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Geochemistry of sediments from the Lui drainage, Braemar, Grampian

Geochemistry
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This report relates to work carried out by the British Geological Survey on behalf of the Department of Trade and Industry. The information contained herein must not be published without reference to the Director, British Geological Survey.

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SUMMARY

Stream sediments from the western headwaters of the Lui Water all contain markedly high amounts of niobium and some bear anomalous levels of cerium, yttrium, thorium or zirconium. Most of this composition is attributable to the presence of a refractory mineral suite presumed to be derived from nearby granitic rocks.

The tenor of these elements, however, offers somewhat meagre prospect of any significant concentrations of industrial or ore minerals within the local bedrock.

INTRODUCTION

In 1971 Dr.T.Deans submitted for semi-quantitative XRF analysis nineteen panned heavy mineral concentrates collected from Glen Lui, near Braemar in Aberdeenshire. High values of Nb were recorded. A mineralogical examination of ten of these concentrates was carried out in 1974 by Dr. L. Haynes who found grains of cassiterite, columbite or fergusonite in many of the samples.

In 1978, M.J. Bennett collected a further twenty six stream sediments from the drainage of the Luibeg Burn above its confluence with the Derry Burn (Fig. 1). A small sub-sample of the -100mesh BSS fraction from each was submitted for XRF determination of Ba, Ce, Nb, Rb, Sn, Sr, Th, Ti, U, Y and Zr. Although panned heavy mineral concentrates were derived from the -10mesh material at each sampling site, these have been neither chemically nor mineralogically examined.

EARLY STUDIES

It is not clear why the streams were sampled by Dr. Deans, though the presence of bands of skarn in the area (Fig. 1) and vague reports of soda metasomatism at the margins of the Cairngorm Granite may have attracted his attentions. Only limited semi-quantitative XRF analyses were requested. The detailed analytical results are no longer available but they were reported by Dr. Haynes as showing generally high Nb levels with some high Sn values.

In Fig. 1 shows the sites for only those ten samples which were mineralogically examined. All but two were collected from the Luibeg Burn; these two were from streams not directly draining the granite. Sample GL5 comes from the Lui Water downstream of the granite contact, but its concentrate is composed predominantly of granite-derived mineral grains.

A summary of Dr. Haynes' findings is given in Table 1. From this it can be seen that the granitic minerals xenotime, fergusonite, and cassiterite are absent from concentrates GL18 and GL23 but in the latter monazite is found in trace amounts and, surprisingly, columbite more commonly. Concentrate GL5 shows a mainly granitic suite, though with abundant garnets presumably from the Dalradian schists. Of the concentrates obtained from granite locations that from site 7 is unusual in that it displays a totally metamorphic suite even though

several of the higher tributaries of the Derry Burn are wholly in granite.

Table 1. Partial mineralogy of stream concentrates (After L. Haynes)

Species	5	7	8	9	13	15	16	17	18	23
Spessartine	m	m	-	-	-	-	-	-	m	-
Almandine	m	tr	m	tr	-	-	-	-	m	M
Grossularite	M	M	-	-	-	-	-	-	M	M
Rutile	m	tr	m	m	M	M	M	m	m	tr
Anatase	m	m	m	m	m	m	m	m	-	tr
Ilmenite	M	m	M	M	M	M	M	-	m	m
Ilmenorutile	-	-	-	tr	-	tr	tr	tr	-	-
Columbite	-	-	tr	m	-	-	-	-	-	-
Fergusonite	tr	-	tr	-	tr	-	m	-	-	-
Cassiterite	tr	-	tr	-	tr	tr	m	m	-	-
Monazite	tr	-	m	m	M	m	M	m	-	tr
Xenotime	tr	-	m	m	m	m	m	m	-	-
Zircon	m	m	m	M	M	M	M	M	m	m
Chrysoberyl	m	-	tr	-	m	m	-	-	-	-
Topaz	-	-	-	-	-	-	m	-	-	-

Abundances: M = major; m = minor; tr = trace

In addition Dr. Haynes makes the following observations:

GL 5 - The sample has a mixed granitic and metamorphic derivation and includes magnetite, goethite, altered pyrite, hypersthene, epidote, augite, vesuvianite, kyanite, sphene and amphiboles.

GL 7 - Concentrate mainly of non-magnetic minerals. Also includes amphiboles, apatite, sphene, kyanite, hypersthene, augite and iron oxides.

GL 8 - Small heavy mineral concentrate of granite provenance. Also contains iron oxides, biotite, apatite and one grain of kyanite.

GL 9 - Again a poor heavy mineral crop from a sample of clear granite derivation. Other minerals include iron oxides and biotite; some of the xenotime is metamict.

GL13 - Heavy minerals mainly magnetite and its decomposition products. Remainder also includes biotite and sphene. Some of the zircon is metamict. Granitic provenance indicated.

GL15 - Also of granitic origin and again with abundant magnetite and some of the zircon metamict.

GL16 - Granitic provenance. Abundant magnetite and iron oxides, some metamict xenotime, pyrite, barite and a possible bismuth mineral. Some of the cassiterite grains are magnetic.

GL17 - Essentially similar to GL15 and 16.

GL18 - The heavy minerals are dominantly non-magnetic. Additional species include hypersthene, diopside, a little epidote, augite, altered pyrite, black amphibole and iron oxides. The source rocks are probably metasedimentary and metavolcanic types.

GL23 - Mainly of metamorphic origin and with a heavy crop of garnets. Also includes iron oxides, altered pyrite, amphiboles, kyanite, sillimanite, and sphene,

In discussing the relationship of geochemistry to mineralogy, Haynes emphasises that several of the elements determined are present in more than one mineral phase.

Tin is present predominantly as cassiterite, some of which is a magnetic variety. There is also minor substitution of Sn for Nb in the lattices of ilmenorutile, fergusonite and columbite.

Cerium group rare earth elements are dominantly contained in monazite and this mineral is also the major repository of thorium. Yttrium earths occur in xenotime and fergusonite as a major consituent and may also substitute for Ce in monazite or for Mn in spessartine, grossularite or almandine garnets. Some xenotimes are dark red and metamict, indicating that the common substitution of U and Si for Y and P has taken place.

Uranium values do not vary sympathetically with thorium; and they reflect the abundance of metamict zircon, metamict xenotime, fergusonite and monazite.

Niobium is a major constituent in fergusonite, columbite and ilmenorutile, a minor element in anatase and a trace component in some rutile and ilmenite. The concentrates examined by Dr. Haynes were carefully checked for tantalum, but none was found. The presence of Fe-rich Nb-bearing rutiles (nigrines) is interesting in view of the occurrence of grains of weakly magnetic ilmenorutile. It is thought that Nb in columbite-free or fergusonite-free samples may be due to the presence of near end members of the nigrine-ilmenorutile series.

RECENT INVESTIGATION

Location sites for the recent twenty-six stream sediment samples are shown in Figure 1; all are within the outcrop of the Cairngorm Granite. It will be seen that, although there are no true duplicate samples, some of the Bennett (XFC) and Deans (GL) samples are taken from closely adjacent parts of the drainage. An assessment of the mineralogical and exotic element significance of the Bennett samples from Dr. Haynes details of the nearby Deans' concentrates is given later.

A complete listing of the XRF analyses is given in the Appendix to this report and the essential statistics are quoted in Table 2. With a set comprising only 26 samples, there must be some considerable doubt about the value of log distribution plots. Nonetheless, these were prepared for each element (Figs. 2-5) and provide some indication of the number and level of anomalous values.

For barium the plot (Fig. 2) is equivocal but the three highest values appear to be anomalous. The mineral location of this element is uncertain but it is presumed to substitute for potassium in the micas and feldspars and may also be present as traces of barite. Similar comments can be made upon strontium (Fig. 2), though in this case the highest three values are more decidedly anomalous. Strontium is not present as a discrete mineral phase but as a lattice substitute, mainly for potassium. Rubidium (Fig. 2) behaves in a comparable fashion but it exhibits an almost gaussian distribution

with only a faint suggestion of any anomalously high values.

The plots for titanium and zirconium (Fig. 3) both indicate several population sets but this may reflect the small sample population. In each case the highest value set comprises six samples of which the four highest are clearly anomalous; the other two are probably so. Titanium occurs as three major mineral phases - ilmenite, rutile and anatase - and this could account for the multiplicity of population sets. Zirconium, however, is mainly contained in zircon only and it substitutes in minor degree for iron.

Table 2. Elemental statistics (in ppm)

Element	Range	Mean	Std. Dev.	Median
Barium	104-255	173.27	43.98	180
Cerium	91-999	216.38	172.44	173
Niobium	59-258	95.46	41.14	83
Rubidium	287-587	448.77	69.05	435
Strontium	49-197	77.54	28.40	77
Thorium	43-353	105.77	62.05	88
Tin	3-24	14.08	5.10	14
Titanium	1340-6790	2671.54	1387.13	2300
Uranium	14-55	31.27	10.33	31
Yttrium	74-368	153.38	66.23	132
Zirconium	257-2883	853.00	548.53	719

Tin (Fig. 4) yields a simple log distribution plot with the four highest value results (Sn > 20ppm) forming an anomalous set. This element occurs predominantly as cassiterite but trace amounts are present in other opaque minerals. The niobium plot (Fig. 4) is closely similar to that of tin, with the three highest values anomalous.

Of the rare earth elements, cerium (Fig. 5) yields a relatively simple looking log-probability plot with an anomalous set comprising the three highest results. The yttrium results (Fig. 5), however, provide a more complex plot in which the five highest values can be separated as an anomalous set. It may be advanced that this difference merely reflects the fact that cerium occurs almost solely in monazite whereas the yttrium earths are located both in xenotime and fergusonite.

The two radioactive elements, thorium and uranium, exhibit markedly different distributions. The former, occuring predominantly in monazite but also as traces in some of the zircons, yields a near-straight line plot (Fig. 5) indicative of a gaussian distribution. Uranium, on the other hand, gives a plot (Fig. 4) with two inflection points defining a highly anomalous population at levels above 42ppm U and another, also apparently anomalous, between 35 to 42ppm. It is perhaps surprising that uranium, which occurs as a trace element in monazite, xenotime, fergusonite and zircon, does not yield a more complicated distribution plot.

When applied to the individual samples, the foregoing interpretations of anomalous values show that there are nine samples with non-anomalous contents of all the elements and five in which the contents are doubtfully anomalous (Table 3). Three samples are anomalous in five or more elements. A visual scan of this table confirms that the only obvious elemental associations are those which might be expected from geochemical considerations, namely Ti and Zr, Nb and Y, and Ba and Sr.

Table 3. Distribution of anomalous values

Sample	Anomalous Elements	Sample	Anomalous Elements
XFC 2	Ce, (Ti?), U, (Zr?)	XFC 17	Ba, Sr, Ti, Zr
XFC 3	Sn, (U?)	XFC 18	(Ti?), (U?), (Zr?)
XFC 4	Ba	XFC 19	Ce, Nb, Sn, Ti, U, Y, Zr
XFC 6	(U?)	XFC 21	Ce, Nb, Ti, (U?), Y, Zr
XFC 7	Y	XFC 22	Sn, Sr, Ti
XFC 8	Nb, Y	XFC 23	(U?)
XFC 9	Y	XFC 24	(U?)
XFC 10	Sn, U	XFC 26	(U?)
XFC 15	Ba, Sr, Ti, U, Zr		

(X?) signifies the anomalous status is doubtful

The distribution of individual element anomalous values within the drainage pattern shows no obvious logic. Most of the anomalous samples exhibit no significant clustering or sequential downstream distribution, though the latter pattern may be broadly invoked for the Ti-Zr association. In particular the anomalous values of the potentially economic elements - tin, niobium and the rare earths - are scattered.

Comparison with the concentrates examined by Dr. Haynes is somewhat problematic due to the non-quantativity of his descriptions. There is a fairly clear correlation between the highly anomalous sample XFC19 and the Deans' samples GL17 and GL15, respectively upstream and downstream; the mineralogy also clearly reflects the chemistry of sediments from the several higher tributary streams of Allt Carn a' Mhaim (Fig. 1). The chemistry of XFC23, 24, 25 and 26, on the other hand, reflects less well the mineralogy of concentrate GL16. Stream sediments XFC4 and XFC5, and concentrate GL13, immediately downstream from the previous group, show nothing like the same breadth of anomalous elements.

Samples GL9 and XFC8 were taken from adjacent sites on a small southern tributary of the Luibeg Burn and the mineralogy of the former closely matches the chemistry of the latter. Of particular interest here is the presence of columbite as a major source of the anomalous niobium content. Aspects of these compositions are repeated in XFC21 a short distance below in the main burn. Although XFC22, GL8 and GL7 were taken from sites close to one another the chemistry of the first is not matched by the mineralogy of the last, upstream of it. In particular there is no cassiterite mentioned in the

concentrate though anomalous tin is reported in the stream sediment; cassiterite is a trace constituent of GL8 however.

CONCLUSIONS

The collection of stream sediments from the Lui drainage has not located any source enriched in potentially economic minerals, though individual samples do sometimes exhibit distinctly high levels in some of the interesting elements. Cassiterite and columbite, perhaps the most intriguing of the minerals recognised by Dr. Haynes in panned concentrates from the area, are apparently not present in such quantity nor sufficiently widespread to register clearly as major areas of tin or niobium anomalies in the stream sediments.

Only the granitic part of the drainage was sampled in this investigation; it is probable that some of the thin skarn bands close to the granite contact may also be repositories for cassiterite and the niobium minerals, though Dr. Haynes mineralogical work suggests that the tenors may be no higher than are seen within the Cairngorm Granite. In summation, therefore, it appears that this area is unlikely to contain any mineralisation - disseminated, vein form or skarn hosted - of potential economic interest.

ACKNOWLEDGEMENTS

The authors are grateful to the owners and staff of the Mar Estate whose willing co-operation made this investigation both possible and pleasant. Analyses of the stream sediment samples were carried out by T.K. Smith of the BGS Analytical Unit.

REFERENCE

HAYNES, L. "The identification of heavy minerals derived from tin-bearing rocks in the Cairngorms." Report No. 142 of the Mineralogy Unit, Institute of Geological Sciences. May, 1974.

APPENDIX. XRF analyses of Lulbeg stream sediments (in ppm)

Sample	Ba	Ce	Nb	Rb	Sn	Sr	Th	Ti	U	Y	Zr
XFC 1	121	189	88	432	8	61	98	1860	26	148	687
XFC 2	121	363	112	515	18	66	231	3370	44	173	1306
XFC 3	138	246	100	473	22	63	133	2380	36	171	739
XFC 4	236	234	89	403	9	88	102	2500	27	134	818
XFC 5	220	189	90	392	19	84	91	2540	24	124	735
XFC 6	227	140	101	359	9	82	68	2630	39	136	792
XFC 7	183	221	81	496	17	62	103	2040	33	226	704
XFC 8	170	194	128	393	3	66	99	2450	31	304	744
XFC 9	113	146	77	502	14	56	82	1580	23	209	587
XFC 10	104	91	84	587	24	49	58	1340	43	129	257
XFC 11	180	108	70	468	14	77	63	1520	23	120	383
XFC 12	203	133	80	482	15	84	86	2220	29	140	456
XFC 13	146	132	62	439	12	78	81	1700	20	97	446
XFC 14	136	191	75	502	7	61	97	1630	31	170	756
XFC 15	243	251	93	426	20	97	140	4300	51	121	1540
XFC 16	188	111	67	394	9	87	59	2430	19	74	691
XFC 17	255	267	108	412	12	107	128	4700	21	123	1527
XFC 18	180	212	92	426	17	82	115	3250	39	122	1122
XFC 19	181	299	258	388	21	85	353	6790	55	368	1883
XFC 20	230	115	76	395	10	88	57	2110	14	87	531
XFC 21	184	386	188	392	14	83	147	4490	35	220	1715
XFC 22	210	121	59	287	21	197	43	5600	14	80	823
XFC 23	128	146	78	521	11	55	82	1560	35	174	519
XFC 24	148	127	64	454	12	57	67	1420	37	104	415
XFC 25	128	158	79	568	14	51	83	1640	25	104	512
XFC 26	132	154	83	562	14	50	84	1410	39	130	490

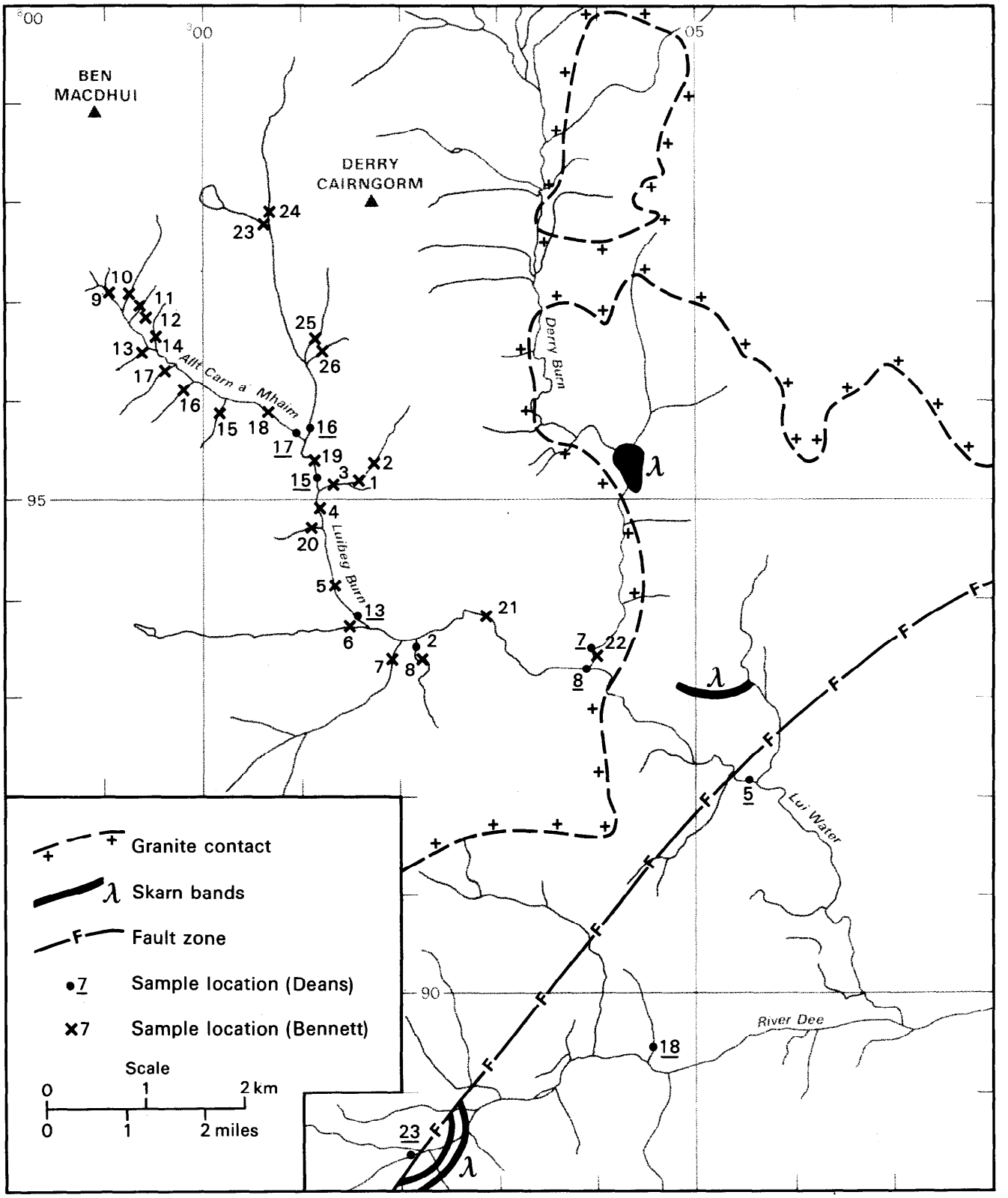

Figure 1 Outline geology and sampling locations

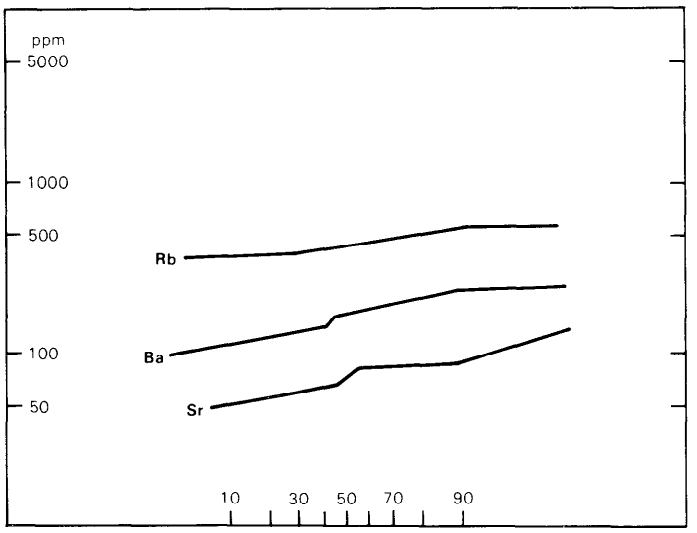

Figure 2 Log-probability plots for Ba, Rb and Sr

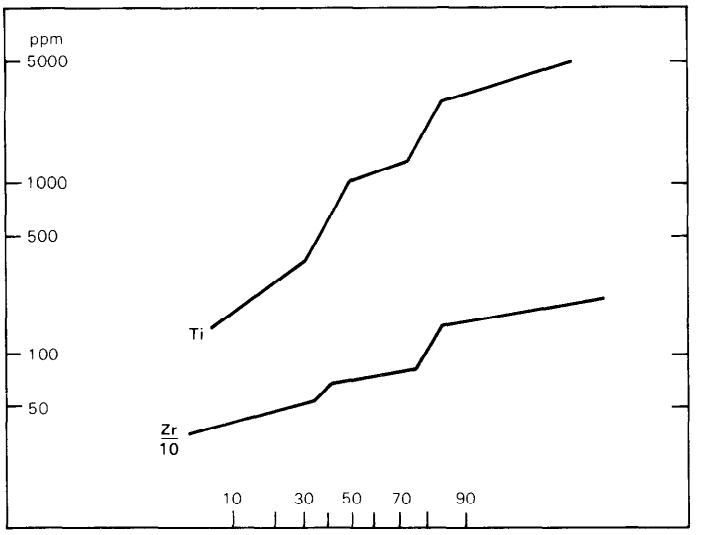

Figure 3 Log-probability plots for Ti and Zr/10

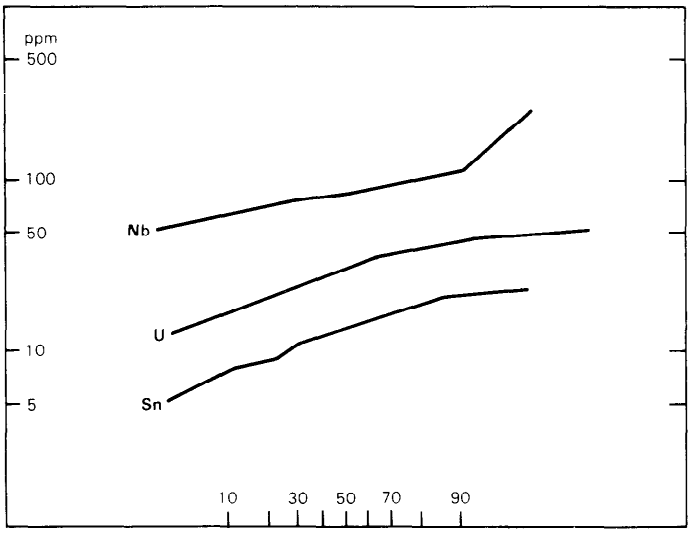

Figure 4 Log-probability plots for Nb, Sn and U

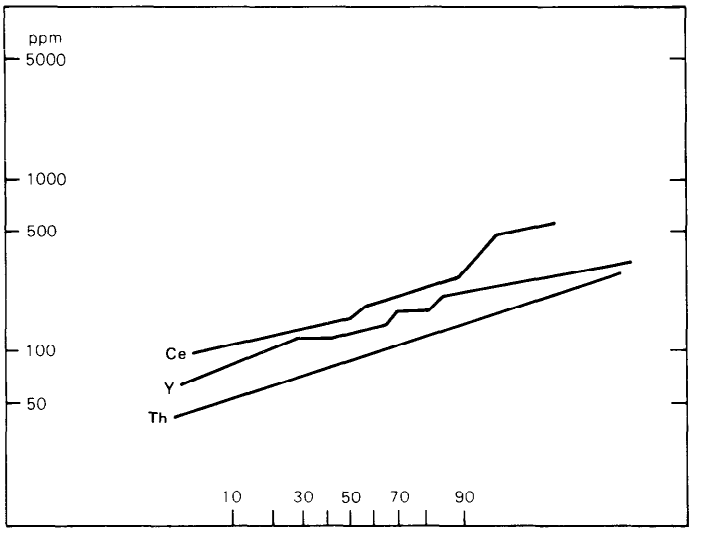

Figure 5 Log-probability plots for Ce, Th and Y