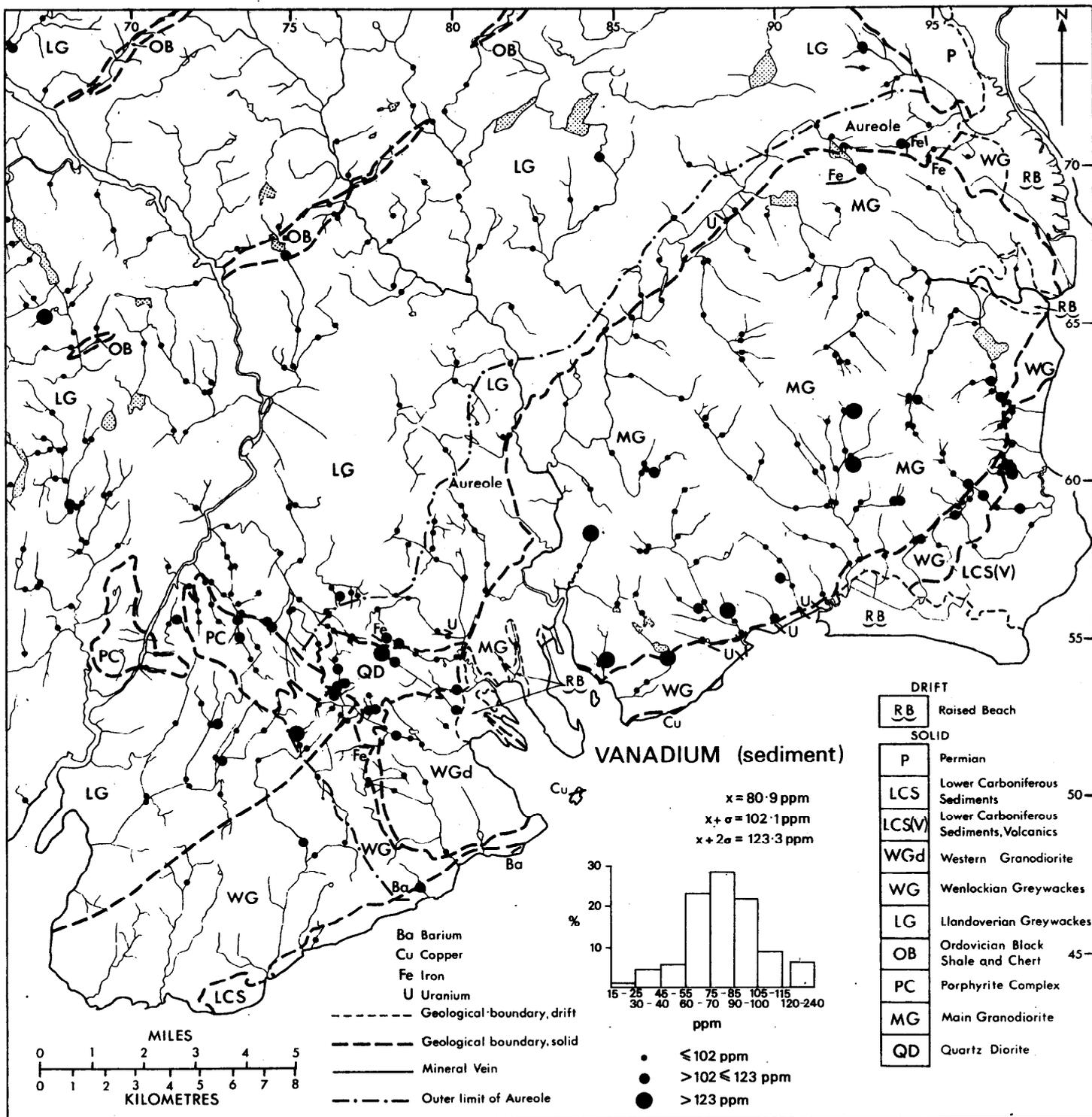


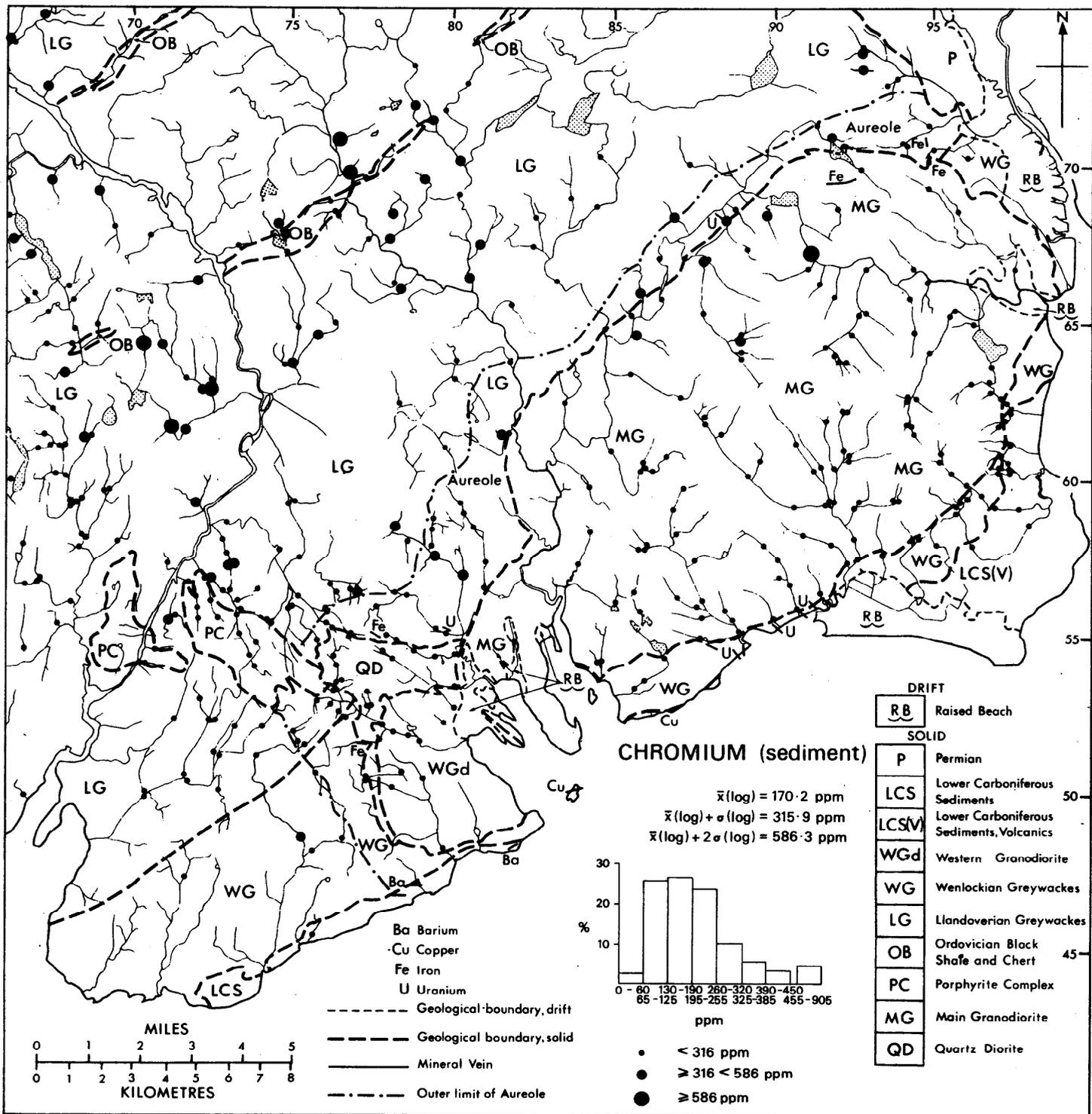


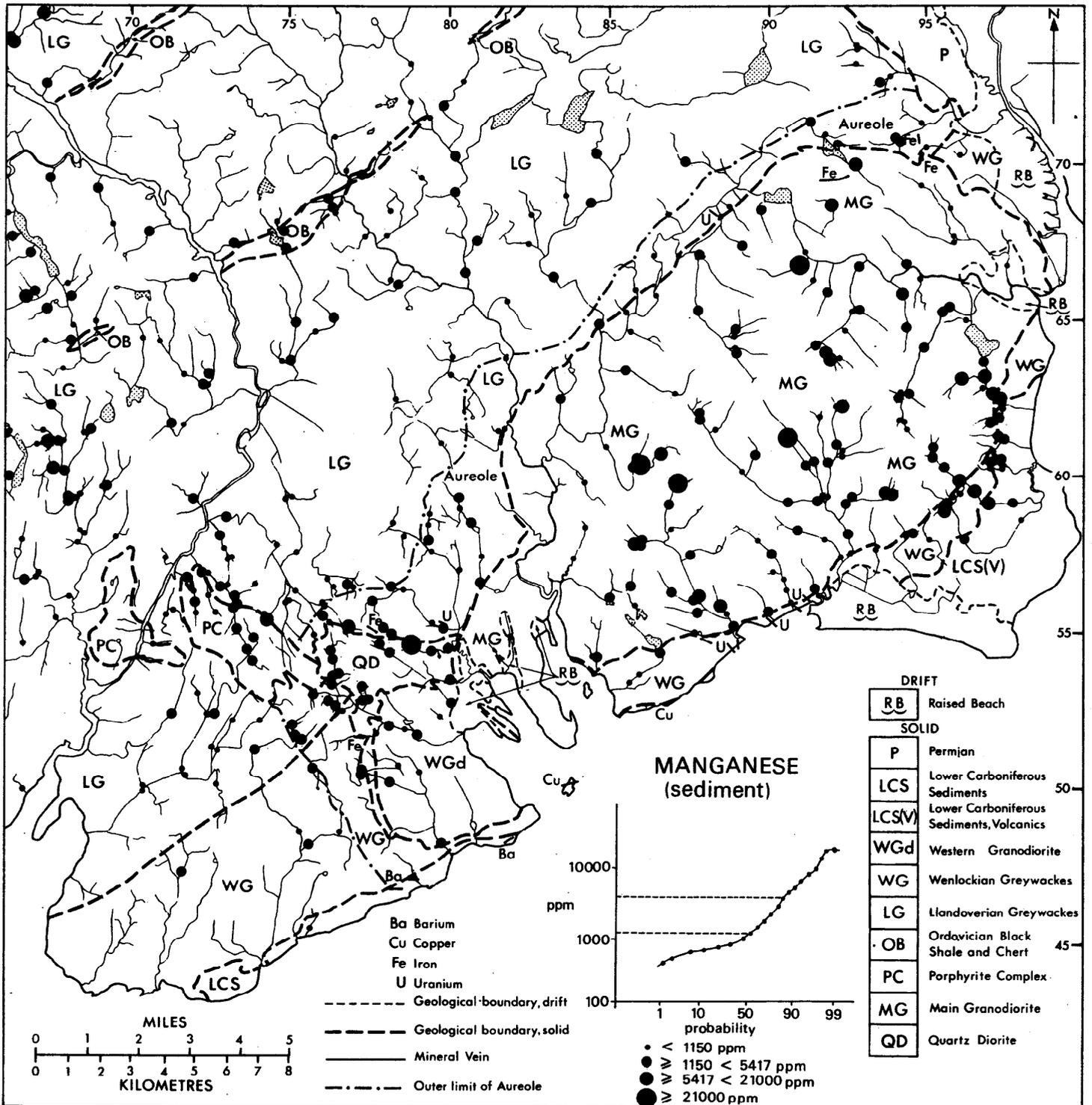


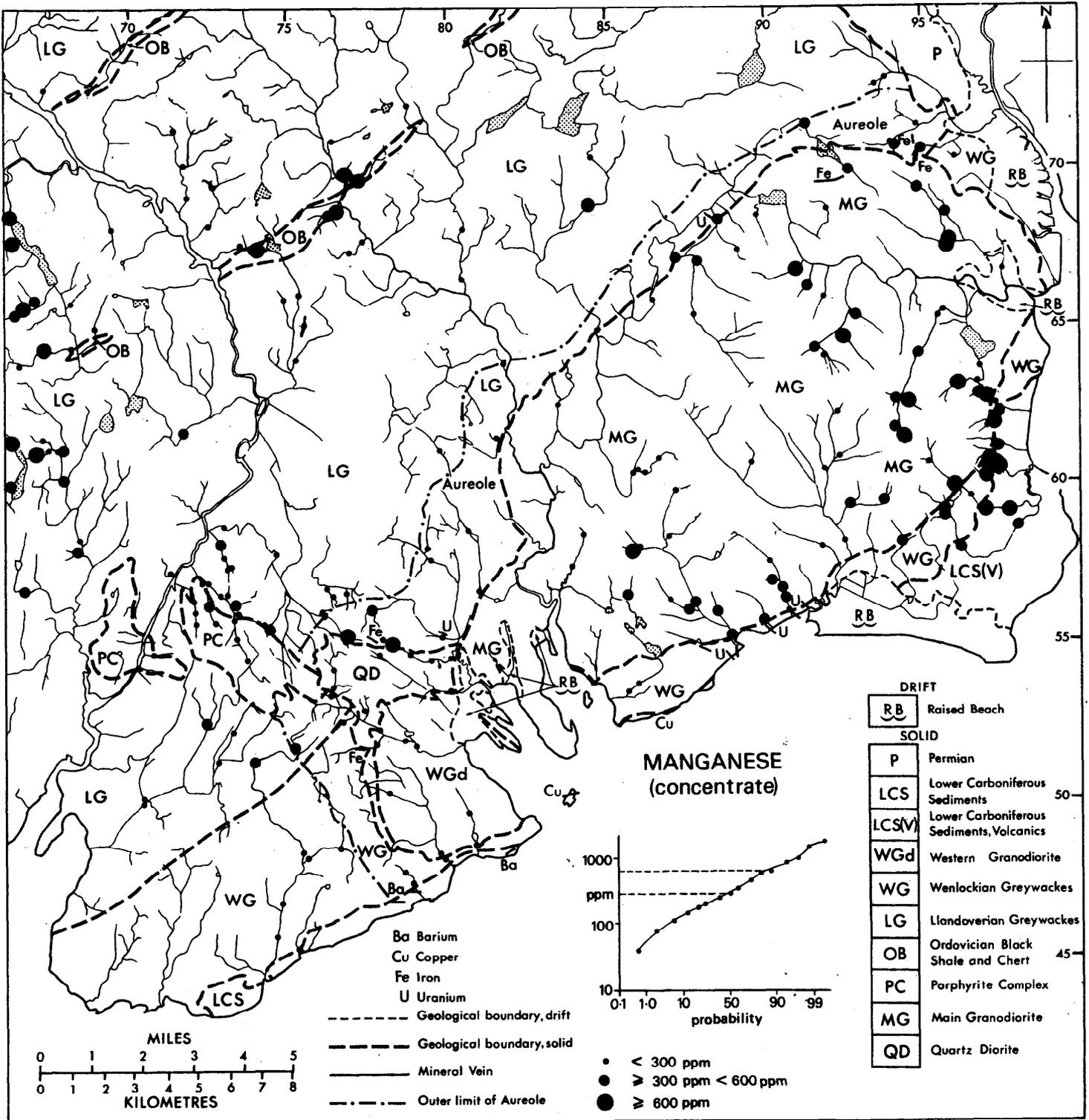


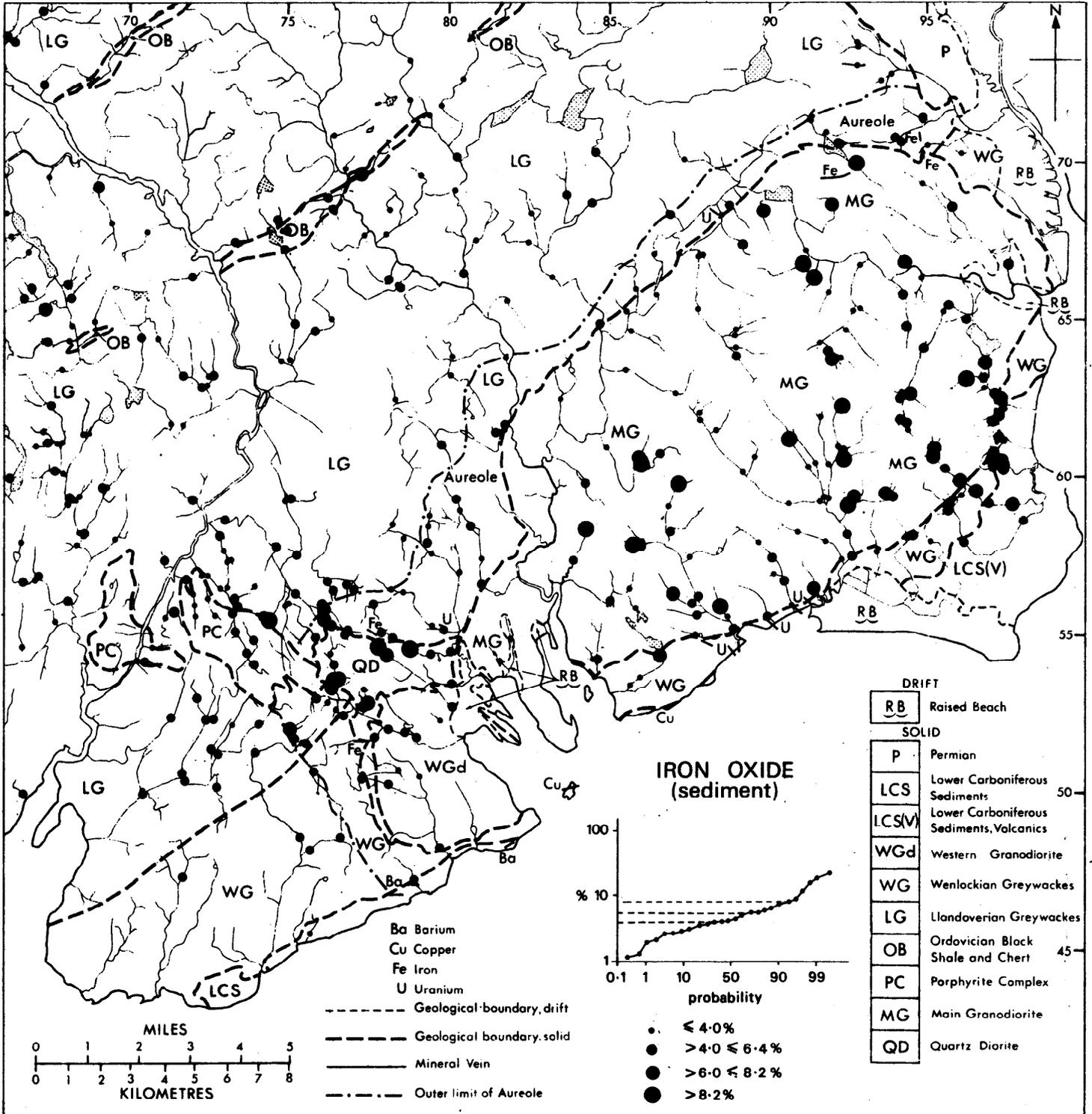


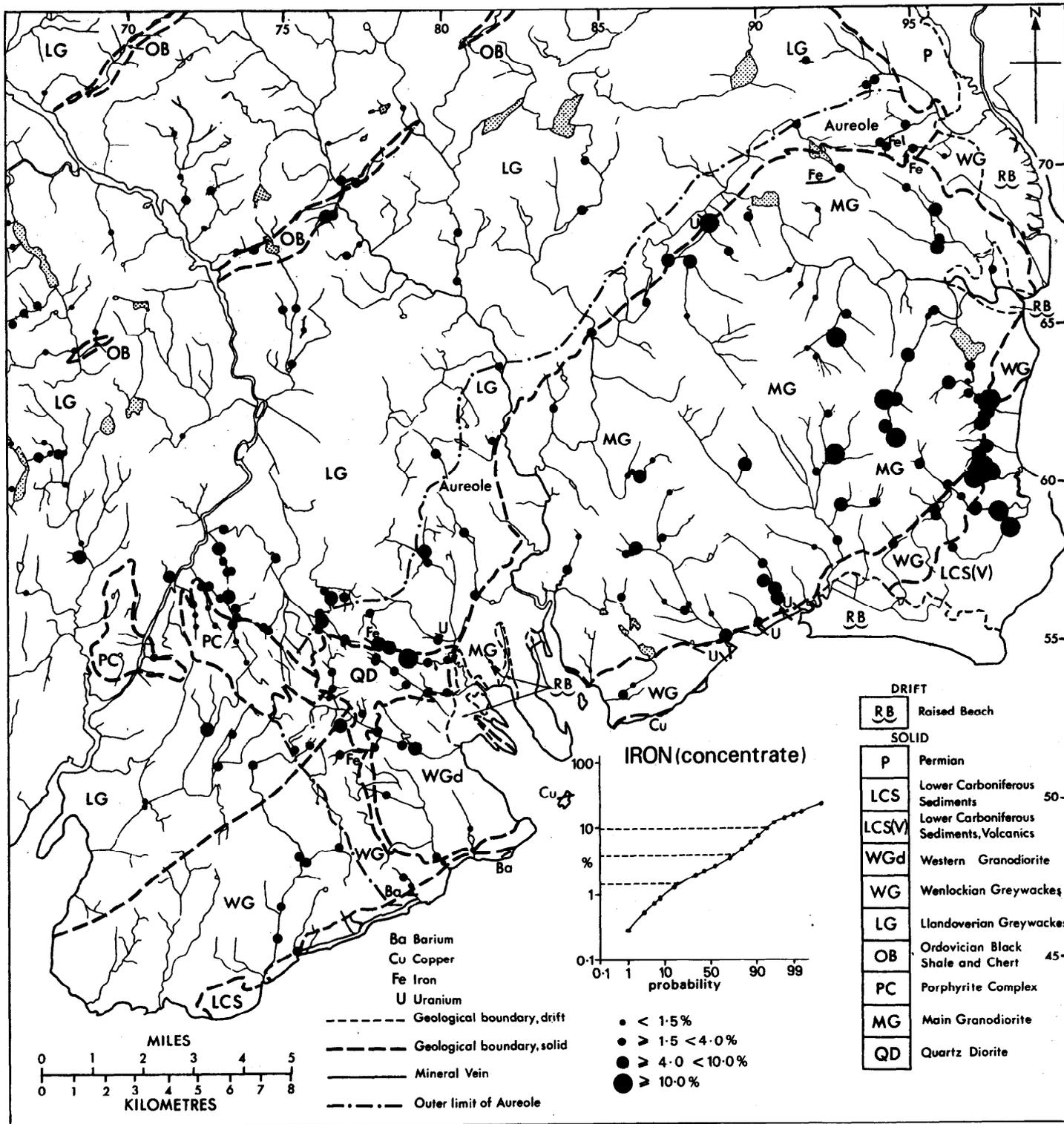


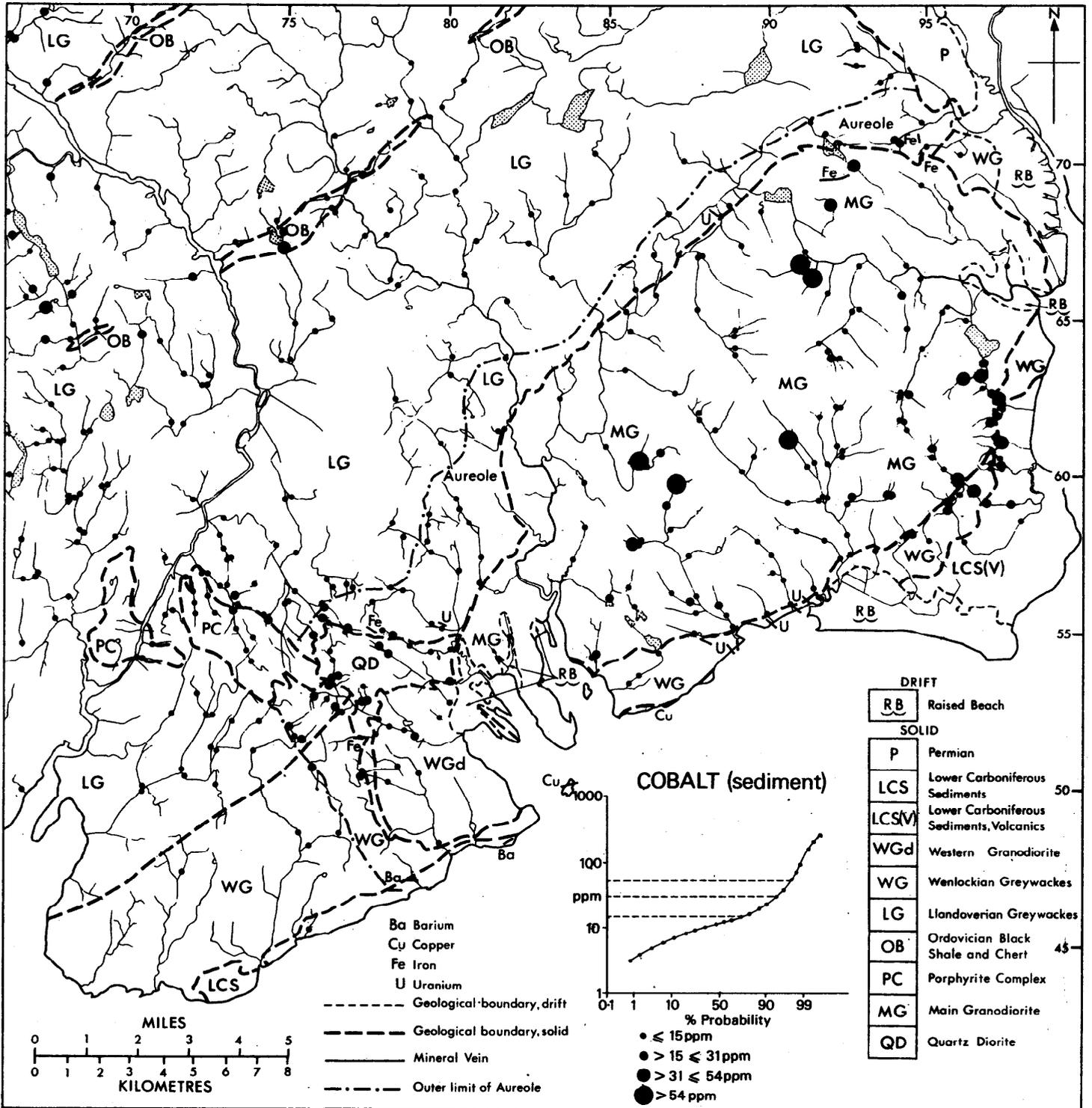


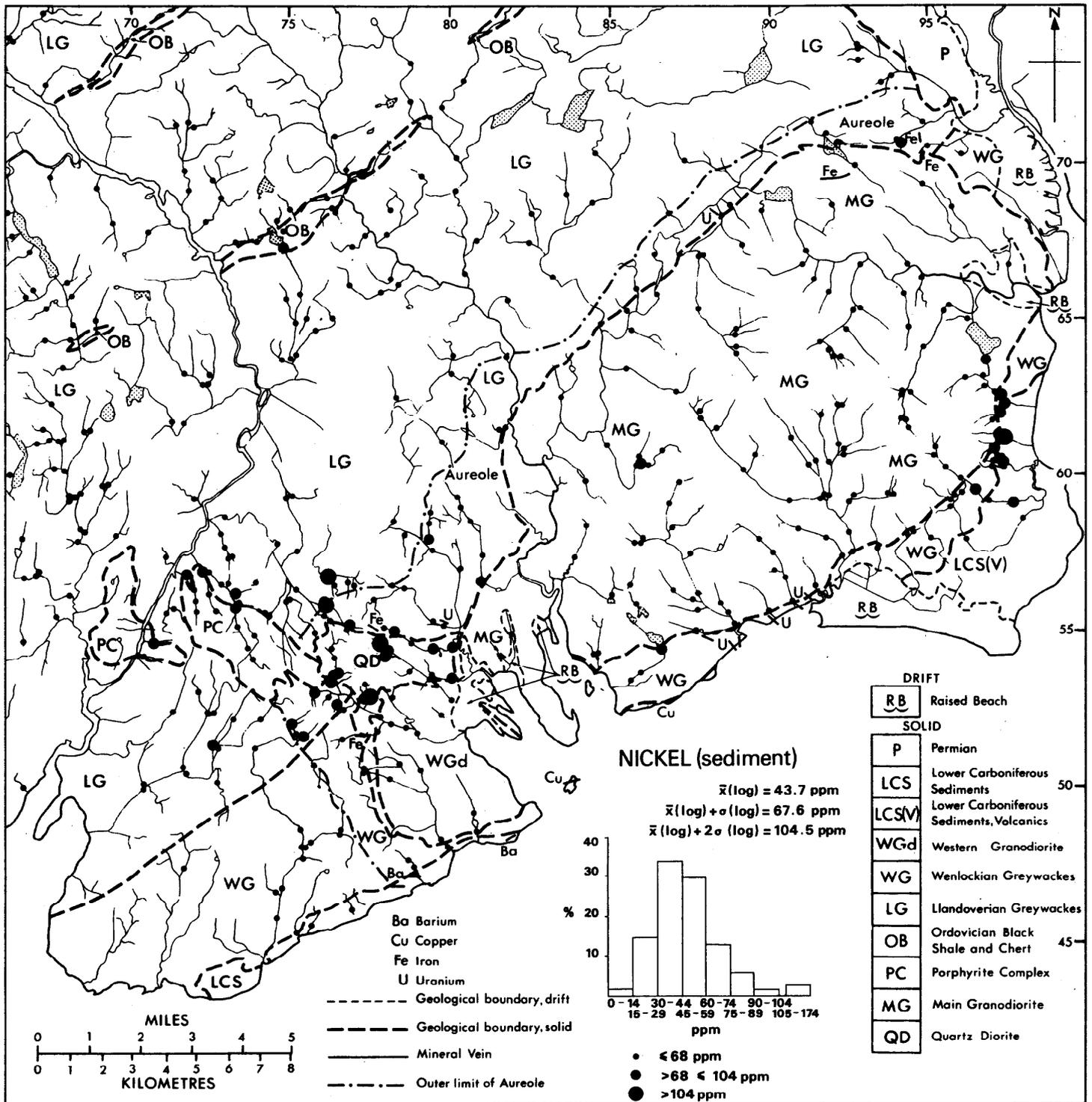


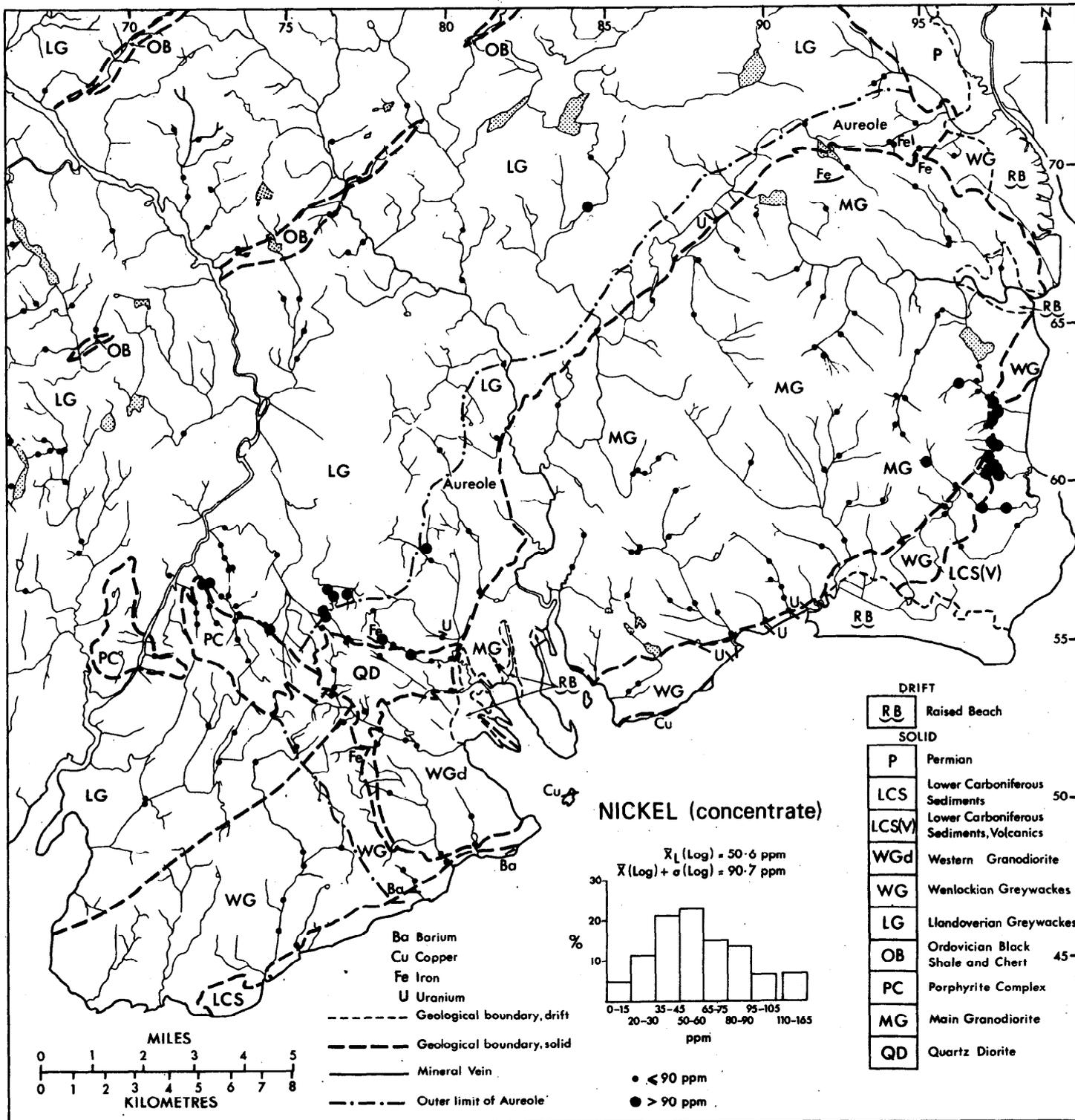


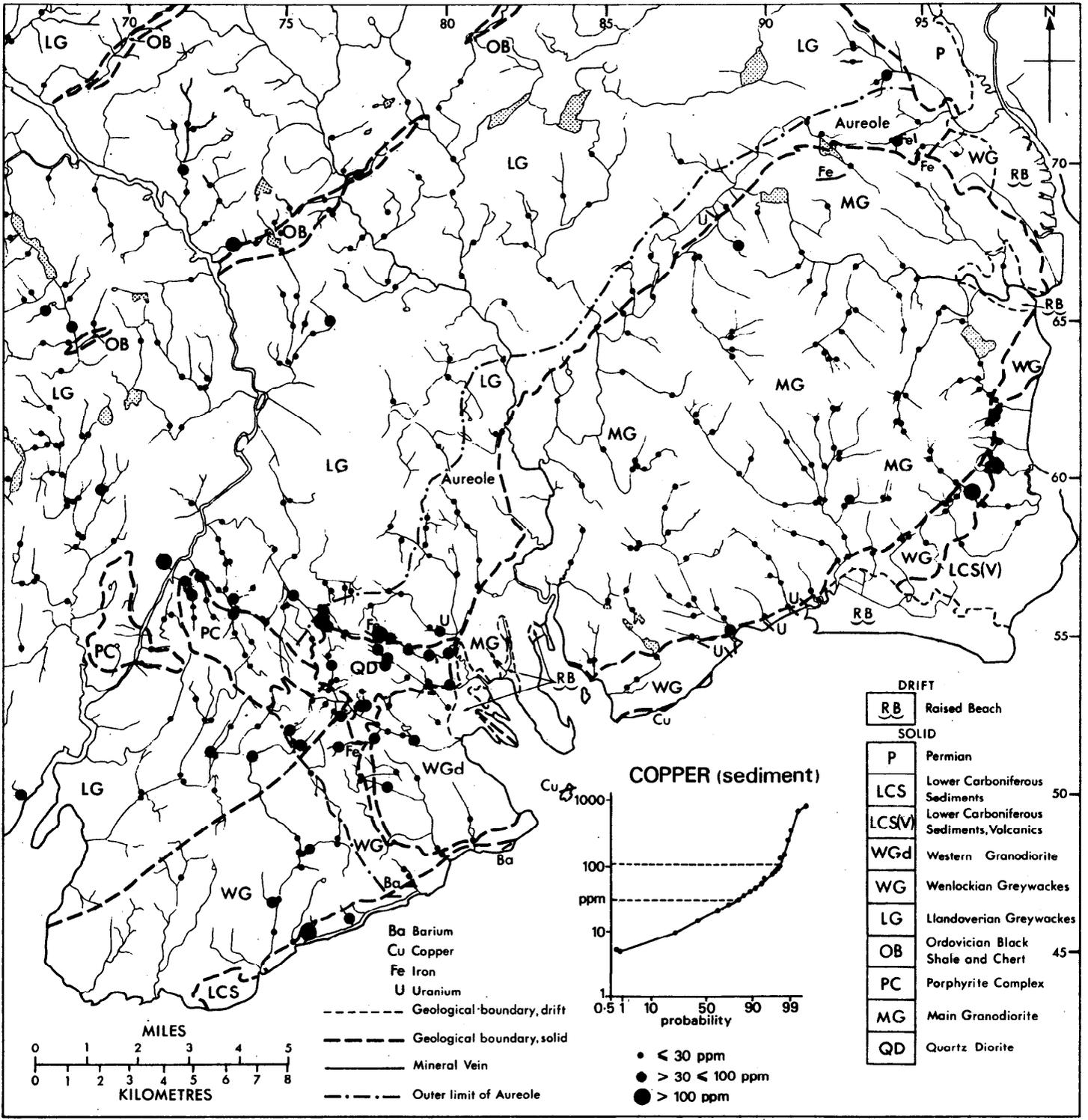


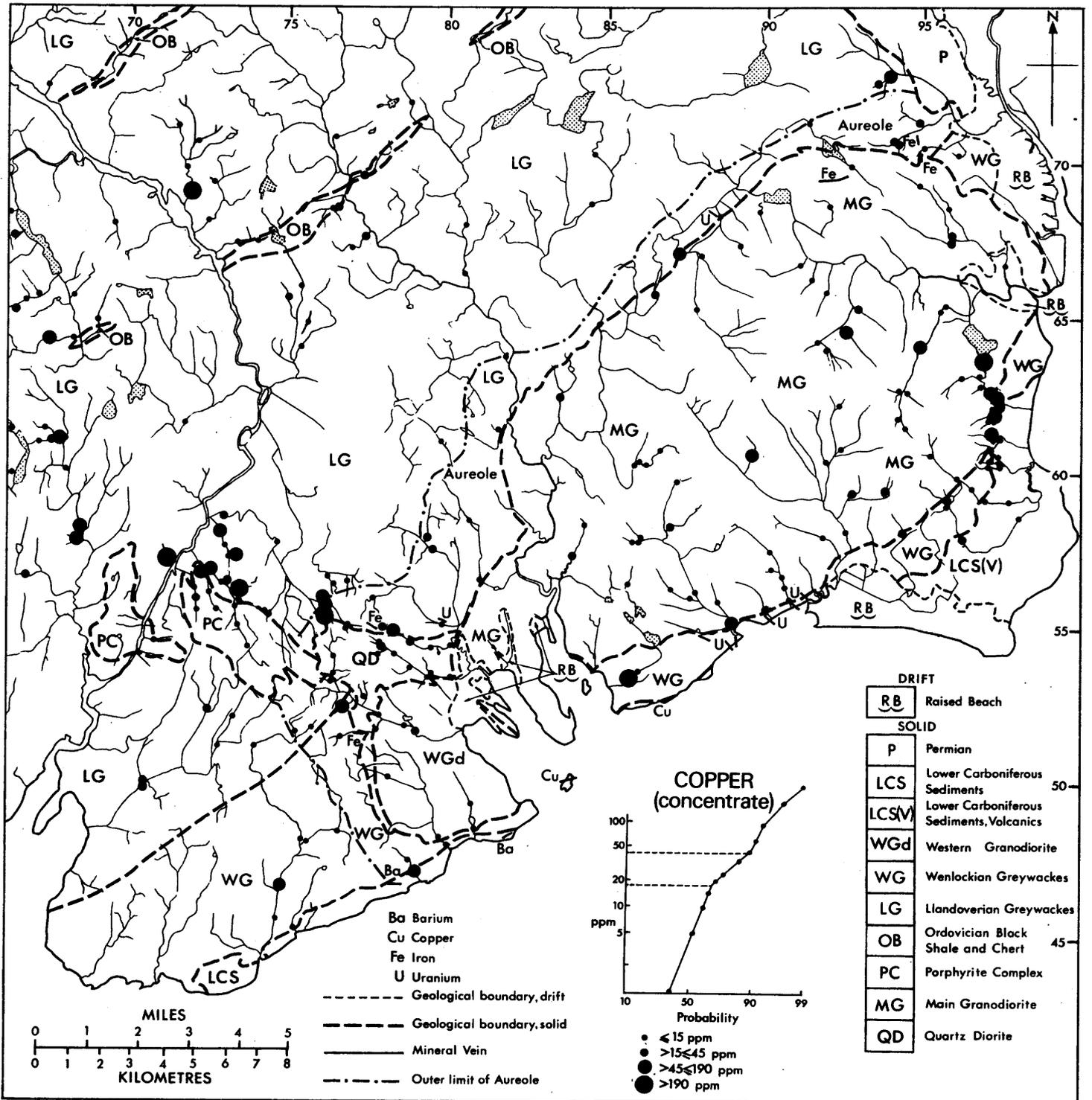


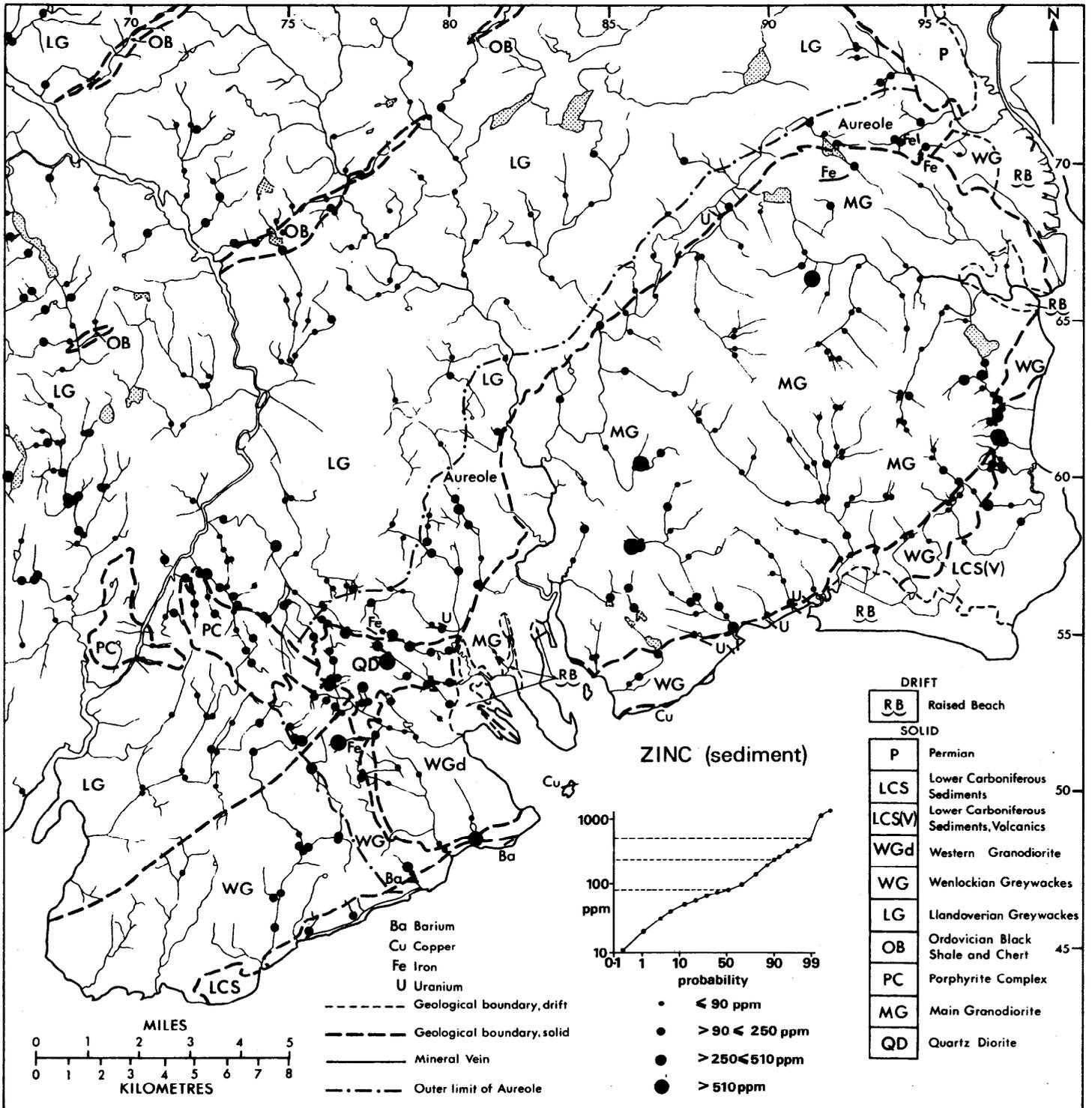


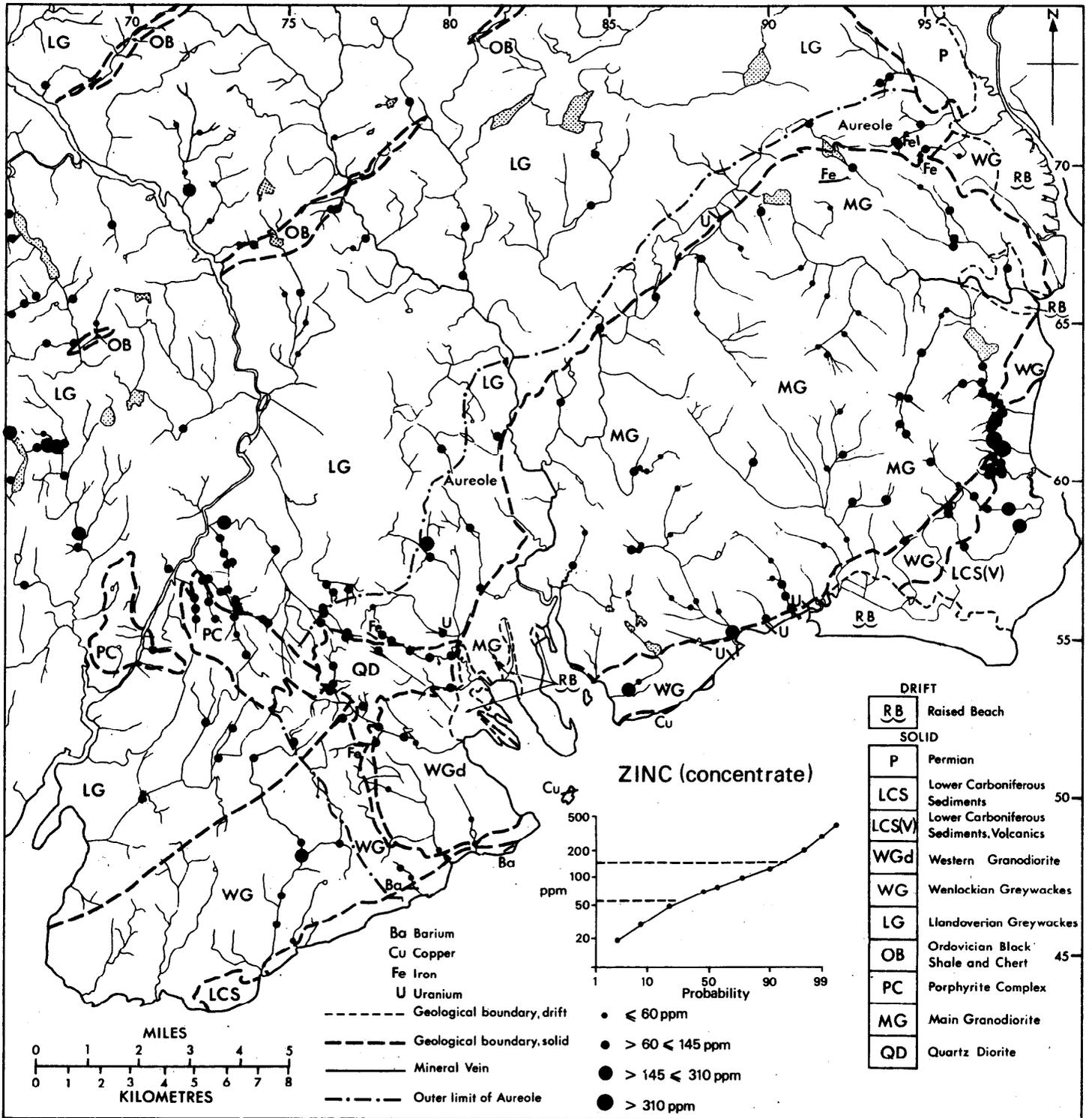


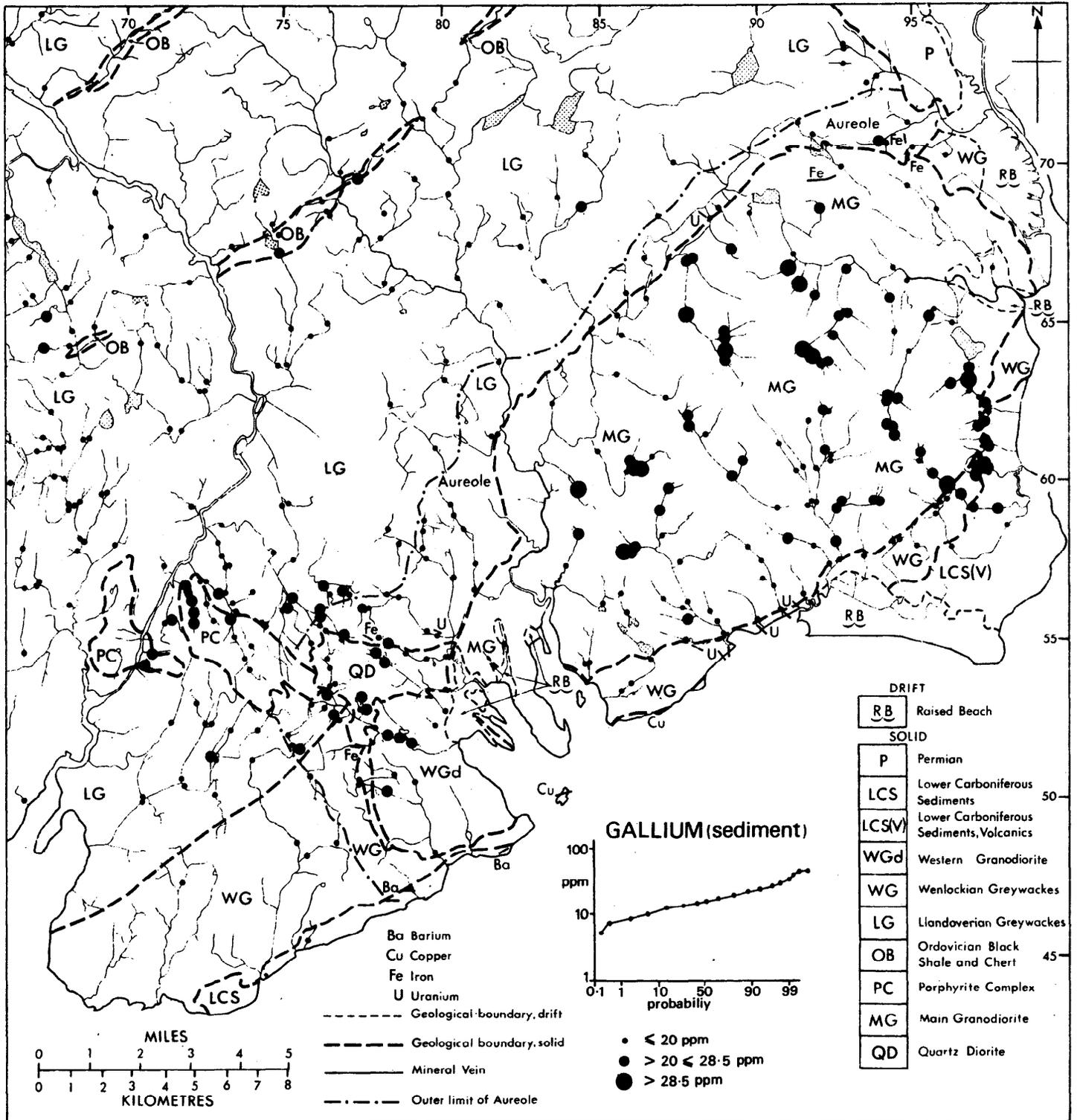


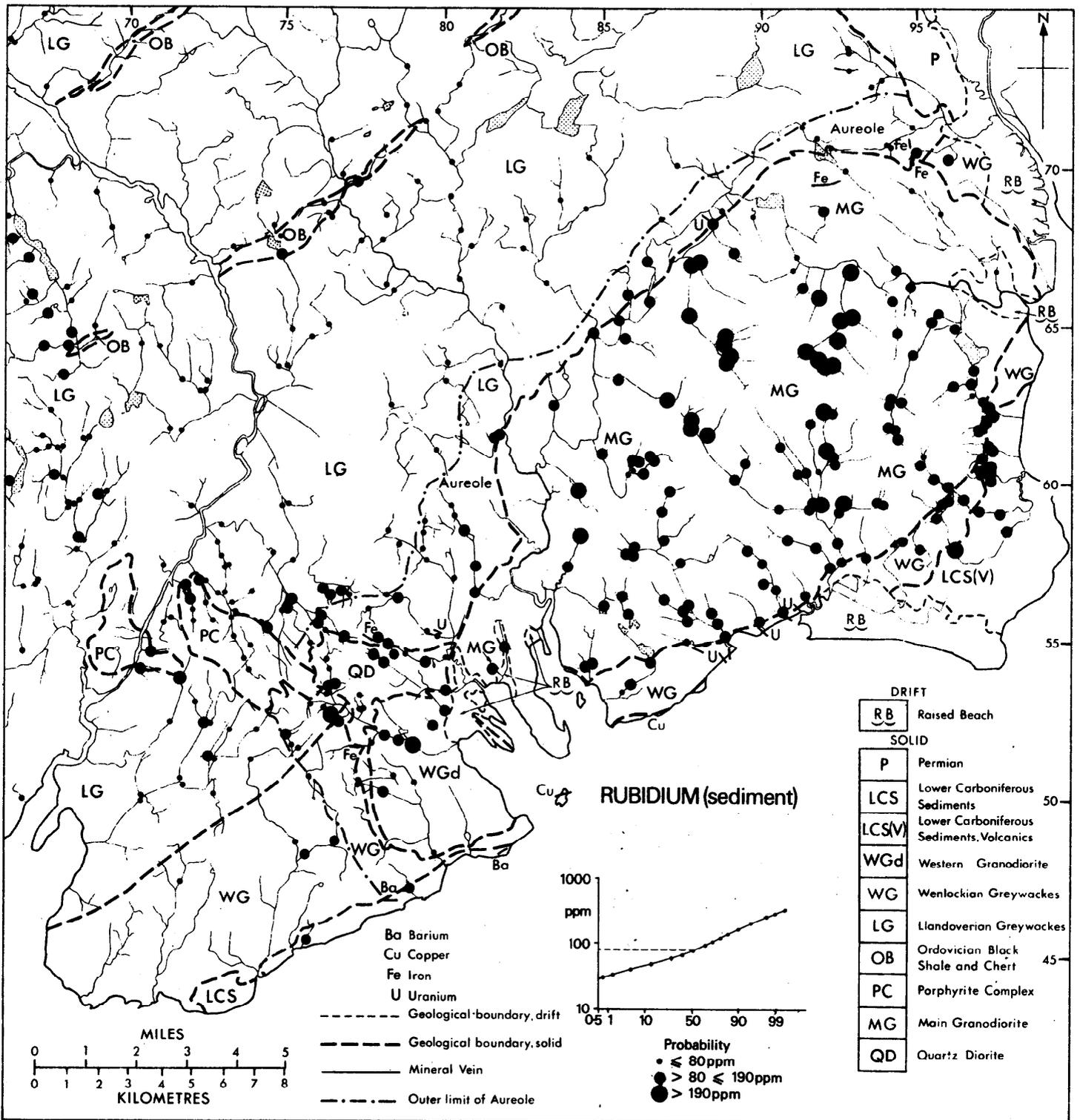


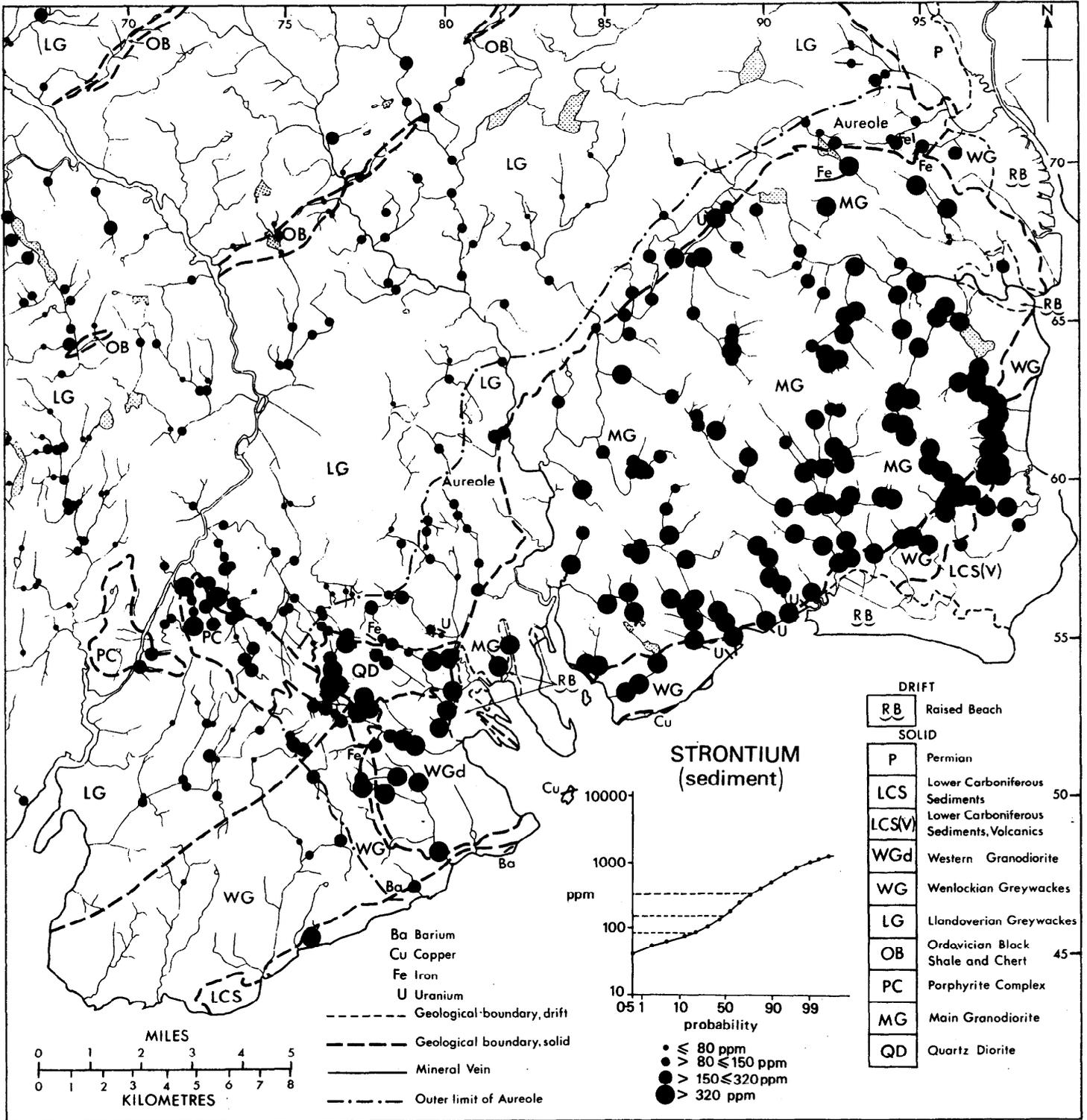


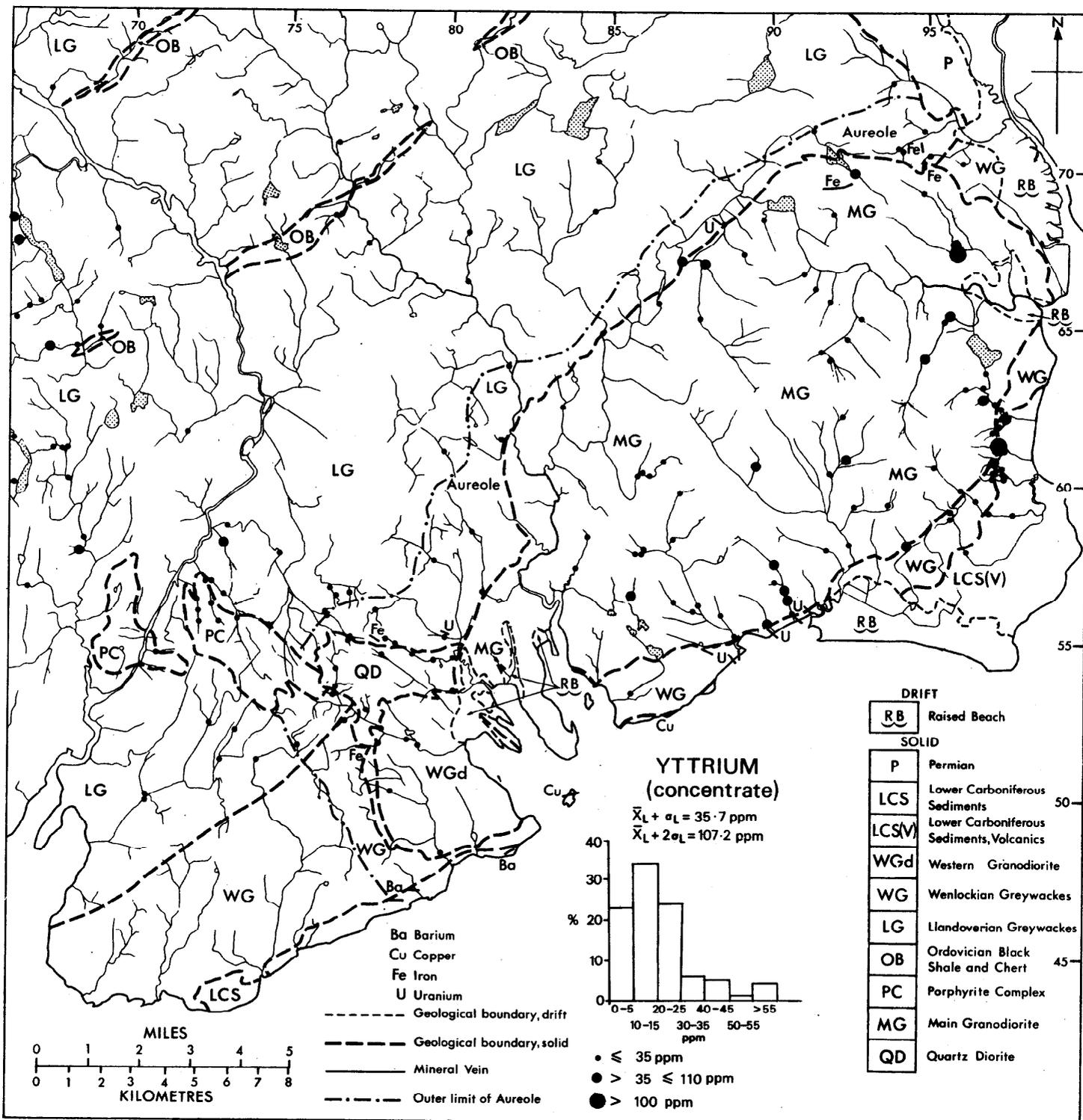


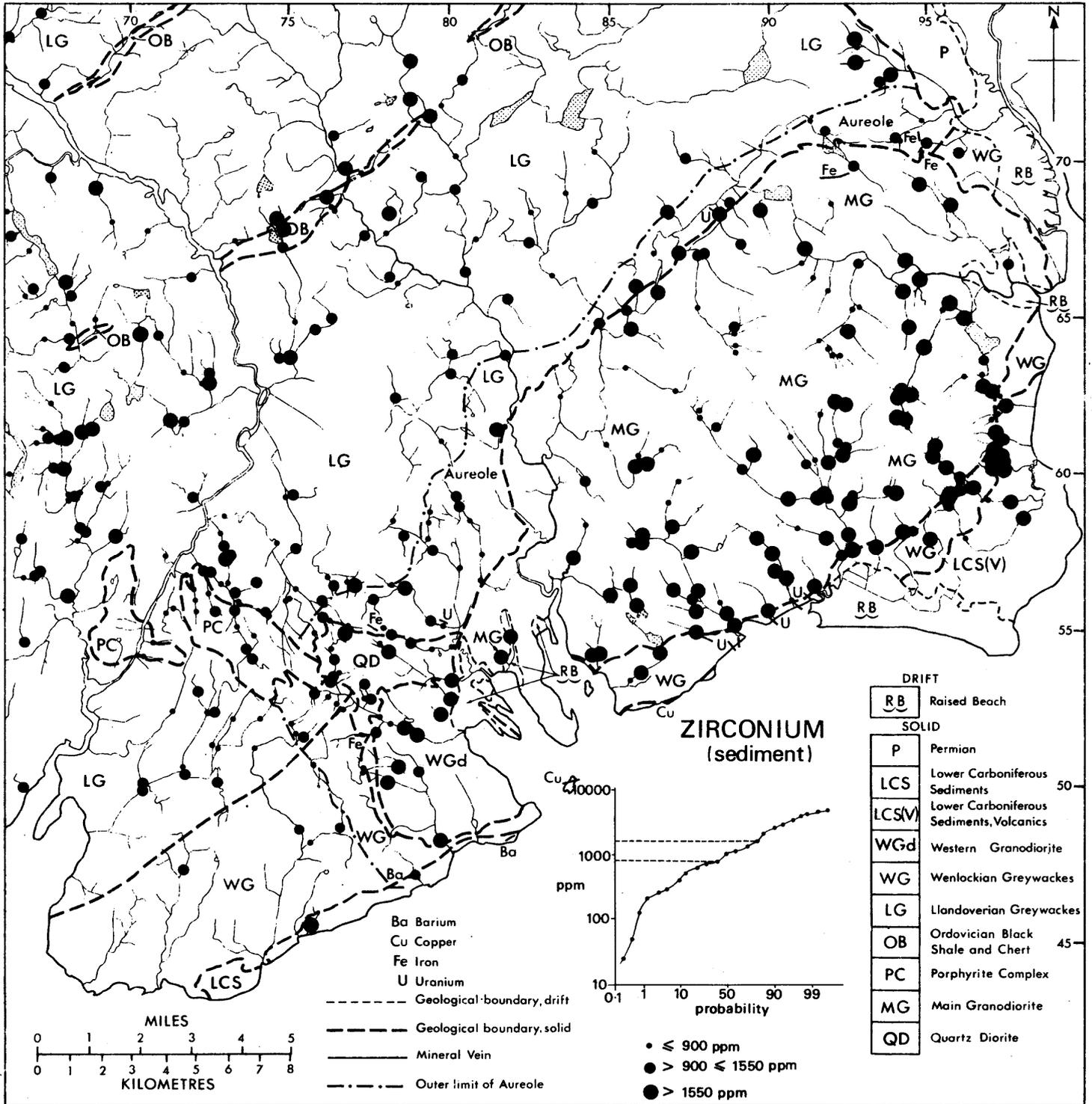


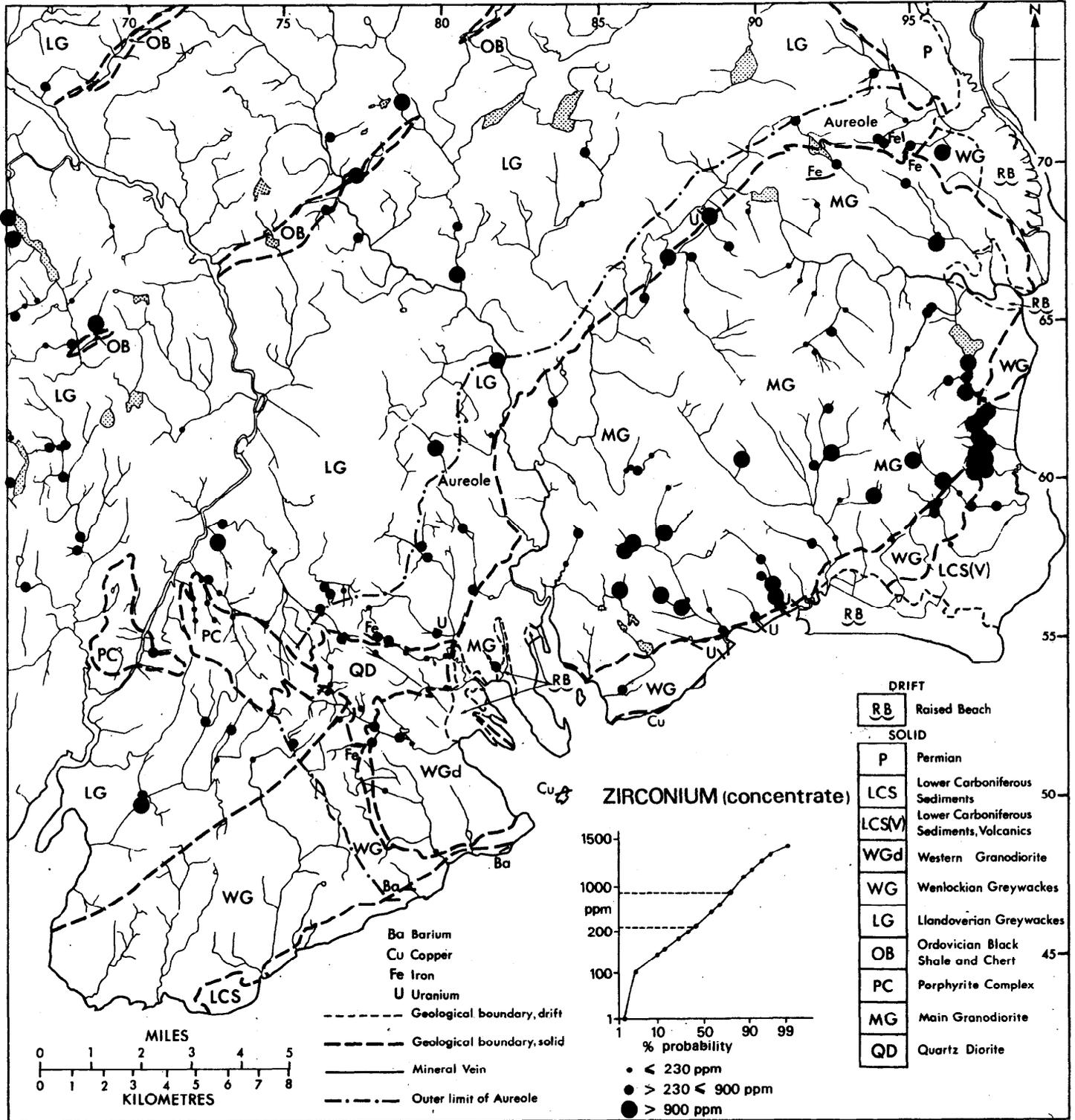


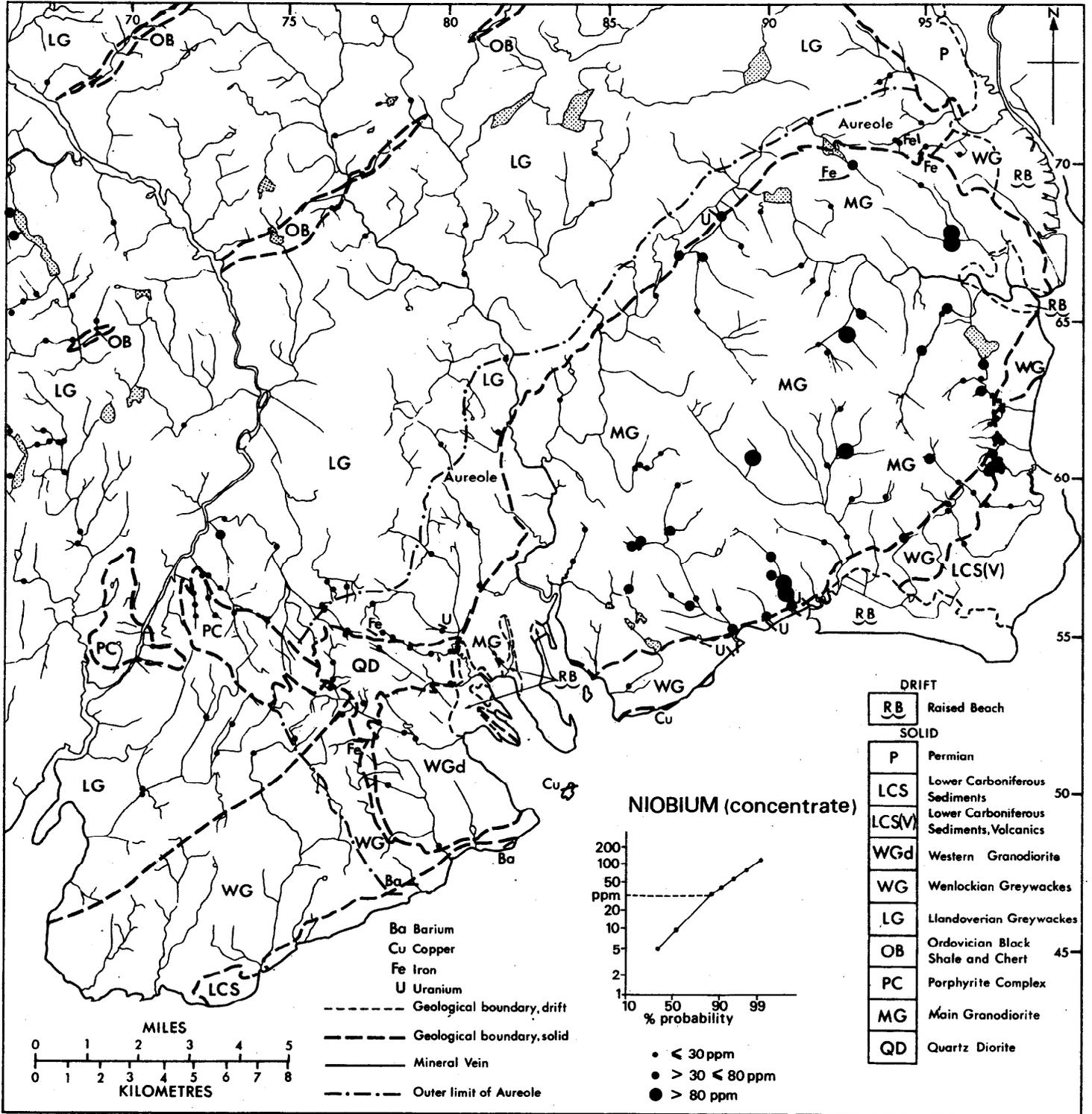


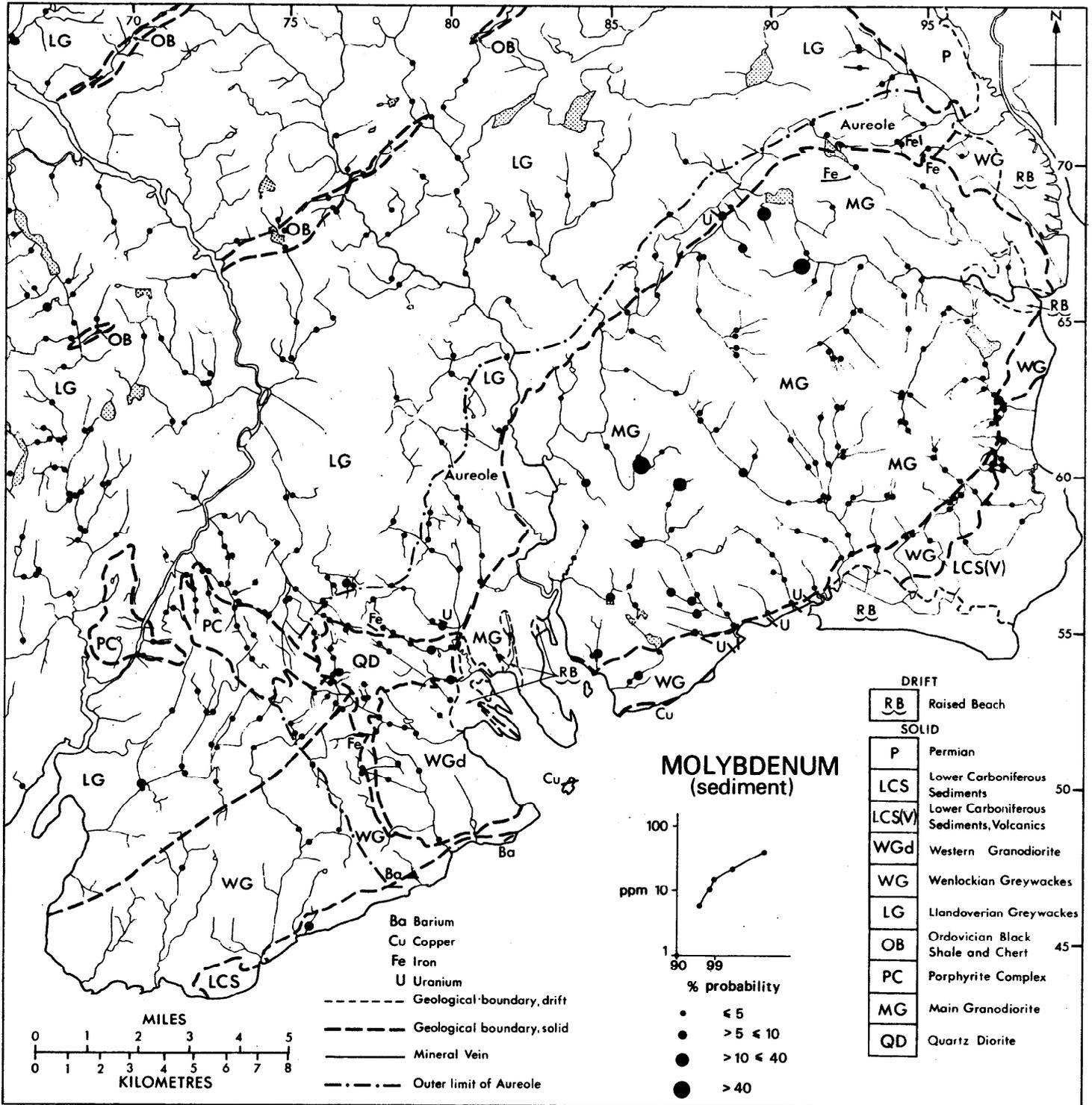


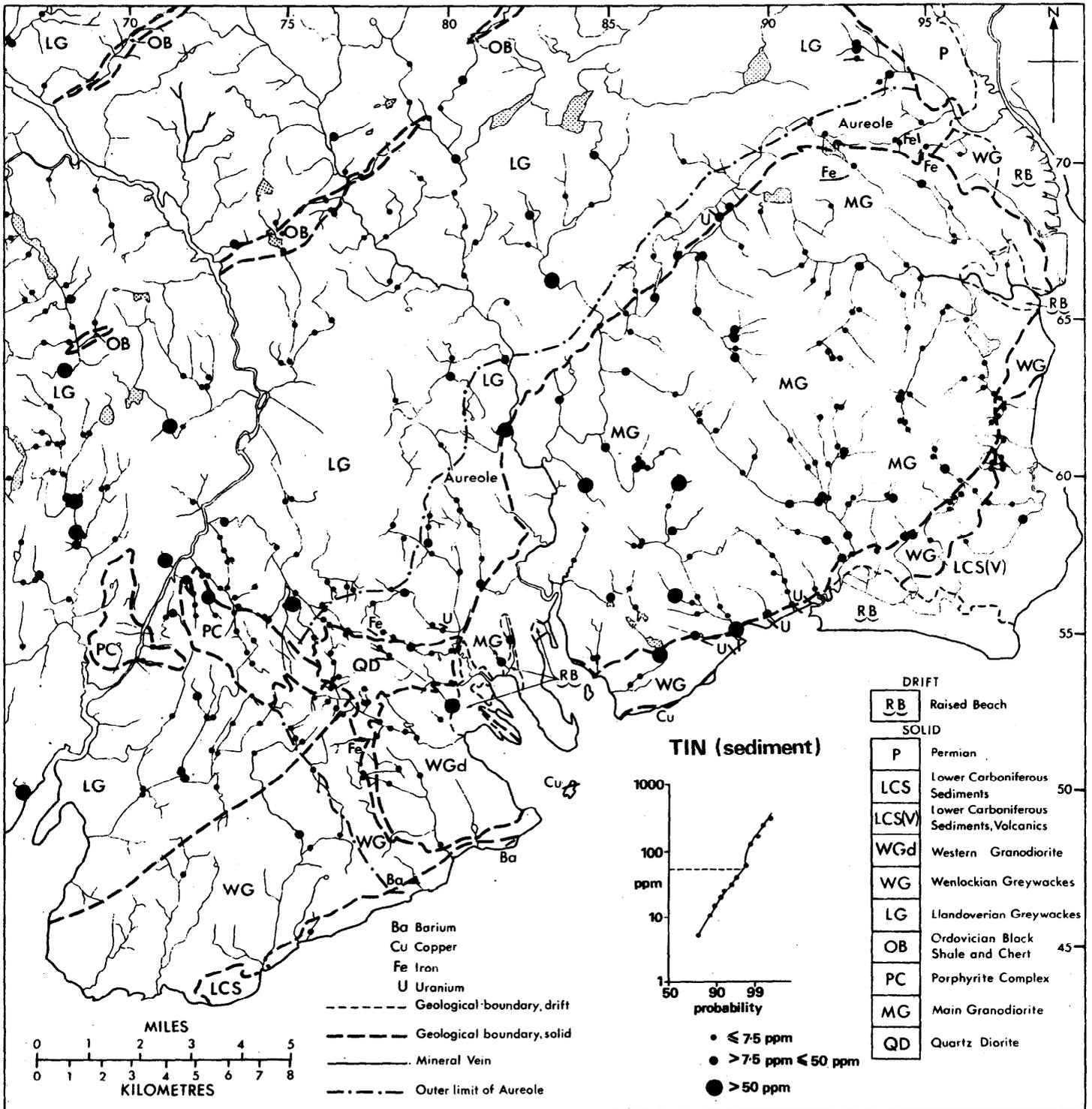


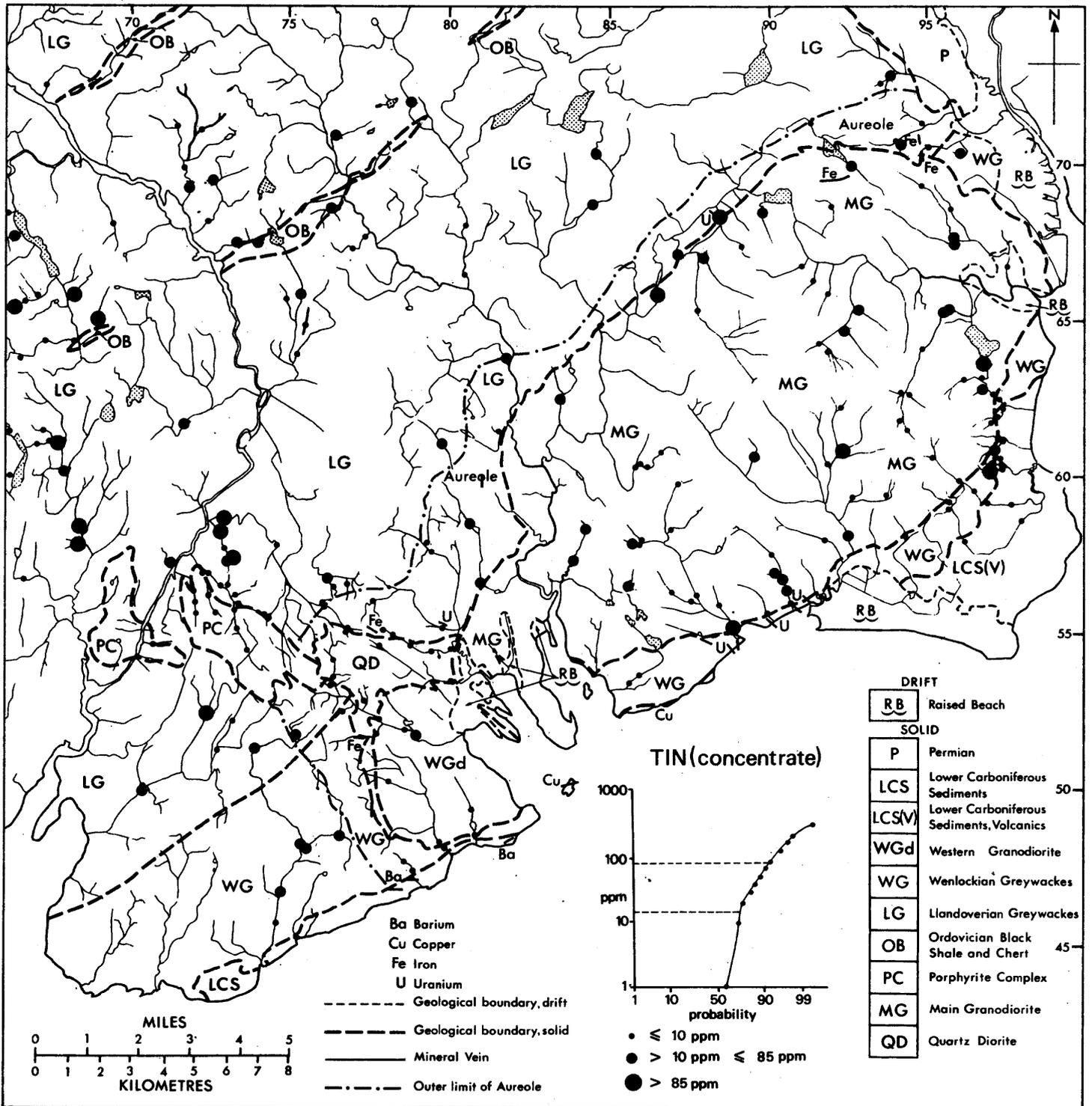


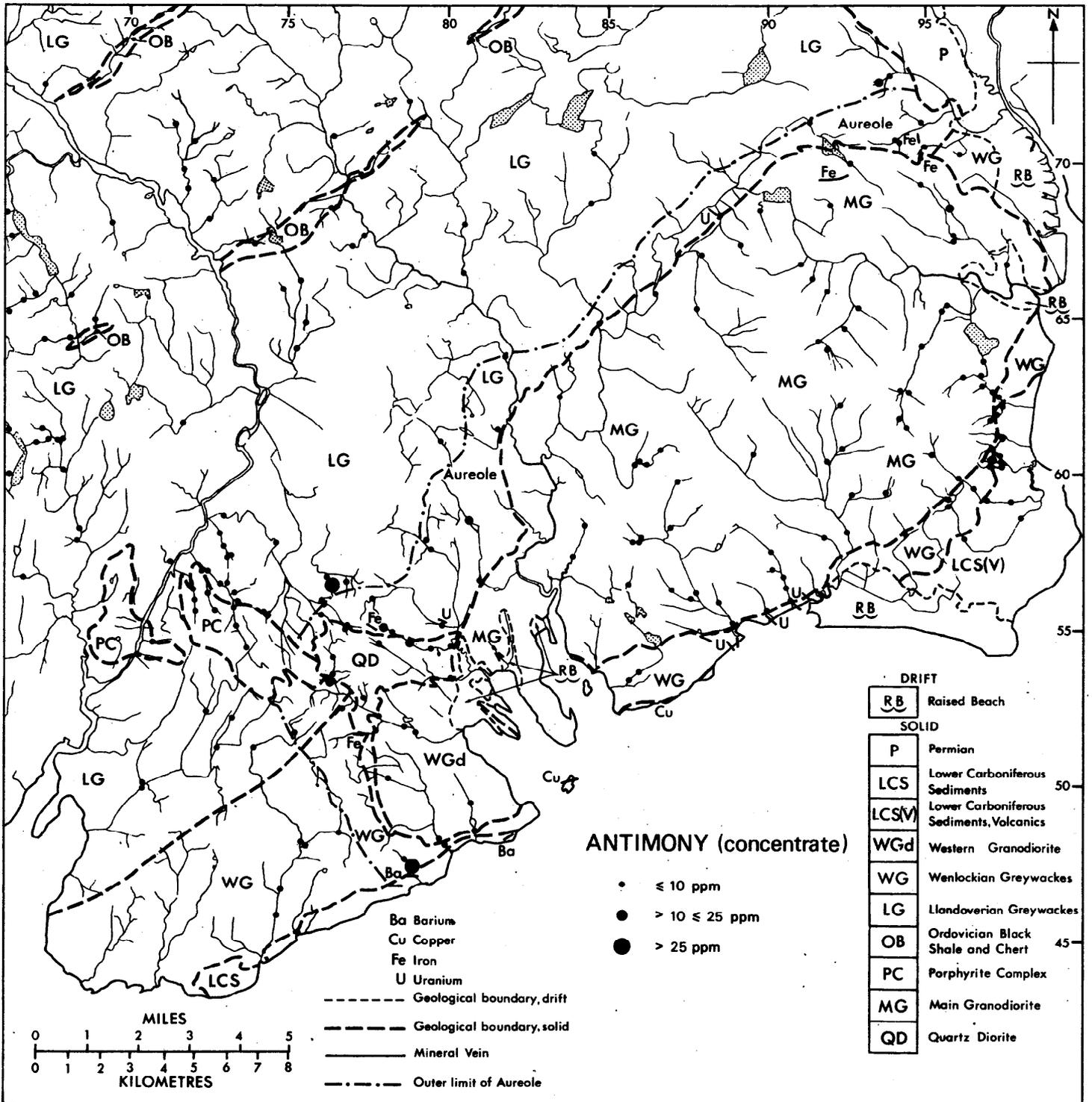


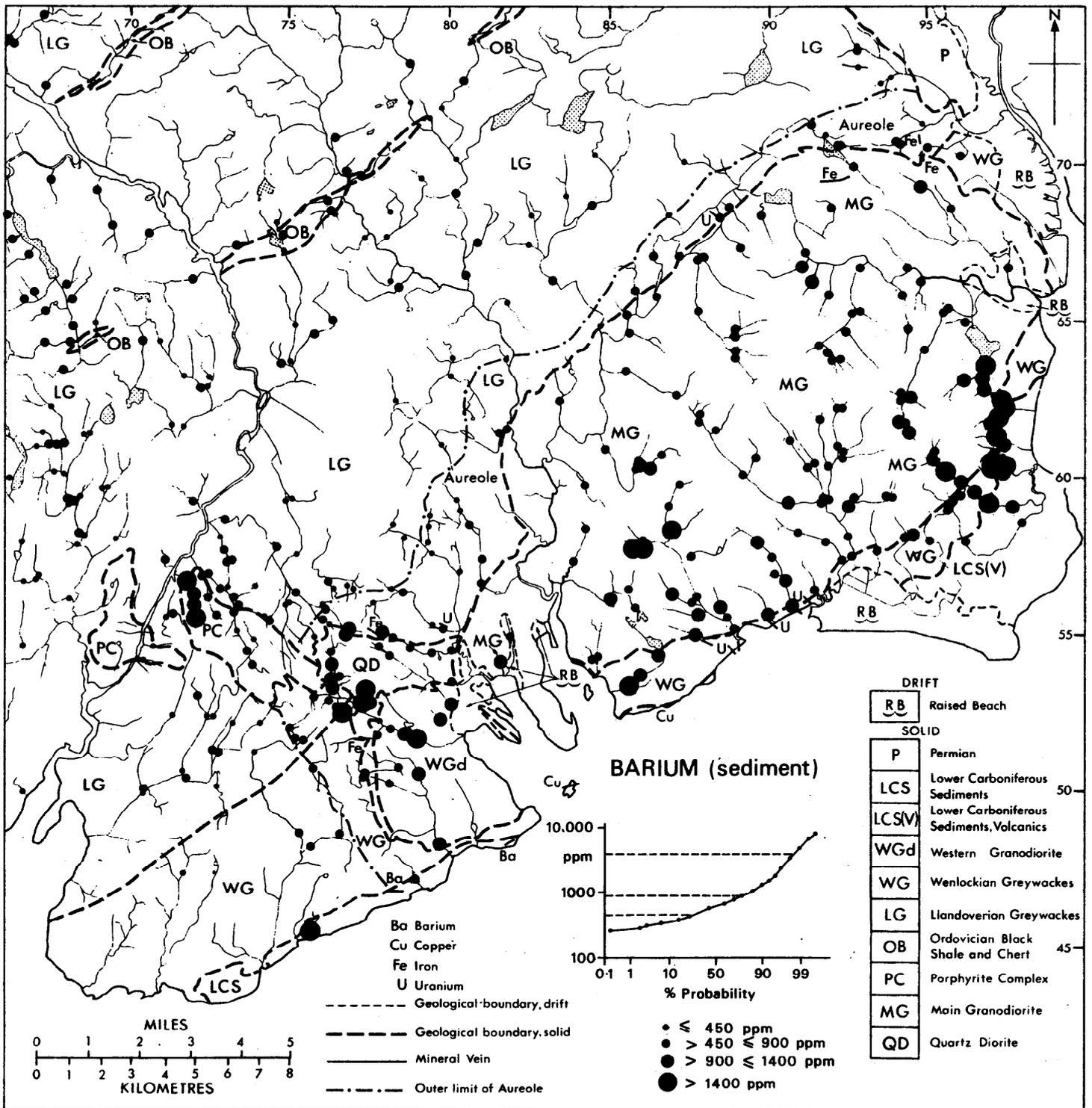












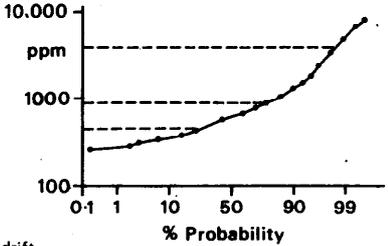
DRIFT

RB Raised Beach

SOLID

P Permian
 LCS Lower Carboniferous Sediments 50
 LCS(V) Lower Carboniferous Sediments, Volcanics
 WGd Western Granodiorite
 WG Wenlockian Greywackes
 LG Llandoveryan Greywackes
 OB Ordovician Black Shale and Chert 45
 PC Porphyrite Complex
 MG Main Granodiorite
 QD Quartz Diorite

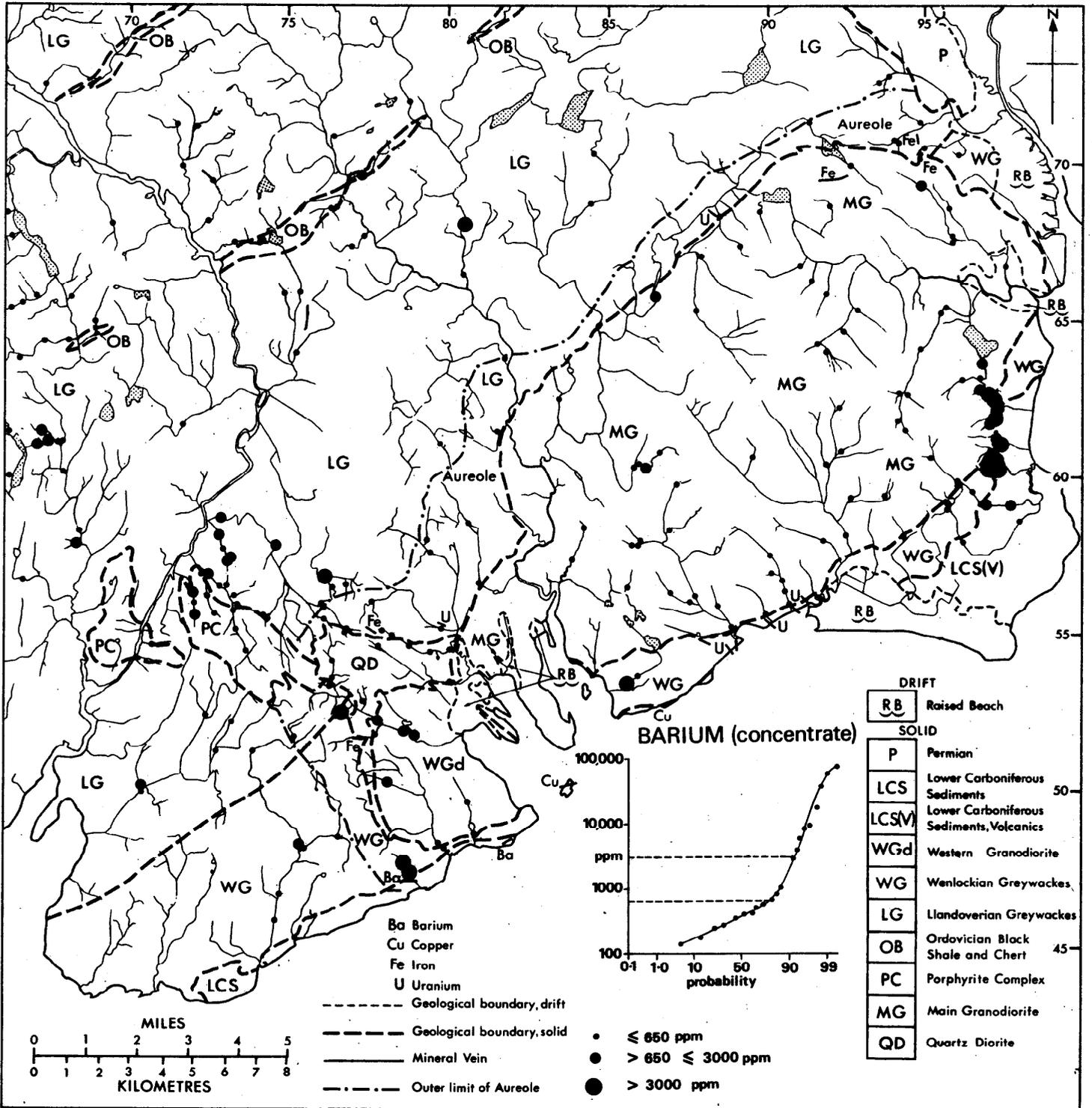
BARIUM (sediment)

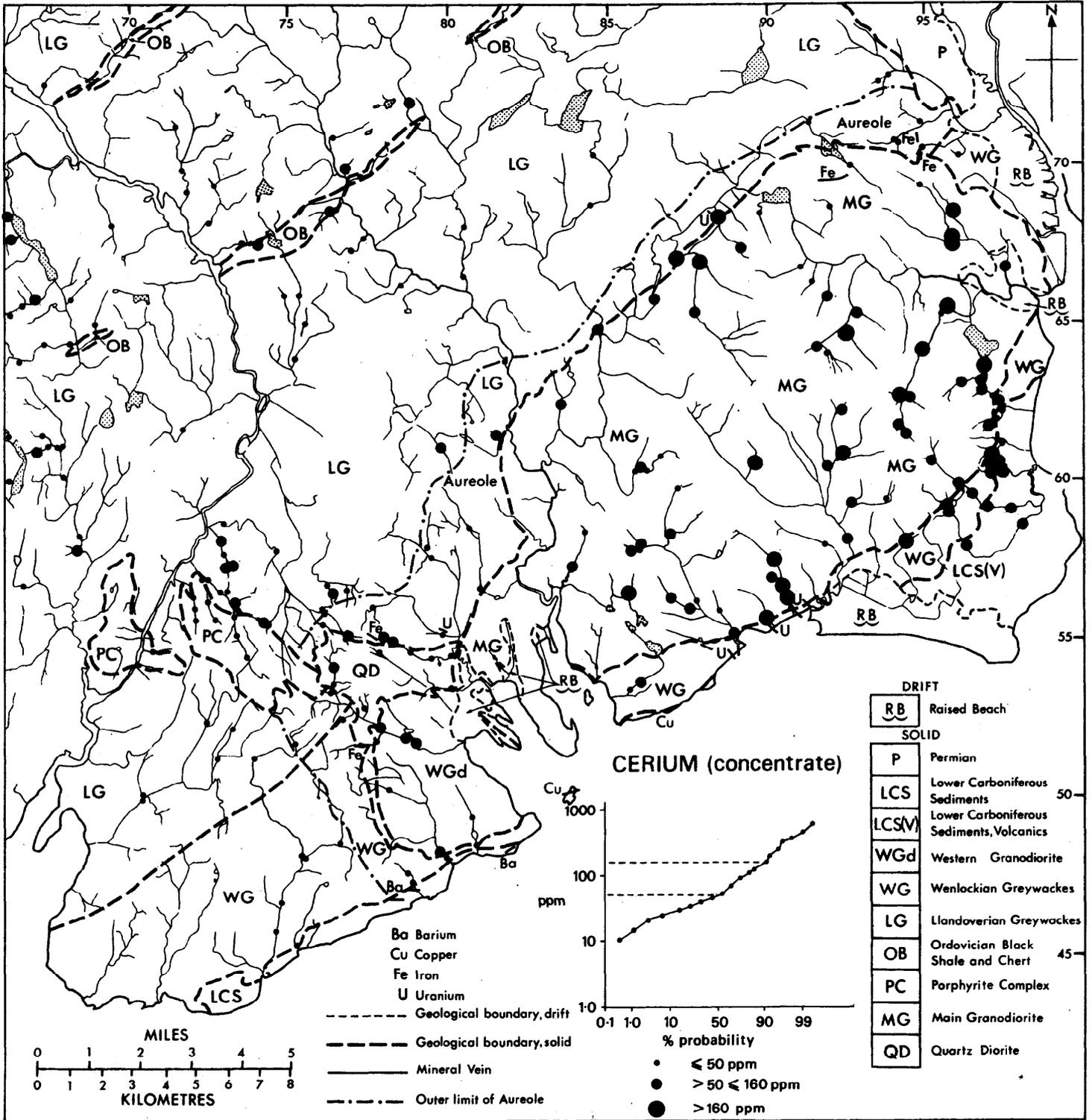


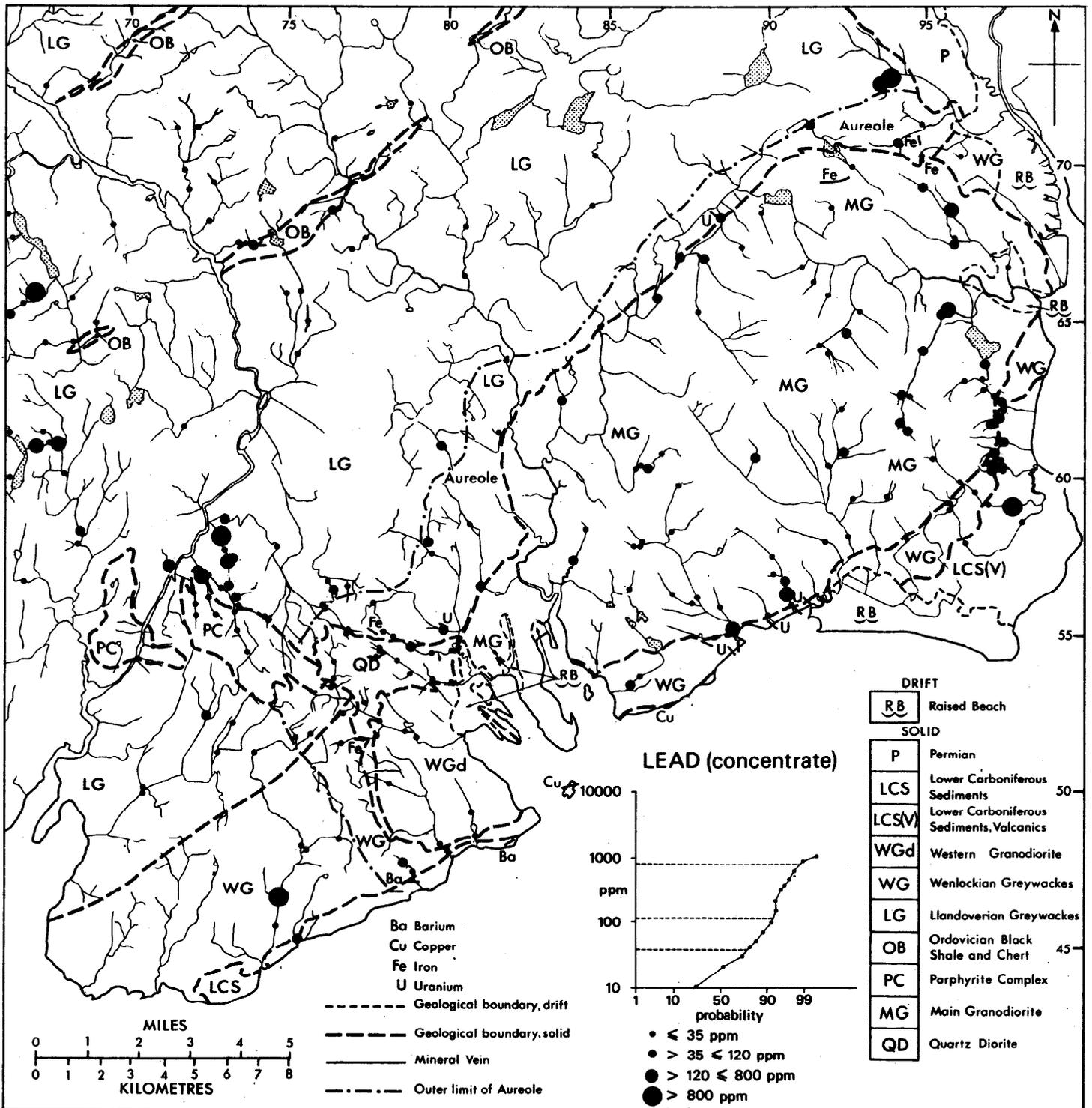
• ≤ 450 ppm
 ● > 450 ≤ 900 ppm
 ● > 900 ≤ 1400 ppm
 ● > 1400 ppm

Ba Barium
 Cu Copper
 Fe Iron
 U Uranium
 - - - - Geological boundary, drift
 - - - - Geological boundary, solid
 — Mineral Vein
 - · - · - Outer limit of Aureole

MILES
 0 1 2 3 4 5
 KILOMETRES
 0 1 2 3 4 5 6 7 8







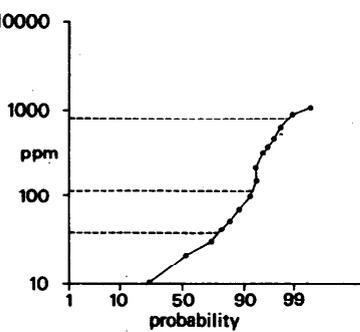
DRIFT

RB Raised Beach

SOLID

P Permian
 LCS Lower Carboniferous Sediments
 LCS(V) Lower Carboniferous Sediments, Volcanics
 WGd Western Grandiorite
 WG Wenlockian Greywackes
 LG Llandoverian Greywackes
 OB Ordovician Black Shale and Chert
 PC Porphyrite Complex
 MG Main Grandiorite
 QD Quartz Diorite

LEAD (concentrate)



• ≤ 35 ppm
 • $> 35 \le 120$ ppm
 • $> 120 \le 800$ ppm
 • > 800 ppm

Ba Barium
 Cu Copper
 Fe Iron
 U Uranium

----- Geological boundary, drift
 ----- Geological boundary, solid
 ----- Mineral Vein
 - - - - - Outer limit of Aureole

MILES
 0 1 2 3 4 5
 KILOMETRES
 0 1 2 3 4 5 6 7 8

