PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

Regional Geochemical Mapping and Interpretation in Britain [and Discussion]

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Regional geochemical mapping and interpretation in Britain

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[Plates 1 and 2]

Regional geochemical atlases of Britain and the British North Sea prepared by the Institute of Geological Sciences are discussed with special reference to their environmental significance. Factors affecting the selection of sample types are considered, and sample preparation, analytical procedure and monitoring error discussed. Stream sediment is shown to be the optimum sample type for regional geochemistry in areas of upland Britain underlain by crystalline bedrock, although soils may provide the optimum sample medium in areas of intensive agriculture. Geochemical mapping of the continental shelf is based on superficial seabed material obtained by grab or cone dredge.

Examples of geochemical maps of northern Scotland for several elements of environmental significance including Cu, Mo, Pb and U are considered in relation to geology, topography, vegetation, land use and the chemistry of surface waters. Geochemical maps are shown to provide the best available source of information on chemical variations in bedrock, although there are many difficulties in relating geochemical or biological activity to the total trace element values. In any attempt to correlate trace element levels with disease, careful consideration must be given to factors affecting the availability and flux of the trace elements if meaningful associations are to be obtained. Geochemical maps of the North Sea indicate that the contents of Cu, Pb, Zn, Cd and Hg are uniformly low over most of the offshore area although higher concentrations occur in coastal samples. The highest concentrations of Cu, Pb and Zn occur off the Tyne estuary while the highest values for Cd and Hg occur further south.

1. Introduction

In the late 1960s the Institute of Geological Sciences initiated a programme, subsequently sponsored by the Department of Industry, to prepare geochemical maps of the land area of Britain. The principal purpose was to supplement available geological information and provide regional geochemical data for studies of crustal evolution and ore forming processes. In addition it was expected that the programme would provide quantitative information on natural elemental levels, thus allowing contamination to be assessed. It was also anticipated that lithological, compositional and structural variations in bedrock which are difficult to detect by visual mapping procedures would be more clearly defined and that data obtained would be of importance in identifying new occurrences of metalliferous mineralization as well as in studies of the relation between trace element levels and diseases in crops, animals and man. The production of geochemical maps of the continental shelf for several elements of environmental significance including Cu, Pb, Zn, Cd, Hg and Mn began late in 1971. The main aim of this survey was to obtain quantitative data on the distribution of toxic elements, particularly Hg, in the superficial sediments of the British continental shelf.

The Institute's geochemical mapping programme has been aimed at collecting standardized data of high quality to provide a quantitative basis for existing geological information and to identify features revealed by geochemistry that are not indicated by the geology as mapped. The data for the land area are published in the form of geochemical atlases at a scale of 1:250000. The distribution of up to 30 elements is plotted as point source information on a modern geological base map, and generalized contour plots of the geochemistry and maps of some surface features such as topography, vegetation, land use and the pH and conductivity of surface waters are presented with interpretative notes (Institute of Geological Sciences 1978*a*). The technical difficulties in obtaining a standardized system of mapping elemental levels and some of the scientific problems of interpreting the geochemical data over the variable and complex offshore and land area of Britain are the subject of this paper.

2. Geochemical mapping procedures

(*a*) *Continental shelf*

(i) *General*

Geochemical mapping of marine sediments of the British continental shelf was directed initially towards the North Sea and east coast estuaries since research on the west coast, for example in the Bristol Channel and Liverpool Bay, was being carried out by University departments. Because of the high cost of ship time, low density sampling was planned on a systematic 10 mile (*ca.* 16 km) grid from the coast to the median line of the continental shelf. This was maintained as the basic unit of mapping for offshore areas although in shallow waters, principally those offshore of the Wash, some distortion of the grid was found necessary. A higher sample density was used for near coastal sediments which were also sampled first since they were expected to have higher contents of heavy metals and to pose a greater potential threat to human health. The first cruises were therefore designed to collect samples along the 10, 20 and 30 fathom (*ca.* 18, 36 and 55 m) contours with stations at approximately 5 mile (*ca.* 8 km) intervals along the lines. Estuaries of the Tyne and Tees were sampled at 1 mile (*ca.* 1.6 km) intervals across the mouths and those of the Humber and Thames in a less systematic manner. In addition to these surveys the data were supplemented whenever joint cruises with other organizations could be arranged. The sector between 51 and 58° N has so far been covered.

(ii) *Sampling procedures*

Sample stations were occupied and Decca Main Chain navigation was used, since the broad scale of the survey did not justify more expensive navigational aids. Initially, sediment samples were taken using a Shipek grab; however, the only grabs available were cadmium plated and were therefore a potential source of sample contamination. Further, significant quantities of fine sedimentary material were shown to be lost in passage from the seabed. The grab was therefore replaced by a cone dredge; although some fine material was lost from a cone dredge owing to turbulent flow, the yield was usually higher than with a grab. Neither of these devices gives a representative sample of bottom sediment under all conditions, however, and the application of a box corer for sample collection is currently being investigated.

Immediately after collection, samples were transferred to clean polyethylene or polypropylene containers and deep frozen at -30 °C to minimize losses of volatile constituents and to prevent decomposition of organic material. In the laboratory, analytical subsamples were freeze dried to prevent loss of mercury and ground to less than 104 μm diameter. Additional subsamples were taken for sizing into gravel (more than 2057 μm), sand (between 2057 and 66 μm) and mud (less than 66 μm) fractions. In the early stages of the programme, before freeze drying of samples was used, a further subsample was ground in its wet state for determination of moisture, mass loss on ignition, and Hg before being dried at 110 °C and ground to less than 104 μm for determination of Cu, Pb, Zn, Cd and Mn.

(iii) *Chemical analysis*

Cu, Pb, Zn, Cd and Mn were determined by conventional atomic absorption spectrophotometric methods on portions of dried ground sample decomposed by heating with a 3:1 mixture of nitric acid and perchloric acid. Excess acid was removed by evaporation and the solutions diluted and centrifuged. Hg was determined on separate subsamples. Initially this was by the cold-vapour flameless atomic absorption method described by Head & Nicholson (1973), but it is now determined by the modified technique of Nicholson (1977). Loss of mass on ignition at 450 °C was also determined to give an indication of organic matter content, and at 1050 °C to give an approximate value for carbonate content.

(iv) *Results and discussion*

One of the most important features shown on the geochemical maps of the continental shelf is the relatively high trace element levels which occur seawards of the major estuaries. Coastal samples generally contain higher levels of heavy metals than those from offshore areas and fall within the ranges 5–410 parts Cu/10^6, 5–320 parts Pb/10^6, 20–2240 parts Zn/10^6, 0–3 parts Cd/10^6, 0.01–0.59 part Hg/10^6 and 170–2750 parts Mn/10^6. The maximum values recorded for Cu, Pb and Zn occur off the Tyne estuary, that for Cd is somewhat further south, approaching midway between the Tyne and Tees, while that for Hg is off the Humber estuary. Maximum values for Mn occur in a long strip off the Yorkshire coast and might be derived from terrigenous material weathered from coastal exposures of the clay-ironstones of the Middle Lias. Samples consisting of clean sand with traces of silt, sometimes with quantities of shell debris, collected from the fishing grounds of the Dogger Bank, have very low trace metal contents. Typical values are less than 5 parts Cu and Pb/10^6, 10 parts Zn/10^6, less than 1 part Cd/10^6, less than 0.01 part Hg/10^6 and 120 parts Mn/10^6.

Statistical analysis of the results shows a significant correlation between Hg and the content of material smaller than 66 μm, confirming earlier results by this laboratory (Smith *et al.* 1973) that Hg is strongly associated with fine particulate matter. Cu and Zn were strongly correlated but neither was significantly correlated with amounts of material smaller than 66 μm.

Data for Hg in the Thames estuary study, showing total Hg contents of the sediments ranging from 0.012 to 0.55 part/10^6, have been reported already. Little overall difference in Hg content was found between fresh samples and a collection of samples assembled over the last 45 years by the British Museum (Department of Mineralogy) (Smith *et al.* 1973).

(*b*) *Land area*

(i) *General*

In order to meet the specific objectives of the Institute's programme for the land area of Britain, sampling procedures were required to be as precise as possible, sensitive to changes in the chemical composition of catchment areas, practical and robust. Absolute accuracy is difficult to obtain, particularly in sampling, but an estimate of overall accuracy is required for comparison with other data sets and the relative accuracy should be maintained at a constant level throughout the mapping programme to avoid recording spurious variation in elemental levels.

Several types of sampling media were considered, including rocks, soils and stream sediments. Rocks are unsuitable for a regional survey owing to their limited exposure at surface, the occurrence of areas of deep alteration and weathering particularly in Scotland, the problem of representing heterogeneous assemblages such as the Lewisian or Dalradian by statistically valid sampling models, and the difficulty of obtaining samples from faults and other structures which are often areas of low topography infilled with thick overburden.

Soil sampling presents considerable problems for regional geochemical mapping because of the variation in soil types, the limited soil cover in upland areas, the wide variation of pH and *Eh* in soils, which critically affects the solubility and concentration of metals (Baas Becking *et al.* 1960), and the difficulty of ensuring consistent sampling of specific soil horizons by inexpert sampling teams. Work carried out in collaboration with the Department of Agriculture, Oxford University, however, suggests that soils may be the optimum medium in agricultural areas of England particularly for larger scale geochemical maps. Both rock and soil samples provide information of limited areal extent and large numbers of samples are required, making geochemical mapping based on either of them relatively costly.

The Institute's geochemical atlases are therefore based on stream sediment samples, which have clear advantages in systematic regional mapping. Each sample is considered to approximate to a composite sample of weathering products upstream of the sampling point and hence reflects the concentrations of metals in rocks of the catchment area (Hawkes & Webb 1962). Many studies of the application of stream sediment sampling to exploration geochemistry (see, for example, Webb *et al.* 1968) and environmental geochemistry (see, for example, Thornton & Webb, this symposium; Webb & Howarth, this symposium) have shown that analysis of a portion of the unground, *ca.* 190 μm, fraction of 'grab' samples of stream sediment provides an effective method of broad scale geochemical mapping where individual values are averaged by statistical procedures (Howarth & Lowenstein 1971; Webb & Howarth, this symposium).

These methods, designed for primary broad-scale reconnaissance, are not sufficiently precise and accurate, however, for maps intended to show point source data at a scale of 1:250000. An orientation study directed towards development of more suitable procedures was, therefore, undertaken (Plant 1971). An area of northern Scotland was selected for the study (and for the first series of geochemical atlases) because the low levels of industrial contamination enable information on the natural variation of element levels to be obtained. Furthermore, the hydrological conditions which consist mainly of surface run-off are considerably less complex than in England and Wales where water flow varies from predominantly surface run-off in the Lake District, Wales and southwest England to intergranular aquifer flow in the areas underlain by Carboniferous and Mesozoic successions over south Wales and most of England (Institute of Geological Sciences 1977).

The aim of the research was to develop a general approach rather than a standard method since certain features of the sampling procedures may have to be varied, depending on the area being surveyed.

(ii) *Sampling procedures*

Existing stream sediment sampling procedures were evaluated by investigating the dispersion of elements in natural steam channels (Plant 1971) to identify processes that modify the levels of trace elements relative to those of bed rock and to assist in the development of methods which take account of such effects. An additional aim was to select sampling procedures that reduce sampling error relative to geochemical variation and to determine the optimum sampling interval for identifying regional trends in the geochemistry and local anomalies.

Study of the distribution of trace elements in relation to the size fraction of sediment showed that several elements, including Mo, Cu, Zn, Co, Mn and Fe, are concentrated in the finest fractions of the sediment, particularly over areas of mineralization. The finest fraction that it is practical to collect, however, is material finer than 150 μm (very fine sand, silt, clay and colloids); and over the area mapped to date this material has been shown to include all size fractions in which elements are concentrated. Studies of the speciation of elements in stream sediments carried out in collaboration with M. B. Hayes and B. A. Toms of the Department of Chemistry, Birmingham University, confirmed these results but indicated that the recovery of size fractions by dry screening is not quantitative owing to the agglomeration of fine material to form larger particles which are then screened out in varying amounts. A system of wet screening on site, devised by B. A. Toms, with the use of the minimum amount of water, is now employed routinely to collect the fraction of sediments smaller than 150 μm. Parallel studies (Peacock & Michie 1975) also indicate that wet screened samples of the fraction of stream sediment smaller than 150 μm give improved contrast.

In areas of upland Britain (much of Scotland, Wales, the Lake District and parts of southwest England) elemental levels in stream sediments can be enhanced relative to bedrock because of coprecipitation with hydrous manganic and ferric oxides (Nichol *et al.* 1967) which occurs where reduced, acidic water bearing Fe and Mn from peat flows into streams where the pH is higher and the water is in equilibrium with atmospheric oxygen. Collection of samples containing quantities of these precipitates results in elemental values which may not only be spuriously high but also highly variable.

Studies of natural stream channels in the Scottish Highlands indicate that the problem is most serious in first order tributaries where the proportion of water in the channel which is derived directly from peat is at a maximum. Furthermore, the precipitates are enriched in the top few centimetres of the sediment profile where the pH and *Eh* tend to be higher. The relation between elemental levels and the size of stream was investigated and although samples collected near stream sources contain abundant secondary oxide precipitates, the sampling of higher order streams draining large catchments failed to detect local anomalies associated with mineralization owing to rapid downstream dilution.

Additional sample types on which studies were carried out included heavy mineral concentrates obtained by panning a portion of sediment in the field (Leake & Aucott 1973) and stream and well waters (Ostle *et al.* 1972). Heavy mineral concentrates provide improved contrast for metals such as Pb or Sn that tend to occur in discrete detrital grains which can be recognized by simple optical methods when anomalous levels of trace elements have been identified in the sample. Studies of water sampling indicated that Cu and Pb were normally below the detection limits of the direct atomic absorption spectrophotometric method used, Zn values were highly variable, but values for U provide useful information, particularly in the presence of high levels of dissolved carbonate which favour formation of the highly soluble uranyl carbonate complex.

A minimum sampling density of 1 per 2 km^2 based on second or third order streams sampled immediately above confluences was selected for the standard procedure. In this, the top few centimetres of sediment are removed before sample collection particularly where magnetic/ferric precipitates are observed and the fraction smaller than 150 µm is collected by 'wet' screening in the field. A heavy mineral concentrate is prepared by panning at a proportion of sample sites and a 30 ml water sample is taken at all sites (Plant & Rhind 1974; Institute of Geological Sciences 1978*a*).

(iii) *Conduct of field sampling*

Field parties normally include a proportion of non-professional sample collectors, usually students, and thus care has to be taken lest they obtain samples from sites that differ from the location recorded on the map. Also, they may use non-standard sampling procedures. To reduce these errors, professional staff of the Institute maintain close supervision with a minimum staff : student ratio of 1:5. Students work in pairs and are interchanged on a daily basis to minimize the likelihood of sampling bias arising from the development and use of modified procedures. Each sampling team of twelve is assigned an area which is irregularly shaped, with boundaries that do not follow mapped geology. Hence variation in element levels related to sampling teams can be identified by overlaying sampling areas over plots of the geochemical data.

At each site where a sample is collected the location, local geology and other features of the site are entered on a computer-compatible data card in a format devised by R. J. Howarth & J. Plant for the National Geochemical Data Bank; the location is also plotted on a 1:50000 Ordnance Survey map. Studies carried out by Rachel Williams (personal communication) into the reliability of field data obtained by student parties indicate that large errors may occur in recording national grid references while qualitative information on sites is poorly reproducible. These data are therefore stored only on in-house files while information on sample sites, vegetation, geology and topography for the atlases is digitized from specialist maps.

The pH, conductivity, dissolved carbonate and fluoride contents of stream waters are determined in the field† but it is not always possible to obtain adequate and meaningful data of this type; pH is particularly difficult. Measurement of pH by using papers or liquids was found to be unsatisfactory in the Scottish Highlands and measurements are now made by using a meter with a glass electrode. Since these are fragile and large errors can be made by inexperienced operators, a skilled member of staff performs the determinations. A number of determinations are made on the site to serve as controls in addition to a much larger number made within a few hours of collection on samples taken by field sampling parties.

As discussed later the information on pH and dissolved carbonate, although general, is of use in indicating some of the constraints on the distribution of elements. Information on electrical conductivity and fluoride levels is also of value for interpretation.

Maps of vegetation kindly supplied by the Institute of Terrestrial Ecology are included in the geochemical atlases wherever possible to indicate the distribution of some species of plants for which the pH tolerance range is known and thus provide information on soil pH.

(iv) *Sample preparation and analysis*

In the field or headquarters laboratory, damp sediment samples contained in Kraft paper bags are dried at approximately 95 °C in large electric ovens equipped with fans. Sediments containing appreciable clay-fraction material dry in lumps which are difficult to disaggregate.

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† A full account of the procedures used is given in each of the geochemical atlases (Institute of Geological Sciences 1978*a*, *b*, 1979).

Trials with freeze-drying, now used as a standard procedure for marine sediment samples, produce a friable powder with almost all samples tested, and routine drying by this method is being introduced. An additional advantage of freeze-drying is that no special treatment is required for samples in which Hg is to be determined.

In order to satisfy the analytical requirements of the programme it was necessary to employ rapid, inexpensive, multi-element methods and it was considered that some form of d.c. arc emission spectrographic technique would best fulfil these objectives. Although there have been changes in the instrumentation employed since the programme began over 9 years ago, the d.c. arc emission technique is still regarded as the most appropriate means of providing the required analytical data.

The subsample taken for arc emission analysis is small, only 15 mg being introduced into the electrode, and subsampling is therefore likely to be an important source of error (Gy 1967; Plant 1971). Although the fraction finer than 150 μm employed for this programme is finer than is normally collected for geochemical exploration, it nevertheless contains a heterogeneous mixture of detrital minerals and rock particles, clays, organic materials and precipitates and requires further particle-size reduction.

In the grinding method currently in use, about 15 g of sediment is ball-milled for 30 min. Repeated tests on a variety of samples show that this treatment yields a product with greater than 95% having a particle size of less than 53 μm so that error will be significantly less than for surveys involving analysis of material of coarser size fractions, particularly where this is unground.

In the initial stages of the survey, a spectrographic technique with a Hilger Large Quartz instrument with photographic recording was employed. Element concentrations were estimated by visual comparison of spectral lines from the samples with standard spectra by use of a Jarrell-Ash spectrum-projector comparator.

In 1975 a major change was made in the analytical system and all regional geochemical survey samples were subsequently analysed by using direct reading spectrometry. The spectrometer, a Jarrell-Ash 1.5 m Atomcounter which incorporates forty channels, is on-line to an IBM 1130 computer and options for data output include hard copy from a Friden Flexewriter, lineprinter, card punch, paper tape punch or magnetic tape.

A 100 mg subsample of ignited material smaller than 53 μm is mixed with an equal mass of spectroscopic buffer comprising a 1:1 mixture of pelletable graphite and sodium fluoride containing In, Eu and Pt as internal standards. A 30 mg pellet of the mixture is arced for 99 s at 12.5 A with the use of anode excitation in a jet of argon:oxygen (75:25) to improve stability, to suppress CN band emission and to reduce general background radiation.

The importance of adequately researching interelement effects and introducing appropriate computer correction procedures for direct reading spectrographic analysis is shown in table 1 where apparent levels of Pb are doubled by interference from Mn. The type and magnitude of interferences vary according to the spectral lines used and for different instruments. Calibration of the data obtained by direct reading spectrograph in the Institute's laboratories is performed by polynomial regression on data obtained for synthetic reference materials prepared by a coprecipitated gel technique (Date 1978) after correction by using data from synthetic standards of wide compositional variation, and international standard rocks. The trace elements that are corrected for major element interferences on the basis of data obtained for the synthetic matrix reference materials are shown in table 2.

Relative standard deviation of ten determinations over 5 months is 10% or better for 17

Table 1. Jarrell-Ash 1.5 m Atomcounter: major element interference correction

(Pb 405.7 nm: correction for Mn interference.)

[Mn]	10^6[Pb] uncorrected	10^6[Pb] corrected	10^6[Pb]†
5.2	206	165	140
5.4	61	16	20
5.6	82	34	50
5.6	64	17	50
6.0	54	0	20
6.6	87	23	60
9.5	116	20	30
5.4	86	49	50
5.2	84	50	60
7.9	178	100	80
7.1	76	13	20
15.3	162	31	40
	105	43	52

† Result from atomic absorption spectrophotometry.

Table 2. Direct reading spectrometry: matrix correction

analyte	interfering element	approximate effect
Ga	Mn	—
Ge	Mn	—
Sn	Mn	—
Pb	Mn	—
B	Fe	20 % Fe = 20 parts B/10^6
Zr	Fe	20 % Fe = 200 parts Zr/10^6
V	Ca	—
Mo	Ca	20 % Ca = 30 parts Mo/10^6
Li (2)	Ca	—
Sn	Mg	—

Based in part on A. R. Date and J. S. Coates (personal communication).

elements and 25 % or better for 8 elements at average concentration levels for the sediments. Results obtained from the spectrometer are routinely checked against determinations performed by analytical procedures based on different principles such as atomic absorption spectrophotometry and neutron activation analysis on in-house standard samples.

Until recently, Pb and Zn were determined by atomic absorption spectophotometry on a separate subsample after decomposition with a 3:1 mixture of nitric and perchloric acids. Research by Date and coworkers in 1977, however, enabled both these elements to be brought into the emission spectrometer programme by using the 405.8 nm line for Pb and 334.5 nm line for Zn. A correlation plot of Zn values obtained on a series of samples by atomic absorption spectrophotometry and by direct-reading spectrometry is shown in figure 1.

Sensitivity for U by emission spectrometry is inadequate for the purposes of regional surveying and a delayed neutron method based on that of Amiel (1962) is used for both sediment and stream water samples. The method has a detection limit of about 0.001 part U/10^6 in sediment.

(v) *Error control*

A constant check on errors is necessary to obviate false trends or anomalies on geochemical maps. An example of a false trend for Ba is shown in figure 2, plate 1. A system to monitor error

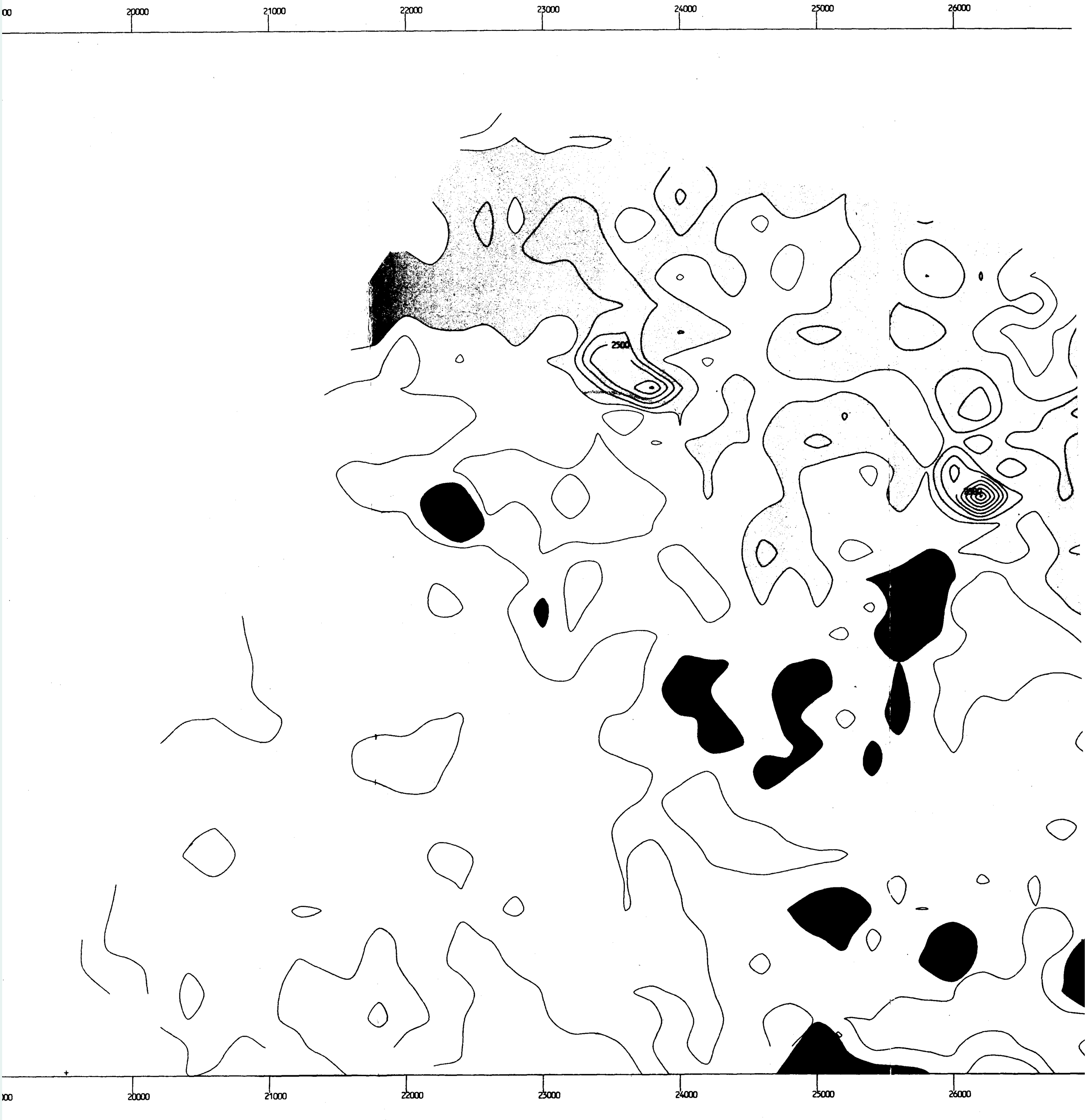
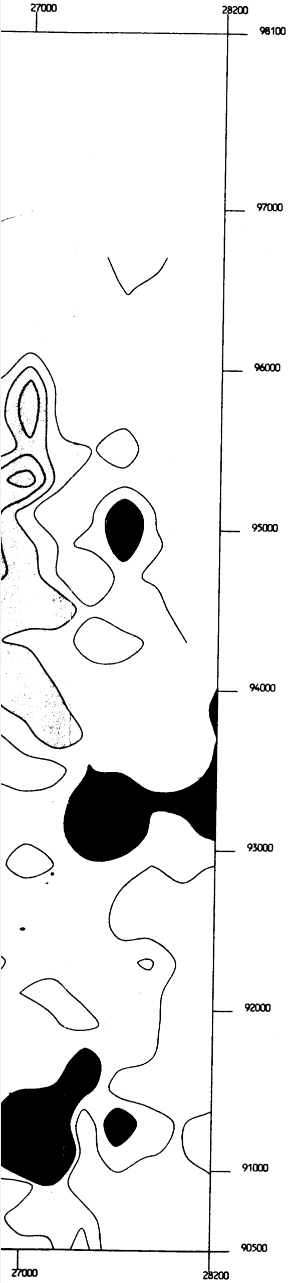


FIGURE 2. An example of systematic error in the geochemical map of Ba in northern Sutherland. Brown, levels of Ba thought to be related to bedrock geochemistry; blue, high levels of Ba related to systematic in sampling or analysis.


27000
28200
98100
97000
96000
95000
94000
93000
92000
91000
90500
27000
28200

high
error

PHILOSOPHICAL TRANSACTIONS —OF— THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

planation of geological signs and colours

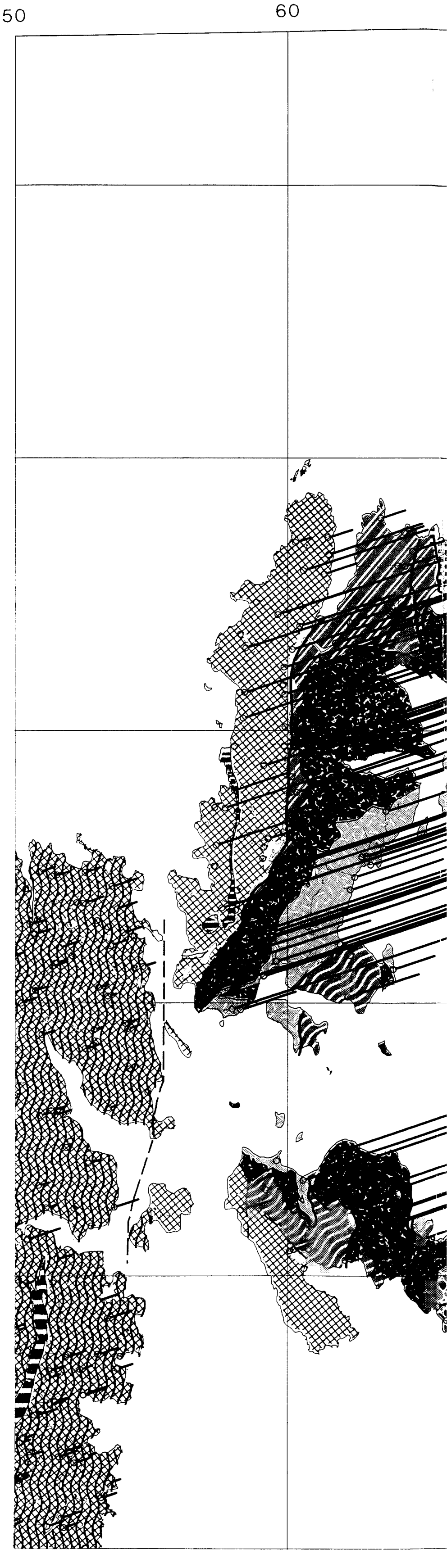
Metamorphic Rocks

Unst-Fetlar Nappe Pile

- ▩ Funzie conglomerate
- ▒ 'Greenstone' (metagabbro)
- ■ Serpentinite
- ▦ Skaw 'granite' (granite-gneiss)
- ≋ Phyllite, hornblende- and graphite-schist etc
- ▨ Schists and flags of Saxa Vord block

Yell, Western Unst and Fetlar and adjacent islands

- ░ Scatsa Division and schists and gneisses of Valla Field (Unst) and Lamb Hoga (Fetlar) blocks and E Yell; ▬ Limestone
- ≋ Yell Sound Division and gneisses of Yell; ▬ Quartzite
- ▩ Permeation belts and vein complexes (overprint)
- - - - - - Major fault
- ——— Thrust



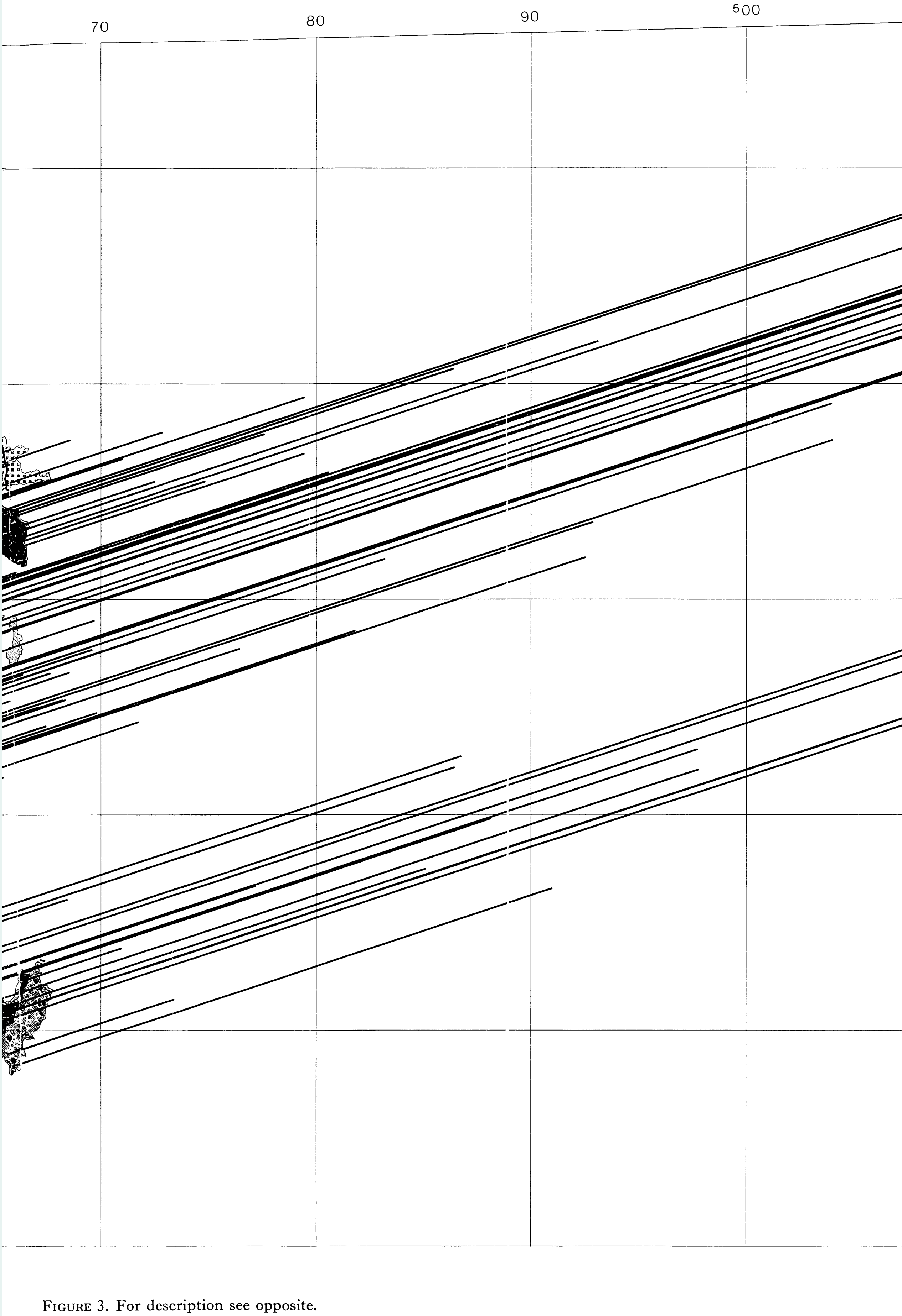
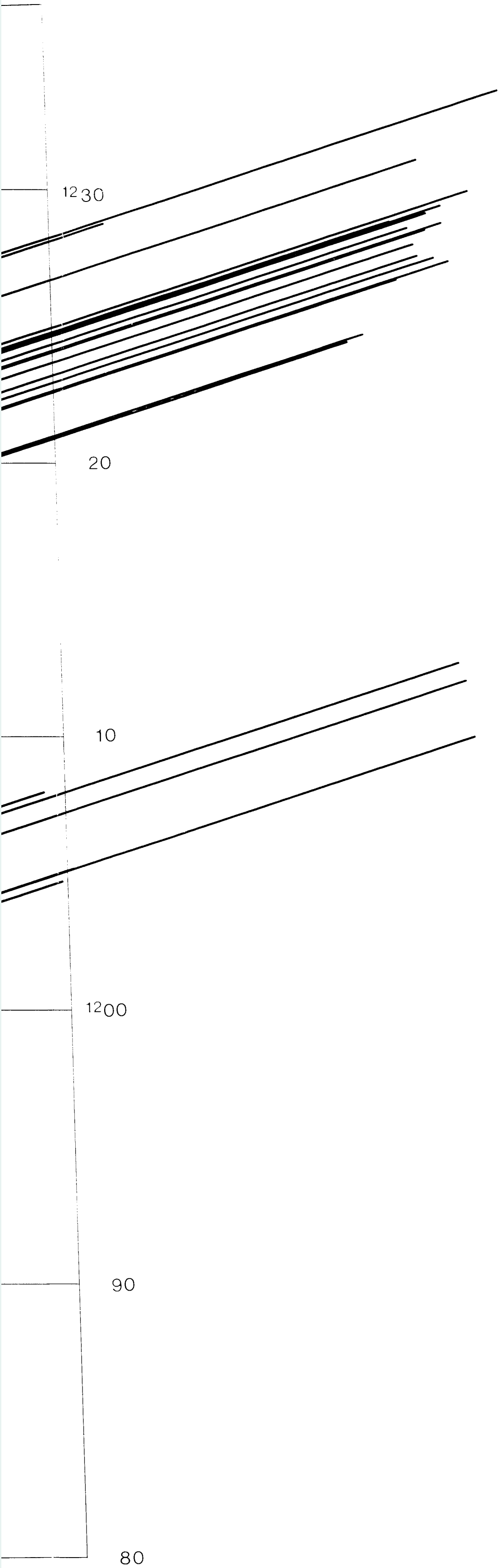


FIGURE 3. For description see opposite.


1230
20
10
1200
90
80

in sampling and analysis is therefore used (Plant *et al.* 1975). Monitoring systematic error in field sampling or analysis is based on a system with randomized sample site numbers (Plant 1973) with standards to monitor analytical error between batches of samples.

This is considered to have advantages over systems where sample numbers are randomized before analysis because error in sample preparation and subsampling is monitored in addition to analytical error. It is also preferred to systems where large numbers of samples are each assigned a field number and different analytical number since renumbering could be associated with considerable error as discussed in §vi.

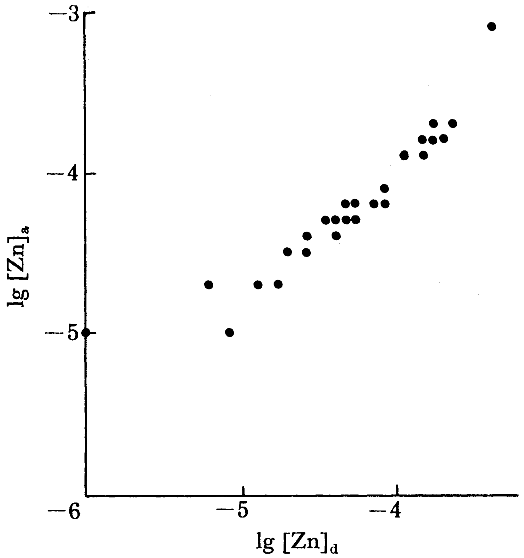


FIGURE 1. Comparison of Zn concentrations obtained by direct reading spectrography, $[Zn]_a$, and atomic absorption spectrophotometry, $[Zn]_d$.

Randomly numbering sample sites is aimed principally at determining within-batch error such as instrument drift or contamination and should be used only as part of a system in which error is monitored between batches with the use of standards. Standard stream sediment samples prepared in-house and rock standards calibrated against international standard materials are used to monitor analytical accuracy. These are randomly numbered and not distinguishable to the analyst. The accuracy of the data for Co, Mn, V, Mo and Ba, which can be determined by instrumental neutron activation analysis (Plant *et al.* 1976), is established by analysis of randomly selected samples by this technique and samples of deionized water are included in batches of water samples to be analysed for U by delayed neutron activation analysis to serve as blanks.

Sampling and analytical precision is monitored by using a procedure based on analysis of variance. Duplicate samples are collected a few metres from the routine samples at

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DESCRIPTION OF PLATE 2

FIGURE 3. Part of the geochemical map for Cr in Shetland from the Institute of Geological Sciences regional geochemical atlas series. The arm scale represents Cr concentration at indicated sites; 1 mm = 40 parts/10^6. The abrupt change in the level of Cr over the northern islands of Shetland would be obscured by smoothing techniques. Map scale 1 : 250000.

approximately 2% of the sites and the between-site variance (geochemical variation) and the within-site variance (total error, including errors in sampling, sample preparation and analysis) are determined by using a single-factor analysis of variance model (Koch & Link 1971). *F* tests are not performed because the data do not satisfy the assumptions required for formal analysis of variance. Furthermore, the test is sensitive to the number of sites duplicated, which varies considerably for different atlases. The mean squares for between-site variance and within-site variance are therefore given as percentages (Bølviken & Sinding-Larsen 1973) and provide a general indication of the reliability of the element distribution maps. The method is preferred to those where only analytical error is calculated since it enables both sampling and analytical error to be estimated and their significance for different geological and surface environments to be assessed. For example, in Orkney high within-site variance for U is related to its low concentration in stream sediment as a result of the high levels of bicarbonate in surface water rather than to a change of analytical precision.

(vi) *Data processing*

Locational information for up to 10^4 sample sites and analytical data for up to 35 elemental determinations for each of the sites are processed each year, making a total of 350000 items of information. An analysis of the sources of typographic error for 2000 early samples taken from Orkney and Shetland was performed by M. D. Forrest & R. T. Mogdridge (personal communication) who showed that the initial error rate associated with recording and card punching of analytical or locational information was approximately 20% (table 3). This confirmed the findings of the experiments of Rachel Williams which demonstrated high levels of error in recording field data. Forrest & Mogdridge also showed that the percentage of locational error could be reduced to less than 1% where sample site locations were entered into computer records by digitizing from maps of sample sites, while the error associated with transcription of analytical data could be eliminated by recording data directly on to a magnetic disk for processing and storage.

TABLE 3. SOURCES OF TYPOGRAPHIC ERROR IN GEOCHEMICAL DATA PROCESSING

(From 2000 samples from Orkney and Shetland.)

	percentage error
(1) recording National Grid Reference	8.9
(2) punching from field data cards	1.2
(3) plotting maps of sample sites	5.2
(4) digitizing sample sites from maps	0.7
(5) punching and sequence error in analytical data	4.0
total	**20.0**

From M. D. Forrest & R. T. Mogdridge (personal communication).

The following system is therefore used. In the field office, sample site locations are plotted daily on stable base plastic 1:50000 Ordnance Survey maps by using both the field copies of the Ordnance Survey maps and the data cards prepared by students. Sample sites for digitizing are plotted in red and sample numbers for error control such as duplicates, which are not digitized, are plotted in green. National grid references recorded on data cards are checked and corrected by the field assistant. Sample sites are digitized at the Experimental Cartography Unit, London, with the use of a high accuracy digitizing table and recorded on to magnetic tape. The digitized data are checked automatically against corrected National Grid References and manually by comparing overlays of computer plotted sample sites with the master plots of sites. Analytical data are transferred directly to magnetic disk, and after manual checks on the results of approximately 1 % of samples which are selected randomly, locational and analytical results are merged. A final check of the data is made before plotting on hard copy by displaying geochemical maps with a c.r.t. display facility. The corrected data set stored on magnetic disk is used for plotting and for statistical analysis.

(vii) *Data presentation and analysis*

Map presentation and statistical analysis have been restricted to preparing interpretations of individual elements in relation to geology, and surface features of relatively small regions rather than performing multivariate statistics of large data sets over the area of Scotland mapped. The data are stored and plotted as point source information and the distribution of each element is shown on separate maps by lines orientated in a particular direction and with a length proportional to the element concentration. The geochemical data are plotted in black over a modern compilation of the geology prepared as a single colour plot. In addition, generalized contour maps and 'geochemical landscapes' prepared by the SACM program and using a very limited amount of averaging are now included in the geochemical atlases to indicate general trends.

The use of proportional line symbols has been criticized by Howarth (1977) and by Meyer *et al.* (1977) on the grounds that assessment of background levels is difficult (Rhind *et al.* 1973), although such symbols are useful for identifying high values.

Proportional point source symbols were adopted as the principal method of presentation by the Institute since contouring or smoothing procedures (which are appropriate for broad scale mapping at scales greater than 1:1M) would have removed local variation from the data and may be too sensitive to sample point distribution at the 1:250000 scale adopted. Further, the choice of parameters such as class intervals or cell size for averaging can affect the patterns represented which will also have different levels of confidence in different areas. Nor is it possible to assess the variance of sample values from maps prepared by techniques such as moving average or contouring; and sample variance, where levels of procedural error are low, provides an indication of the nature of processes operating in the surface environment. Also, it is considered essential to distinguish general increases in background levels from apparent increases produced by averaging a few very high values with several low values.

Sinding-Larsen (1975, 1977) has demonstrated that regression techniques (as well as factor analysis or any method employing the variance–covariance matrix) for estimating the contribution to the trace element value from the environment can be misleading if the elements show different geochemical behaviour within the survey area. Thus while multivariate analysis of trace element data and disease patterns is desirable, the geological and geochemical processes operating in different regions should be borne in mind in selecting data for correlation. As discussed in §vi the Institute's geochemical atlases are prepared by using digitized information for geological and environmental factors. It is therefore possible to create files of data from a particular lithological unit. For example, a file of Cu, Mo, pH and HCO_3^- values over the outcrop of the Old Red Sandstone of Scotland could be prepared.

(viii) *Results and interpretation in relation to biological and medical studies*

The geochemical maps of Scotland precisely reflect known changes in bedrock composition and many geochemical features previously unrecorded. Levels of several elements, including the essential elements Co, Cr and Cu, vary widely. For example, over the Tertiary basalts of Skye and the Lewisian Complex of the Hebrides and northwestern Scotland the levels are relatively high and frequently in the range 30–280 parts Co/10^6, 100–700 parts Cr/10^6 and 25–200 parts Cu/10^6, while over the agricultural areas of Easter Ross-shire, Cromarty and Inverness-shire, which are underlain by Old Red Sandstone, the values for Co and Cu are generally low and in the range 1–10 parts Co/10^6 and 1–15 parts Cu/10^6. An example of variation in the levels of these elements at a local scale occurs in the northern islands of Shetland (figure 3, plate 2) with approximately 50–180 parts Co/10^6, 300–10^4 parts Cr/10^6 and 25–200 parts Cu/10^6, over the island of Unst, and less than 15 parts Co/10^6, 50 parts Cr/10^6 and 10 parts Cu/10^6 over much of the adjacent island of Yell.

Some of the highest levels of the potentially toxic elements Mo (6–20 parts/10^6) and Pb (100–200 parts/10^6) occur over Caithness and southwest Orkney respectively. In addition there are many local anomalies associated with mineralization, for example Mo and Cu in the Lairg area of Sutherland, which were discovered during the course of the regional geochemical mapping programme. U, of which some of the daughter products are of physiological significance, also varies widely from levels below 1 part/10^6 over the Lewisian Complex of northwestern Scotland and the Hebrides to values in the range 20–40 parts/10^6 over the Helmsdale and Cairngorm granites.

Examples of variation in the elemental levels within the mapped geological units of northern Scotland include those over the Caledonian granites and the Old Red Sandstone. Values of crustal abundances lower than average for granites occur over several intrusions which are geochemically similar to the Moine metamorphic assemblage. The Grudie granite in Sutherland, however, is associated with levels of Mo of 10–300 parts/10^6 and Cu of 5–100 parts/10^6; the Laxford granite with levels of Mo up to 53 parts/10^6, and of U of 2–35 parts/10^6; the Helmsdale granite with U values of 4–40 parts/10^6 and the Cairngorm granite with high levels of U, Li and Be. These fundamental geochemical differences, which probably reflect differences in genesis of the intrusions (Simpson *et al.* 1979, Watson & Plant 1979) had not previously been recognized.

Variations in the levels of the first row transition elements, Mo, Pb and U, within the outcrop area of the Old Red Sandstone of Orkney, Caithness and the Moray Firth are related to the palaeogeography of the sedimentary basin and to occurrences of metalliferous mineralization, several of which were discovered during the course of the programme. More detailed interpretations of the principal regional and local features of the geochemistry are given in the published atlases (Institute of Geological Sciences 1978*a*, *b*, 1979).

In favourable circumstances, geochemical mapping is capable of indicating changes in the chemical composition of bedrock which could not be deduced from the geological map. There are many difficulties, however, in relating biological or geochemical activity to the total concentrations indicated on geochemical maps. Some of the inorganic geochemical factors that affect the solubility and availability of trace elements are briefly discussed below since they affect not only biological availability but help in interpreting the nature of geochemical anomalies.

The primary mineral phases in which elements occur are important in determining the rate of release on weathering. For example, Zn and Co may occur in mafic silicates in basic or ultrabasic lithologies, while in sedimentary rocks they occur in organic fractions, with clay minerals, or in Fe oxides or sulphides. Significantly larger amounts of elements may be released into surface water and groundwater over metalliferous mineralization owing to the mineral phases in which the elements are held rather than because of the total concentration in bedrock. For example, high levels of U have been recorded in stream sediment and rock samples over the Cairngorm and Helmsdale granites of northern Scotland. In the Cairngorm granite, U is held in primary minerals such as zircon which are resistant to chemical weathering, while in the Helmsdale intrusion U occurs in a variety of secondary minerals such as autunite and Fe oxides as a result of mineralization (Simpson *et al.* 1979). Markedly higher levels of U occur in stream water over the Helmsdale granite than over Cairngorm (Institute of Geological Sciences 1978*a*). Thus the concentration of elements in stream waters only partly reflects total concentration, which may be enhanced or diminished by mineral reactivity.

Areas of natural poisoning of vegetation over various types of mineralization which include sulphides of Cu, Fe, Ni, Pb and Zn have been reported from Norway (Bølviken & Låg 1977), and anomalous vegetation has been reported over many other such areas (Warren 1972), a feature which is utilized in biogeochemical prospecting.

The pH and *Eh* of surface and groundwaters are important constraints on the solubility and availability of trace elements. A pH range of 4–5 occurs over much of the peat-covered areas of upland Britain. *Eh* is also likely to be low in soil and at bedrock surface since free drainage over impermeable crystalline bedrock is limited and microbiological activity in bogs may consume most of the available oxygen. In contrast to these conditions, large areas of southern Britain are underlain by permeable sedimentary rocks overlain by agricultural soils where pH and *Eh* are likely to be much higher. For example, a study of the geochemistry of groundwaters in British Triassic sandstones (Edmunds & Morgan-Jones 1976) indicates that all groundwaters to a depth of at least 100 m below the water table are oxidizing with pH greater than 7. In general terms, Mn and Fe tend to be more soluble at low pH and *Eh*, Cu and Co are moss soluble in conditions of low pH and high *Eh*, while Mo, Se, V and U tend to be more soluble at high pH and *Eh* (Garrells & Christ 1965; Levinson 1974). Thus over much of upland Britain, Mn and Fe will tend to be more soluble, while the Triassic sandstone may be associated with higher levels o dissolved Mo, V, U, Se, depending on their concentrations in bedrock.

Solubility cannot be defined simply in terms of *Eh* and pH, however, and many other factors such as temperature, total dissolved concentration, and the activity of other dissolved species must be considered. In the case of Mo, for example, its solubility at high pH may be limited by the presence of Pb in solution which may cause precipitation as the secondary mineral wulfenite ($PbMoO_4$). Molybdenum also has reduced mobility in the presence of Fe because of sorption of the hydrous Fe_2O_3 or precipitation of ferrimolybdite (Titley 1963; Hansuld 1967). Sorption on to hydrous Fe and Mn oxides or clays limits the solubility of many trace elements, and secondary phosphate, iron and manganese mineral phases are also important controls of the mobility of trace elements in the surface environment.

Dissolved carbonates, chlorides, sulphates and phosphates affect the speciation and hence the availability of several trace elements but the stability of secondary minerals or complexes is dependent on factors such as pH. Thus the solubility of $ZnCO_3$ is low in conditions of high pH but at or below pH 7, values of 1 part Zn/10^6 can occur in surface or groundwater in response to several factors but particularly dissolved CO_2 (Hem 1970). Levels of dissolved carbonates, sulphates, phosphates and chlorides will be generally low over upland Britain, as reflected in conductivity values in surface waters frequently less than 200 μS. Carbonates and sulphates are important locally, however. The pH, conductivity and dissolved carbonate content of surface waters increase over outcrops of calc silicate, marble and serpentinized basic and ultrabasic rocks (Institute of Geological Sciences 1978*a*), while oxidation of sulphides in black shales or associated with mineralization may release large amounts of sulphate, locally increasing the solubility of Co, Cu or Zn. Levels of major anions are much higher in groundwaters flowing through sedimentary aquifers and at the surface where streams contain a greater proportion of groundwater. Over Orkney, for example, measured conductivity in surface waters is 400–1150 μS with bicarbonate levels of 33–236 μg/l and a pH range of 6.8–8.4 (Institute of Geological Sciences 1978*b*). Thus, although relatively high levels of Cu, Zn, Co and Ni are represented on the geochemical map, it is likely that these will occur predominantly as carbonates or phosphates which will be relatively insoluble in the surface conditions of Orkney. On the other hand, Mo, V and U may be more available than generally over northern Scotland.

Where water supply is predominantly from groundwater aquifers there are particular difficulties in extrapolating from surface geochemistry of bedrock and soils to water composition, especially where this is obtained from deeper levels of the aquifer. A change in the concentration of Ca^{2+}, Na^+, HCO_3^-, SO_2^{4-} and Cl^- has been reported over the Middle Jurassic Limestone aquifer of Lincolnshire by Lamont (1959). The water at outcrop is largely of Ca^{2+}, HCO_3^- type with variable amounts of sulphate; further down dip the water undergoes base exchange to Na^+, HCO_3^- type with decreased sulphate; finally at depth the chloride concentration rises markedly. The variation of trace elements across an oxidation–reduction barrier in the aquifer has been investigated by Edmunds (1973) who demonstrated marked changes in the concentration of major and trace cations in the water from different levels in the aquifer.

These are just a few examples of difficulties in relating geochemical activity directly to total trace element content. There are considerable gaps in knowledge of processes in the surface weathering environment, particularly on the stability and rates of weathering of primary and secondary mineral phases, on the thermodynamic and kinetic factors which affect the reactions, and on the speciation of elements and their synergistic effects in surface waters and soils.

3. Conclusions

Geochemical maps produced by government surveys at scales such as 1:250000 are comparable in their reliability and general application to other types of maps such as geological, geophysical or hydrological maps provided that:

(1) sampling and analytical procedures are carefully designed and error is monitored continuously;

(2) field and laboratory operations are carefully designed and well organized;

(3) a high degree of automation is available to reduce error and minimize costs.

Published geochemical maps should give a full and clear account of all procedures used and include an estimate of the accuracy and precision of sampling and analysis.

Geochemical maps prepared in this way provide the best available source of information on the concentration of elements in bedrock for a wide range of investigations including those of biology, agriculture and epidemiology. Interpretation of the maps to determine the availability of elements to organisms through the medium of soils and groundwater must be carefully considered if associations between elemental levels and disease are to be meaningfully correlated. Information on pH, conductivity and dissolved carbonate of surface waters reported in the geochemical atlases published by the Institute, together with maps of geology, mineralization, vegetation, topography and land use provide general information to assist investigations into the association between environmental geochemistry and health.

The programme of geochemical mapping was initiated by the then Chief Geochemist, Dr S. H. U. Bowie, F.R.S., in 1968, who also directed preparation of the geochemical atlases of Shetland and Orkney. The authors thank him for critically reading the manuscript. Jane Plant also thanks Dr John Camac for encouraging her interest in the association between geochemistry and medicine. The paper is published by permission of the Director, The Institute of Geological Sciences.

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Discussion

R. M. S. Perrin (*Department of Applied Biology, University of Cambridge, U.K.*). A difficulty in the investigations described by Professor Webb and Dr Plant is that the minor element composition of an unfractionated stream sediment will depend much on the relative proportions of coarse detrital grain and finer material, particularly clay minerals, iron oxides and associated organic matter. Even in samples finer than 150 μm, variations in the proportions of these components, brought about by differences in stream velocities at different sampling points, can have important effects on gross chemical compositions. It is not easy, therefore, to see how a unique minor element composition can be assigned to a given stream.

Single measurements of pH in unbuffered streams can be misleading since such waters can vary over 2–3 pH units according to time and season.

Jane Plant and P. J. Moore. Dr Perrin's comment that minor (and trace) element concentrations in undifferentiated stream sediment depend on the relative proportion of course detrital and finer material is unquestionably true and we were aware of this problem during the development of our sampling procedure. We have touched on the matter in this paper (see Sampling Procedures, Land Area) but it is discussed in more detail elsewhere (Plant 1971). In the course of orientation studies in northern Scotland, high density sediment sampling was carried out to investigate the influence of stream channel characteristics on trace element concentration in samples. Trace element levels in sediment finer than 150 μm were found to be more uniform than had been expected and to be consistent with the requirements of regional geochemical mapping; it was also observed that in mineralized areas all size fractions show trace element enrichments. Trace element concentration by coprecipitation with Fe and Mn oxides and by incorporation into organic material that results in enhanced trace element values in samples containing a high proportion of fine material is well known. Conditions for such concentration and for the variability in particle size distribution to which Dr Perrin refers were shown to be favoured by grab sampling from the first order streams; a sampling procedure in which sediment collected from second or third order streams immediately above confluences is slurry screened was developed which overcomes many of the difficulties.

Error control monitoring carried out during routine sampling for geochemical map production shows the relatively small proportion of variance in the data attributable to sampling with the methods developed by the Institute. For example, recent work in the Outer Hebrides has shown that for all the elements studied, less than 2% of the total variation in data for replicate samples taken within a stream length of 20 m is due to sampling. In spite of the unexpectedly high reproducibility of sampling, it is not our intention to establish a unique elemental composition of a given stream but simply of an individual sample location.

We accept that measurement of pH in stream waters is probably of limited value and draw attention to this in our paper. Nevertheless, since the data can be conveniently and inexpensively acquired during the field programme we consider it to be worthwhile, since it provides a general indication of regional trends. Apart from changes in geology, the greatest cause of pH variation is probably climatic, with dilution due to rainfall having the greatest single effect. The fact that sample collection takes place with student help, and consequently during 3 months in the summer, tends to reduce this effect. We have not ourselves observed variations as high as 2–3 pH units at a single site and believe that this represents an extreme value, the probability of occurrence of which is reduced by our method of operation. Resampling of randomly selected sites at weekly intervals has yielded results for pH values for individual locations varying within 0.1 pH unit, representing a higher degree of reproducibility than had been expected. Finally, correlations between bedrock geochemistry and the trace element content of surface waters are generally in accord with the observed pH data.

J. S. Webb and R. J. Howarth. In reply to Dr Perrin's question, a clear distinction must be drawn between the objectives of the Institute of Geological Sciences geochemical reconnaissance and those of Imperial College. The former are aimed at providing *point source* data at 1:250000 and the latter aims at delineating broad-scale *patterns* at 1:1 M to 1:2 M wherein to concentrate more detailed studies. Our methodology was therefore constructed to secure the maximum cost-effective balance between rapid sampling and analytical treatments coupled with statistical processing to reduce sampling and analytical noise, while at the same time producing relatively reliable, useful spatial patterns in the geographical distribution of the elements. In this context, each cell in the Imperial College maps is the result of moving average smoothing of, on average, the data obtained on 20 samples resulting in a mean precision of between 10 and 16% per cell for the majority of elements. Subsequent follow-up over the past 5 years has demonstrated the validity of the patterns disclosed. Turning to pH, prior trial surveys over some 7000 km^2 indicated that, while useful in secondary follow-up phases, pH measurements did not contribute materially to interpretation of the primary broad-scale patterns with which we were concerned.

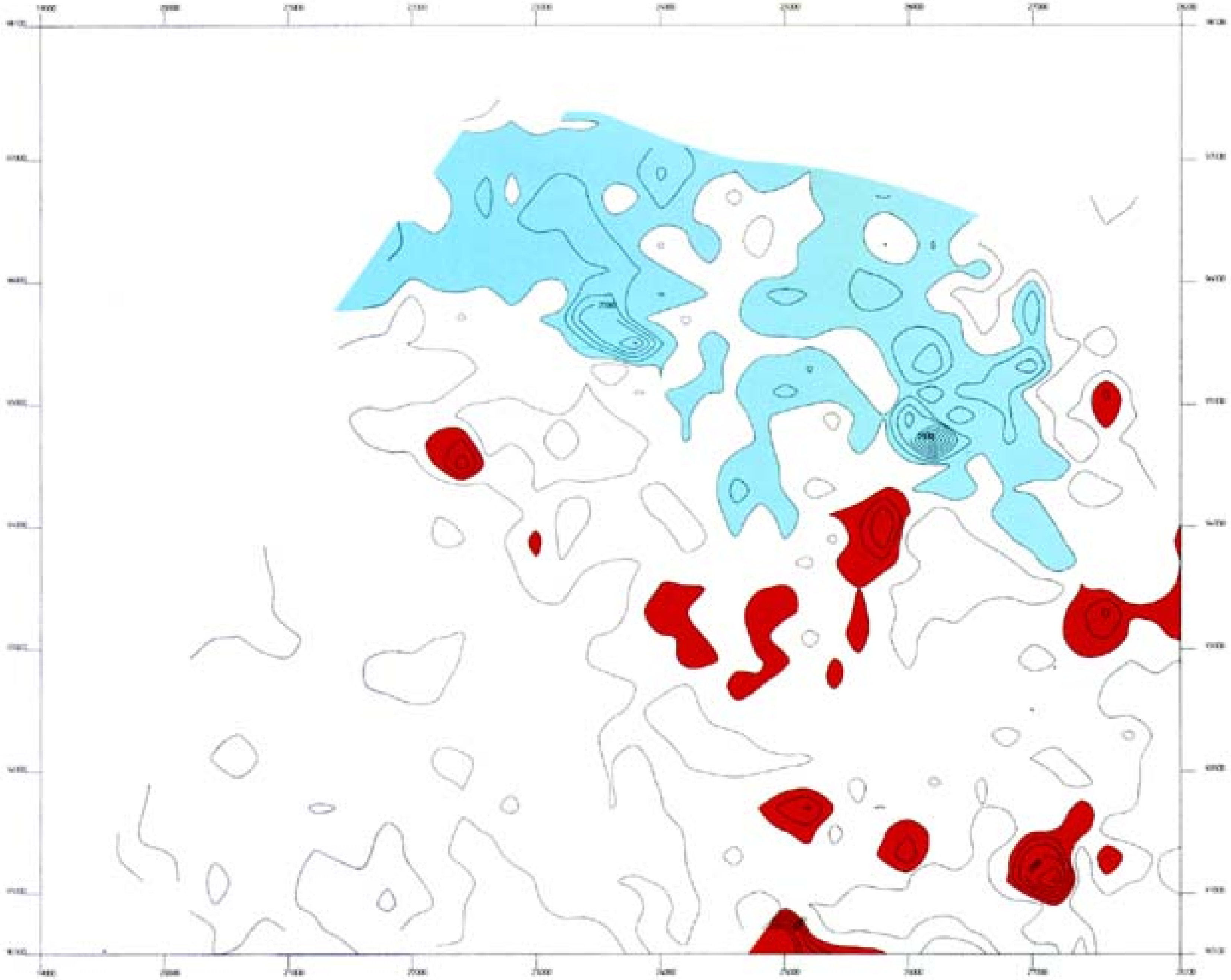
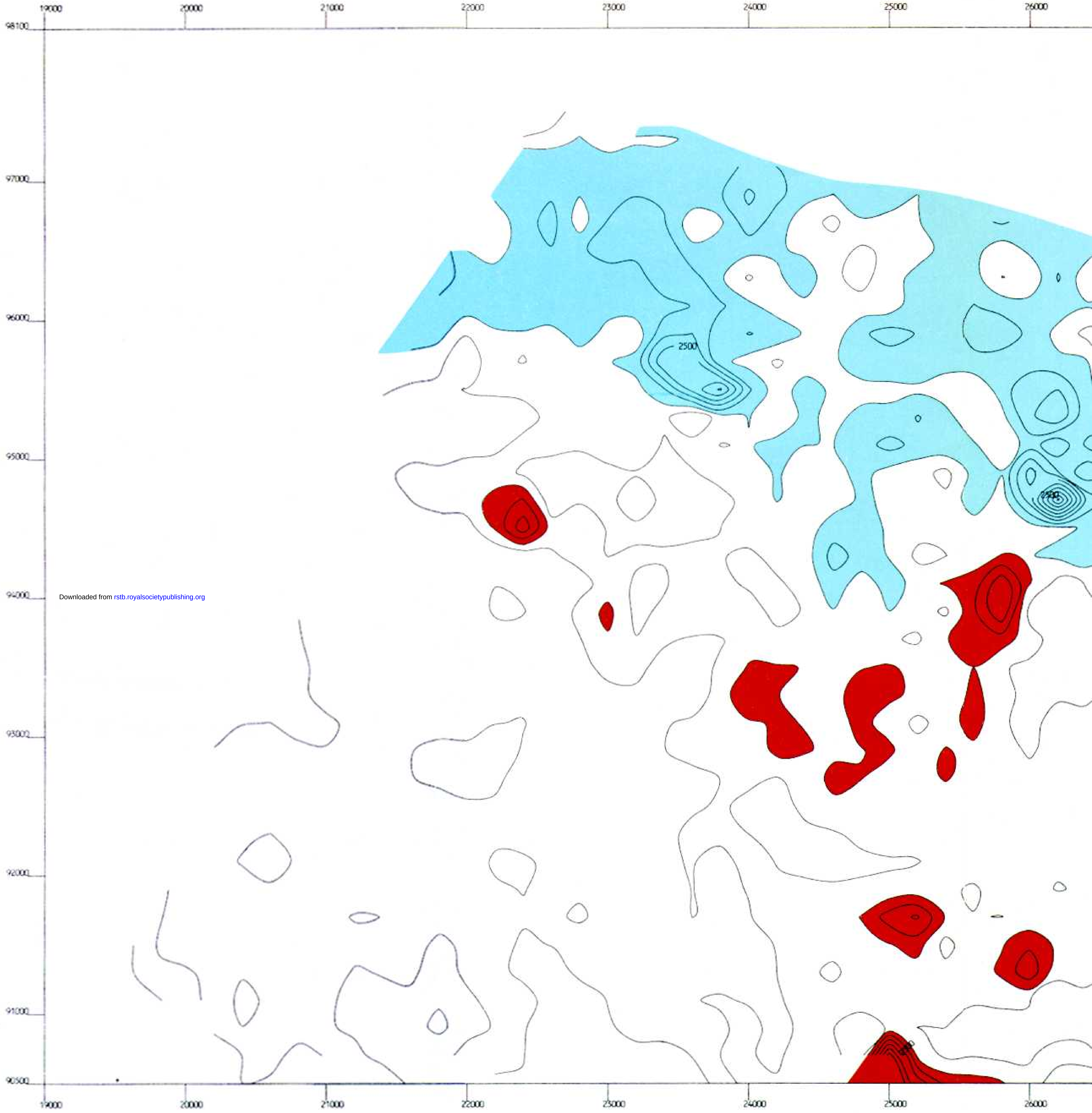


FIGURE 2. An example of systematic error in the geochemical map of Ba in northern Sutherland. Brown, high levels of Ba thought to be related to bedrock geochemistry; blue, high levels of Ba related to systematic error in sampling or analysis.



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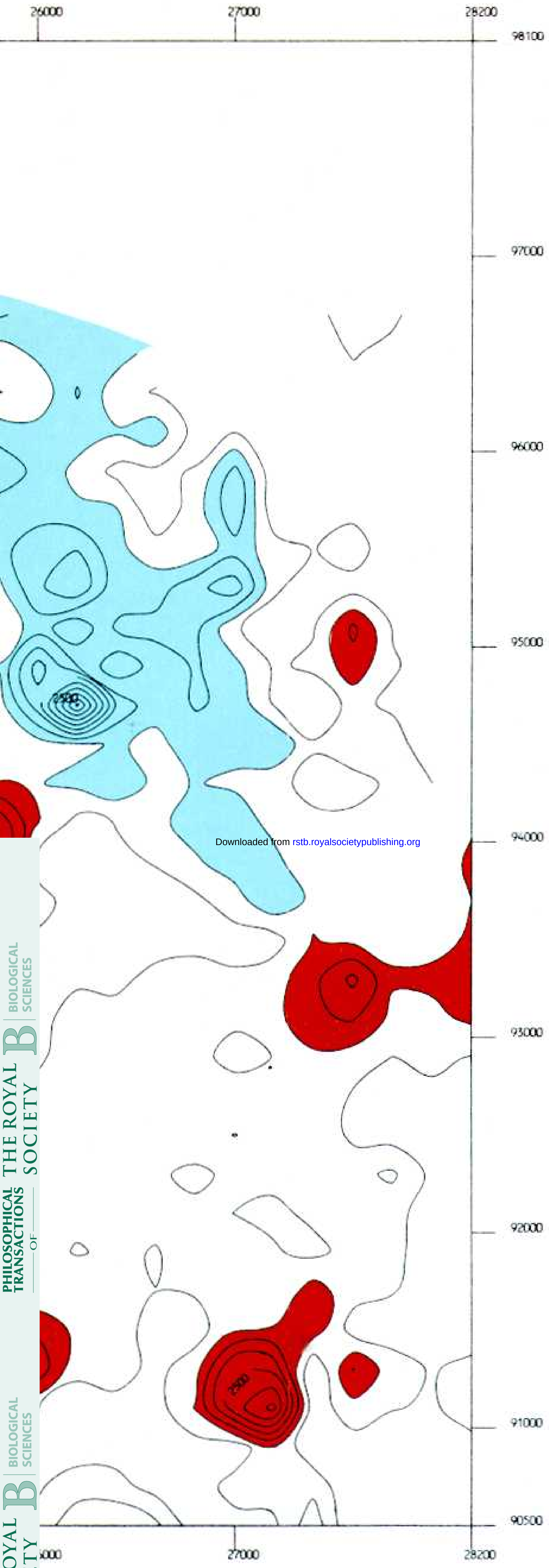


rland. Brown, high
to systematic error

Explanation of geological signs and colours

Metamorphic Rocks

Unst-Fetlar Nappe Pile

▨	Funzie conglomerate
▨	'Greenstone' (metagabbro)
▨	Serpentinite
▨	Skaw 'granite' (granite-gneiss)
▨	Phyllite, hornblende- and graphite-schist etc
▨	Schists and flags of Saxa Vord block

Yell, Western Unst and Fetlar and adjacent islands

▨	Limestone Scatsa Division and schists and gneisses of Valla Field (Unst) and Lamb Hoga (Fetlar) blocks and E Yell
▨	Quartzite Yell Sound Division and gneisses of Yell
▨	Permeation belts and vein complexes (overprint)
- - - -	Major fault
——	Thrust

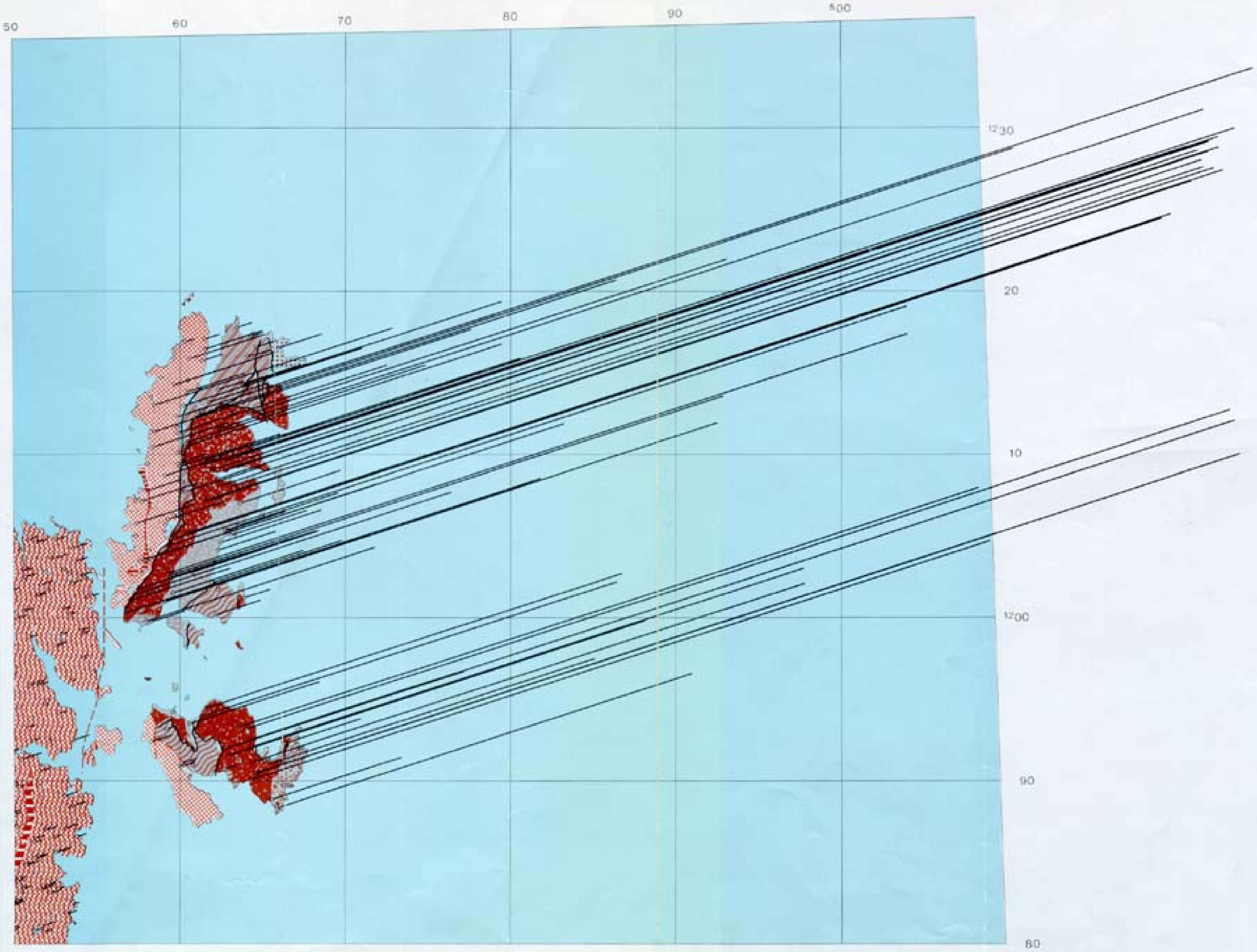


FIGURE 3. For description see opposite.

Explanation of geological signs and colours

Metamorphic Rocks

Unst-Fetlar Nappe Pile

▨ Funzie conglomerate

▨ 'Greenstone' (metagabbro)

▨ Serpentinite

▨ Skaw 'granite' (granite-gneiss)

▨ Phyllite, hornblende- and graphite-schist etc

▨ Schists and flags of Saxa Vord block

Yell, Western Unst and Fetlar and adjacent islands

▨ Limestone

▨ Scatsa Division and schists and gneisses of Valla Field (Unst) and Lamb Hoga (Fetlar) blocks and E Yell

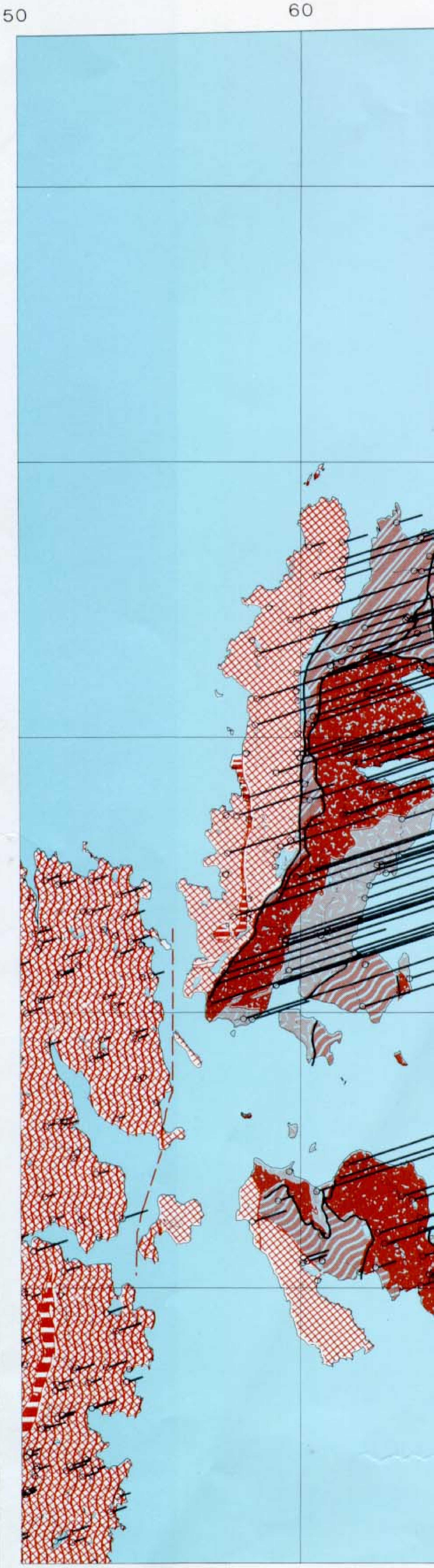
▨ Quartzite

▨ Yell Sound Division and gneisses of Yell

▨ Permeation belts and vein complexes (overprint)

– – – – – Major fault

——— Thrust



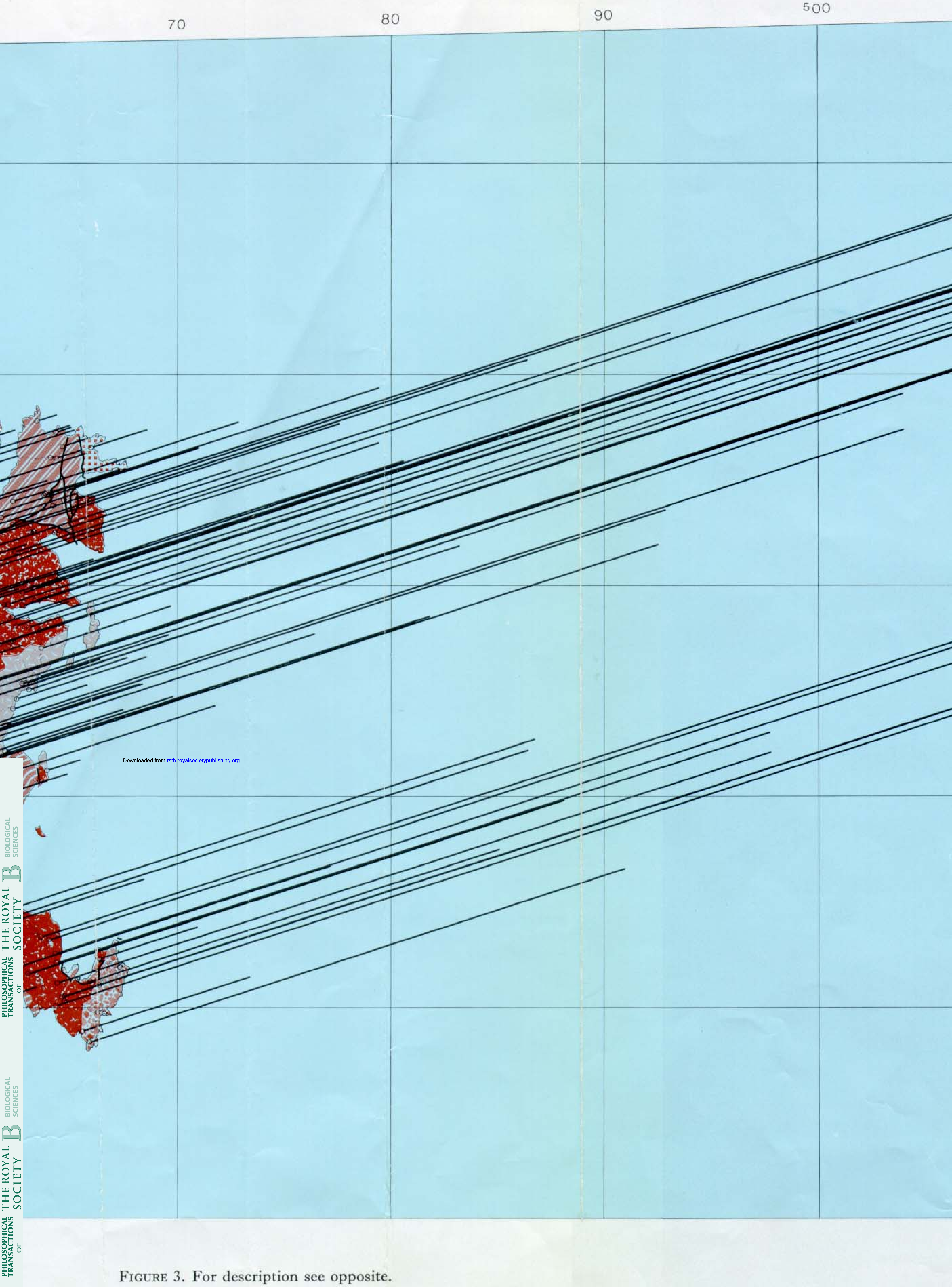
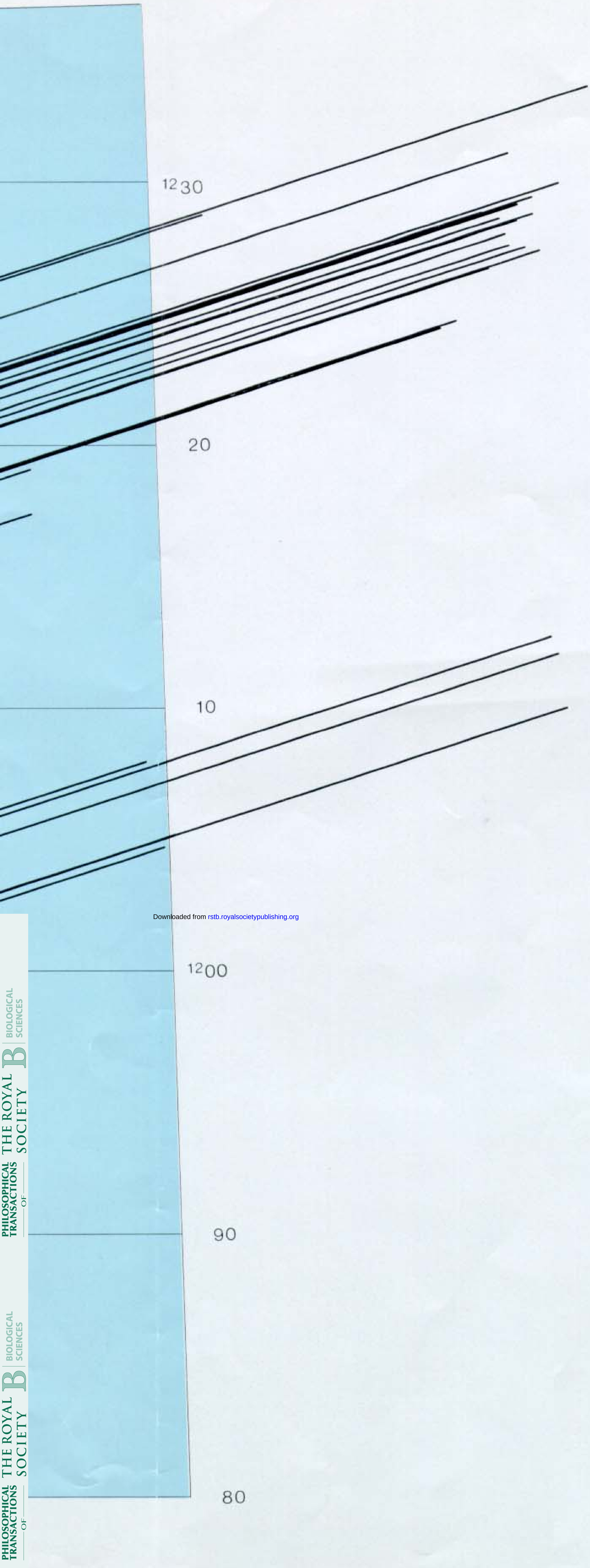


FIGURE 3. For description see opposite.



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