A global geochemical database

for environmental and resource management

Final Report
of IGCP Project 259

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A GLOBAL GEOCHEMICAL DATABASE

FOR ENVIRONMENTAL AND RESOURCE MANAGEMENT

Recommendations for International Geochemical Mapping
Final Report of IGCP Project 259

by
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Preface

“Prevention is better than cure” has been the *leitmotiv* of UNESCO, since its creation, in addressing world problems: prevention through education at all levels and in all sectors, the advancement of science and its applications, cultural development and adequate information. Whether in facing wars, conflicts or in coping with hazards, natural and technological in origin, UNESCO has constantly favoured an educational, scientific and cultural approach that sees anticipation as the only possible solution. It is the only possible cost-effective way of dealing with potential risks and disasters. It is of vital importance that the world community takes the long-term view and learns to be proactive rather than reactive.

Because of the growing demands on mineral and energy resources, water, soils and materials, problems of pollution and waste disposal, on a scale never seen before, and the rise of megacities and human settlements vulnerable to natural and anthropogenic hazards, we require more knowledge of the structure, composition and dynamics of the earth’s crust and of effects upon human life-support systems. A better understanding of natural physical and chemical fluctuations influencing the environment is important in order to elucidate the role of the lithosphere in global change.

There is now a general awareness among policy-makers, planners and the public at large that the environment is inextricably interlinked with economic development and that the present environmental degradation could threaten our very survival. Fortunately, there also seems to be a widespread political will to translate these concerns into action necessary to bring about “sustainable and environmentally sound development”, as advocated in the Brundtland Report of 1987.

In this light, and in the context of follow-up to the 1992 United Nations Conference on Environment and Development (UNCED) and its Agenda 21, UNESCO’s scientific activities are focussing on environmental and developmental issues. This includes work in the earth sciences, notably through the International Geological Correlation Programme (IGCP), a joint activity of UNESCO and the International Union of Geological Sciences (IUGS). This programme contributes to the advancement of knowledge of earth processes and earth resources and to the mutual understanding of the related problems, both scientific and social, among the family of nations.

This particular book, developed as part of the IGCP, is an excellent example of how the earth sciences, and notably geochemistry, contribute to the scientific knowledge required to achieve sustainable development. Its recommendations for a global geochemical database need to be accomodated within any future plans pertaining to the good husbandry and housekeeping of this planet’s environment and resources. This report demonstrates that earth scientists are essential members of the team required to respond to the challenges of “global change”.

We owe thanks to Arthur G. Darnley and his co-authors for writing this book and we very much appreciate the support offered by the Royal Society, various geological survey organizations and national academies, the International Atomic Energy Agency and especially IUGS.

At the present time, we do not have sufficient knowledge or data to be able to assess or predict with any accuracy the implications of human actions on the environment and on our resources. Our reactions to these problems and our feelings about them are defined by our education and our culture. What is needed is some strategy to look into our attitudes and to create some sort of solidarity on a global scale. We hope that the “glue” that can bring about this solidarity and create a partnership of mutual responsibilities is common concern about “global change”. We trust that this book will be a contribution towards that process.

F. Wolfgang Eder
Director, Division of Earth Sciences, UNESCO

Vladislav Babuška
Secretary, IGCP

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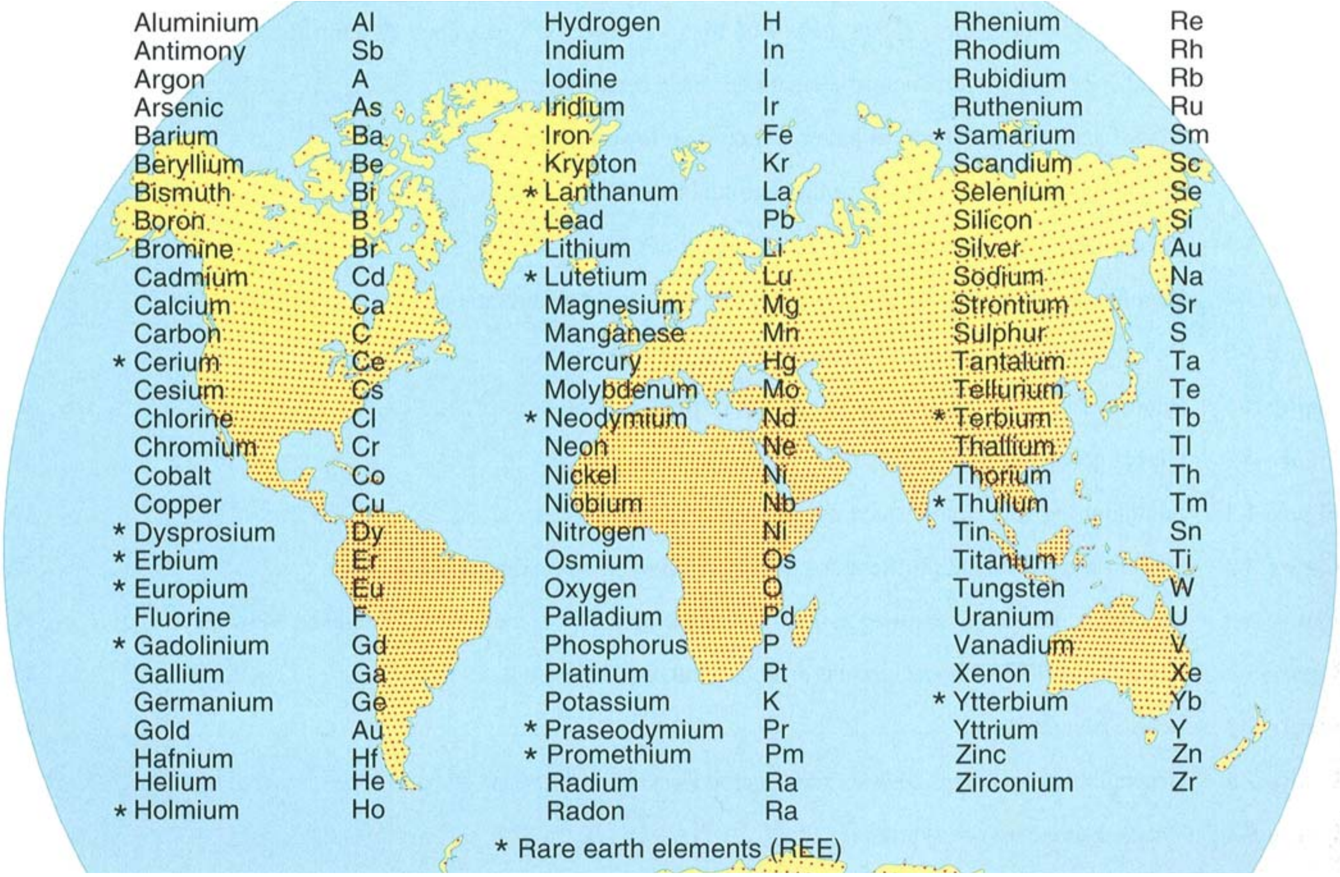
NATURALLY OCCURRING ELEMENTS IN THE EARTH’S CRUST

Constituents of rock, soil, air, water and living matter



Aluminium	Al
Antimony	Sb
Argon	A
Arsenic	As
Barium	Ba
Beryllium	Be
Bismuth	Bi
Boron	B
Bromine	Br
Cadmium	Cd
Calcium	Ca
Carbon	C
* Cerium	Ce
Cesium	Cs
Chlorine	Cl
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Copper	Cu
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Gallium	Ga
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* Holmium	Ho
Hydrogen	H
Indium	In
Iodine	I
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Iron	Fe
Krypton	Kr
* Lanthanum	La
Lead	Pb
Lithium	Li
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Magnesium	Mg
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Mercury	Hg
Molybdenum	Mo
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Neon	Ne
Nickel	Ni
Niobium	Nb
Nitrogen	N
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Potassium	K
* Praseodymium	Pr
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Radium	Ra
Radon	Ra
Rhenium	Re
Rhodium	Rh
Rubidium	Rb
Ruthenium	Ru
* Samarium	Sm
Scandium	Sc
Selenium	Se
Silicon	Si
Silver	Au
Sodium	Na
Strontium	Sr
Sulphur	S
Tantalum	Ta
Tellurium	Te
* Terbium	Tb
Thallium	Tl
Thorium	Th
* Thulium	Tm
Tin	Sn
Titanium	Ti
Tungsten	W
Uranium	U
Vanadium	V
Xenon	Xe
* Ytterbium	Yb
Yttrium	Y
Zinc	Zn
Zirconium	Zr

* Rare earth elements (REE)

Everything in and on the earth - mineral, animal and vegetable - is made from one, or generally some combination of, the chemical elements listed above. Everything that is grown, or made, depends upon the availability of the appropriate elements. The existence, quality and survival of life depends upon the availability of elements in the correct proportions and combinations.

Because natural processes and human activities are continuously modifying the chemical composition of our environment, it is important to determine the present abundance and spatial distribution of the elements across the Earth’s surface in a much more systematic manner than has been attempted hitherto.

This map of the world shows the centres of 5000 equal-area cells which are proposed as the basis for the global geochemical reference network discussed in this report.

1 Executive Summary

1.1 General

Research conducted since 1988 as part of the International Geochemical Mapping (IGM) project has confirmed that the presently available data concerning the geochemical composition of the Earth's surface are substantially incomplete and internally inconsistent. Many of the older data sets have serious deficiencies and do not meet basic requirements for establishing the range of natural geochemical background values. As a result of natural geological and environmental processes, element abundances in natural materials can vary by several orders of magnitude within short distances. These variations are inadequately documented and their existence is often overlooked in the setting of public policy.

A high quality geochemical database is pertinent to a wide range of investigations in the earth and life sciences, and should be considered as an essential component of environmental knowledge. Detailed information about the natural variability of the geochemical background is pertinent to administrative and legal issues as much as to scientific research. Sustainable long-term management of environmental and mineral resources is dependant upon a comprehensive and reliable database. The International Geosphere-Biosphere Program on Global Change requires information on current conditions. Important aspects of change cannot be measured, or their consequences anticipated, unless the present composition of the earth's surface materials is known. To quote a recent Global Change Report (IGBP, 1992),

> *"The availability of data and how they will be managed are two critical facets of future global change research. Global science is data-limited, and therefore new efforts must be engaged which foster the development and validation of global data sets."*

The International Geochemical Mapping project, which was endorsed in 1988 as a contribution to the IGBP (IGBP, 1989), is a multi-stage project established to consider how best to provide quantitative data to portray the geochemical diversity of the earth's land surface.

Participants in IGCP 259 have undertaken a comprehensive review of methods of regional and national geochemical mapping and examined the results obtained. Many problems have been identified and a variety of solutions discussed. Field and laboratory research has been carried out. The resulting recommendations are contained in this report. They are directed towards geochemists and those institutions which have a mandate for providing an earth science and/or environmental database.

The recommendations stem from the conviction that, since geochemical phenomena extend across national borders, and the related information base has multi-purpose, multi-national applications, it is logical, desirable and advantageous to:

(a) establish a common primary database at an international level, and
(b) provide a framework for the adoption of standardized methods and reference materials for detailed regional or national mapping.

These will provide a recognized quantitative base for more specialized local investigations to answer particular environmental and economic problems concerning animal and human health, soil fertility, agriculture, forestry, water supply and irrigation, waste disposal, mineral exploration and mining, industrial pollution and land-use in general.

The detailed recommendations which have been prepared relate to the establishment of a global network of geochemical reference samples; sample collection and preparation specifications; analytical requirements and standards; gamma radiation methods applicable to natural and man-made radioelements; and data management procedures. An appendix contains information to assist readers in developing countries who may not have easy access to supplementary technical literature. Implementation of these recommendations will make it possible to assemble geochemical baseline data for all non-gaseous elements on a systematic global basis. A world geochemical atlas will be one of many possible products which can be derived from these data. The authors of this report believe that a Global Geochemical Database is a necessary and exigent investment for mankind. The cost of establishing the proposed reference network is estimated to be in the range of US$300-400 million, about equal to the cost of launching one NASA Space Shuttle flight.

1.2 Summary of principal recommendations

The authors of this report have identified the following basic requirements as prerequisites for a global geochemical database of permanent value:

- commonly available representative sample media, collected in a standardized manner;
- continuity of data across different types of landscape;
- adequate quantities of the designated sample media for future reference and research requirements;

- analytical data for all elements of environmental or economic significance;
- the lowest possible detection limits for all elements;
- determination of the total amount of each element present, and
- tight quality control at every stage of the process.

The ensuing recommendations have been prepared in order to meet the above requirements in the most practical ways possible. They are presented under six headings.

1.2.1. A global reference network

In order to begin systematic international geochemical mapping it is necessary to establish a primary global geochemical reference network (GRN), analogous to a geodetic grid. Wide-spaced sampling is required over the entire land surface, including regions already surveyed and regions where there is low probability of any geochemical mapping being carried out in the near future. The samples collected will serve as analytical reference materials, so strict procedures must be followed, and adequate quantities must be obtained and retained.

1.2.1.1 Sampling details

(1) the primary reference network will be based on approximately 5000 160 × 160 km grid cells distributed over the land surface (maps showing cell boundaries will be supplied by the international coordinators);

(2) sample sites should be located in several (minimum of 5, 8 are preferred) 20 × 20 or 40 × 40 km subcells within each 160 km cell to permit the application of statistical analysis of variance techniques; access and cost considerations will determine whether the subcells are randomly selected along one or two sampling profiles or road corridors, or randomly distributed in any part of a 160 km cell; in undeveloped regions helicopter-borne sampling profiles are recommended;

(3) several materials are to be sampled from within each cell:

- A_{25} regolith on residual and alluvial surfaces (see Sections 3.2 and 4.5 for further details)
- stream or lake sediment
- C horizon regolith; collection of deep *alluvial* sediment is **optional**
- surface humus, if present
- water, if present

(4) stream sediment samples should be from drainage basins not exceeding 100 km^2; overbank sediment should be taken from an adjacent site;

(5) each sample of each medium at each of the subcell sites should be a composite of a minimum of 5 subsamples; this composite material must be thoroughly homogenized;

(6) floodplain sediment should be taken from large basins, between 1000 km^2 and 6000 km^2 in area; and

(7) gamma ray spectrometer readings should be taken at each site for *in situ* radioelement determination; the acquisition of carborne or airborne gamma ray spectrometry in transit between sample collection sites is recommended to establish a linked data network (see Chapter 7).

1.2.1.2 Sample quantities

(8) sufficient material should be collected to provide, from each cell, 10 l of humus, if present, and 5 kg of < 0.18 mm fraction of sediment and each type of regolith sample;

(9) a bulk A_{25} regolith sample and < 2 mm regolith size fraction should be retained separately (2 kg each) for radiometric and agricultural reference respectively;

(10) if surface water is present, three separate samples are required, about 300 ml in total,

- unacidified, unfiltered, for anion determination
- unfiltered, acid digested for total cations
- filtered (45 micron), acidified, to provide "dissolved" cations.

1.2.1.3 Analytical arrangements

(11) Instructions will be provided by the project co-ordinators concerning which international reference analysis laboratories will receive the samples. A cell-composite sample must be prepared (with equal weights from each sampling site) for each media type within each cell, retaining a minimum of 50 g from each individual site for separate analysis at a later date. Fifty grams of each cell-composite should be sent immediately to the participating international reference laboratories. The bulk of each composite sample should be retained in the country or region of origin in order to provide a range of secondary Standard Reference Materials to standardize future geochemical work in the area. Individual samples from within each cell of the reference network should be analysed at the earliest opportunity.

1.2.2 Field methods for regional surveys

The principal demand for systematic geochemical data collection is at the regional and/or national level. In general, a much greater data density is required than can be provided as part of a global reference network. Thus, national or regional agencies, using methods selected by them, will continue to be the producers of most of the world's geochemical data. It is strongly recommended that the detailed data they collect should be tied into, and be compatible with, the global reference network data, so that data at any level of detail may be compiled and/or compared across organizational and political boundaries. Data collected for detailed national or regional surveys should be compatible, regarding methods and spatial overlap, with those collected as part of the reference network. Therefore, this report provides recommendations relating to the conduct of these more detailed surveys since these should provide the major part of the future global geochemical database.

1.2.2.1 Sample collection:

(1) regional and national mapping should be performed according to internationally compatible standards;
(2) at least one sampling procedure should be applicable and used consistently in any given geographic area, from global to regional scales;
(3) stream sediment samples from tributary drainages are the preferred sample medium, complemented by regolith samples;
(4) water should be sampled in conjunction with stream sediments wherever possible;
(5) if stream sediments cannot be collected, acceptable substitutes are regolith, till or lake sediment;
(6) where a change in landscape requires a change in sample media, sample media collected in neighbouring blocks must overlap to allow comparison of data;
(7) stream sediment catchment basins should be not more than 100 km^2;
(8) analyses should be undertaken on composites of 5 or more subsamples;
(9) duplicate samples should be obtained from at least 3 per cent of sites;
(10) systematic labelling and documentation is essential.

1.2.2.2 Sample preparation:

(11) contamination must be avoided in sample collection, preparation and storage by appropriate choice of tools, equipment and containers;
(12) wet or dry sieving may be employed;
(13) upper limit of drainage sediment grain size fraction analysed should be in the range of 0.18 to 0.10 mm;
(14) a minimum of 100 g of the sieved fraction is required;
(15) non-stream sediment samples should be reduced to < 0.1 mm prior to analysis;
(16) sample material not required for immediate analysis should be archived for future use, in contaminant-free permanent containers;
(17) systematic labelling and documentation is essential.

1.2.3 Geoanalytical requirements

The analytical requirements for the purpose of producing internationally comparable geochemical baseline data are as follows.

(1) Given the many applications of baseline data, a comprehensive multi-element approach is essential. Analytical requirements are considered in two categories,
  (a) for the global geochemical reference network (GRN);
  (b) national or regional surveys conducted by national or international organizations.

(2) Samples collected as part of the GRN should ultimately provide abundance data for 78 elements, i.e., most elements in the periodic table, using methods with limits of detection significantly below presently estimated crustal abundances. Abundance data are not required for the following: H, O; inert gases other than Rn; Tc, Pm, Po, At, Fr, Ac and Pa.

(3) Analytical requirements for national or regional surveys must be fully compatible with those for the GRN. Where possible identical methods should be used, but alternative multi-element schemes based on the techniques of XRF, ICP-AES, NAA etc. can be employed as long as the criteria for precision and accuracy are met. In order to portray the spatial distribution of elements as completely as possible, detection limits must be as low as possible.

(4) A proposal is made for a standard list of elements to be determined; elements are classed into List 1 (51 elements) and List 2 (20 elements) (see Fig. 6-1); Ru, Rh, Re, Os and Ir require the establishment of satisfactory methods and detection limits; Ra and Rn require radiometric methods.

(5) For national surveys, if analytical facilities are insufficient to cover all List 1 elements initially, missing data should be added at a later date. List 2 is of lower priority, but potentially important.

(6) For the purpose of establishing reproducible baseline data of permanent value, analytical methods should be employed which provide the total concentration of each element present. Sample decomposition, where required, must be total.

(7) Partial decomposition (partial extraction) methods have many variants in different laboratories and are difficult to standardize, so they are NOT recommended for any data that may be used for international compilation or correlation.

(8) With respect to national and regional surveys, it is recommended that if more than 20% of the reportable values for any element determined fall below the limit of detection, the results for that element should be considered as unsatisfactory and alternative methods considered.

(9) Strict quality control, through the use of appropriate primary and secondary Standard Reference Materials (SRMs) is essential, and the manner in which SRMs have been used and the resulting quality control statistics must be reported with each data set.

(10) The Chinese series GSD, GSS and the Canadian STSD standard samples are recommended to be used as primary SRMs in international geochemical mapping. For national surveys, primary and secondary SRMs should be used to monitor the analytical accuracy: primary SRMs to monitor the international or interlaboratory bias, and secondary SRMs to monitor the routine between-batch drift within a laboratory.

(11) Radioelements are to be determined by gamma ray spectrometry, according to the procedures recommended in Chapter 7.

(12) Recommendations are made in Chapter 6 concerning arrangements for the analysis of global reference network samples by laboratories to be designated.

1.2.4 Radioelement mapping

1.2.4.1 General:

(1) radioactive elements, both naturally occurring isotopes and anthropogenic products cause particular public concern and their spatial distribution should therefore form part of a comprehensive geochemical database;

(2) gamma ray spectrometry enables the abundance of natural and man-made radioactive elements to be determined in a laboratory, *in situ*, or from a vehicle or aircraft;
(3) an aircraft can provide a continuous quantitative profile of radioelement abundance over any type of land surface;
(4) flight-line spacing can be varied according to the sampling density required;
(5) airborne data may be used to provide an inter- and trans-continental Th reference datum to assist in levelling geochemical maps from geographically diverse regions;
(6) methodologies published by the International Atomic Energy Agency should be followed.

1.2.4.2 Use of existing data:

(7) countries should make an inventory of all airborne and carborne gamma ray spectrometric surveys carried out since 1970;
(8) if necessary, arrangements should be made through the IAEA to establish radiometric calibration facilities;
(9) if necessary, a back-calibration exercise should be carried out to allow the preparation of quantitative maps;
(10) for environmental health radiation monitoring purposes, a map of air dose rate (Gy s^{-1}) or effective dose equivalent (mSv a^{-1}), should be produced;
(11) where sufficient data are available, they should be used to prepare an appropriate grid suitable for the production of a regional or national atlas and ultimately a radioelement map of the world.

1.2.4.3 Collection of new data:

(12) many past radiometric surveys were undertaken with inadequate equipment and insufficient quality control; at best, they were qualitative rather than quantitative; such data are unsatisfactory for baseline purposes;
(13) *in situ* measurements with a field portable gamma ray spectrometer (GRS) should be made at each subsite in the primary 160 × 160 km reference grid wherever a regolith reference sample is collected;
(14) additional information can be obtained by using a portable GRS to obtain a continuous profile whilst in transit in a road vehicle between sample sites (i.e., a carborne survey);
(15) airborne gamma ray spectrometry (AGRS) is the preferred method of obtaining comprehensive radioelement baseline data;
(16) to complement the 160 × 160 km primary reference grid, flight-line spacing should be 80 km, or 40 km or 20 km in populated or contaminated areas;
(17) if funding permits, ground sample collection and AGRS may be undertaken as a single combined operation by using helicopter transportation along regularly spaced cross-country profiles;
(18) a helicopter-mounted combined operation would provide the fastest way of obtaining comprehensive global geochemical coverage, at the same time facilitating the linkage of geochemical with aerogeophysical data.

1.2.5 Data management

1.2.5.1 Databases:

(1) Microcomputers or work stations are acceptable for data management; the following databases should be established;
(2) a Global Reference Database which will contain new data consistent with the proposed GRN specifications;
(3) an index database for administrative and general information;
(4) a block database for averages of elements in large blocks (0.5 × 0.5 degrees spherical rectangles for old compiled data, and 160 × 160 km cells for global reference sampling data) for global presentation;
(5) a bibliographic database for related publications.

1.2.5.2 Quality control requirements for sampling and analysis:

(6) composited sampling to reduce sampling error;
(7) replicate sampling and analysis in an unbalanced 2-fold design for evaluation of geochemical relief in relation to sampling and analytical variability;
(8) SRMs to monitor analytical drift, and randomization to convert any residual systematic drift to non-spatially related analytical variability.

1.2.5.3 Data storage:

(9) miscellaneous recommendations relate to analytical data reporting (maximum of 4 significant figures, and adequate resolution close to the detection limit), data formats, units of measurement, geographic coordinates, data transfer, and the availability of a standard query (command) language.

1.2.5.4 Levelling and normalization of existing data sets:

(10) parametric, linear or non-linear levelling may be used where it is possible to reanalyse some samples or recollect samples from some of the same sites or if reference materials were analysed in both data sets;
(11) in other situations it is necessary to apply non-parametric normalization, using the fractile method or Clarke normalization.
(12) airborne gamma ray spectrometry can be used to overfly adjoining and isolated survey areas to provide an independent Th datum to assist in levelling ground geochemical data sets.

1.2.5.5 Map presentation recommendations:

(13) equal-area map projections for international and global maps (van der Grinten or Goode's Interrupted Homolographic preferred);
(14) coloured surface maps, based on interpolated and smoothed data, are most effective for conveying information.

1.2.6 Implementation

In order to obtain a **global** multielement geochemical database the following practical considerations need to be addressed:
(1) the cost of establishing a complete geochemical reference network, as recommended, is estimated to be in the range of US$300-400 million;
(2) full data acquisition will require a minimum of a decade; given the data's immediate relevance to intensifying land-use problems, early completion (by 2005) is highly desirable;
(3) if a more rapid and relatively low cost global overview is required, a preliminary reconnaissance confined to floodplain sampling could be undertaken. However, floodplain data alone are of somewhat restricted value and the cost of the overall project would be increased by the necessity to re-visit every cell at a later date to collect the other recommended sample media, which better indicate the ranges of element abundance and provide the preferred means of correlating global and national datasets.
(4) irrespective of the rate or mode of progress, the quality and consistency of data must be controlled throughout the acquisition period;
(5) standard reference materials must be provided and renewed as necessary;
(6) a mechanism is required for assessing and introducing new techniques as they become available;
(7) no useful purpose will be served unless global and regional data are readily accessible; and
(8) globally interlinked geochemical data centres are required, which connect to population, environmental, natural resource and global change data centres.

Because the scientific and technical requirements of systematic geochemical mapping have practical significance for all countries:
(9) countries should be encouraged to support and participate in the work and extract maximum value from the information which is obtained;
(10) appropriate training and technical assistance should be made available where needed; and
(11) regional centres should be established to encourage cooperative research and the dissemination and application of geochemical data.

These various considerations lead to the conclusion that:
(12) central coordination is necessary for the duration of the project;
(13) progress must be expedited and facilitated by a small technical secretariat, funded and administered through a recognized international organization.

The work of the International Atomic Energy Agency over the past 25 years in providing a scientific infrastructure relating to radioactive mineral resources, including uranium geochemistry, provides an example of the type of support that is required to establish baseline data concerning the whole periodic table.

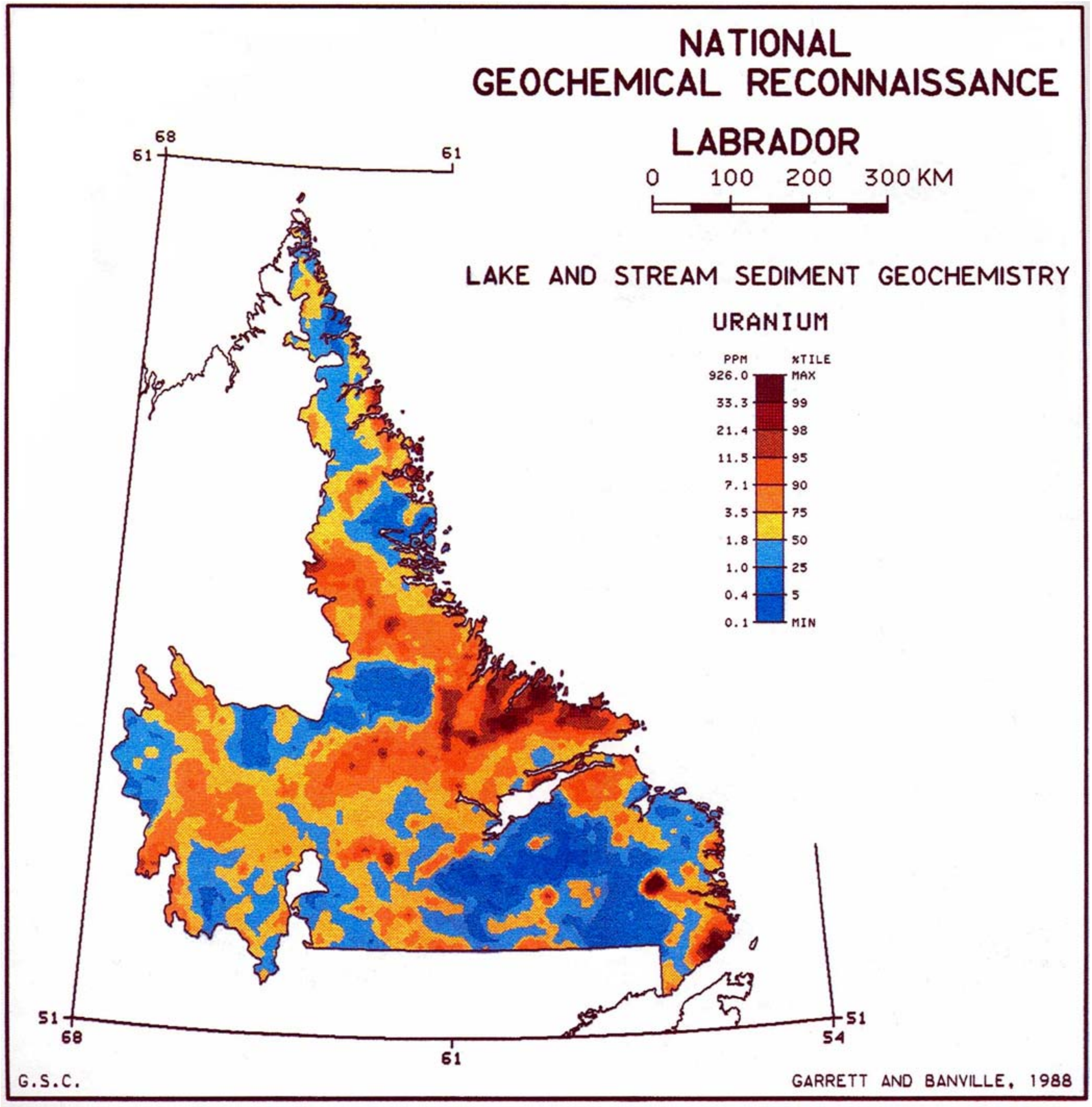


Plate 2-1 *Uranium in Labrador, Canada. From lake and stream sediments, 19 982 sample points (no levelling required). Average sampling density 1/13 km^2. Note range of 3 orders of magnitude.*

from Garrett, Banville & Adcock, 1990

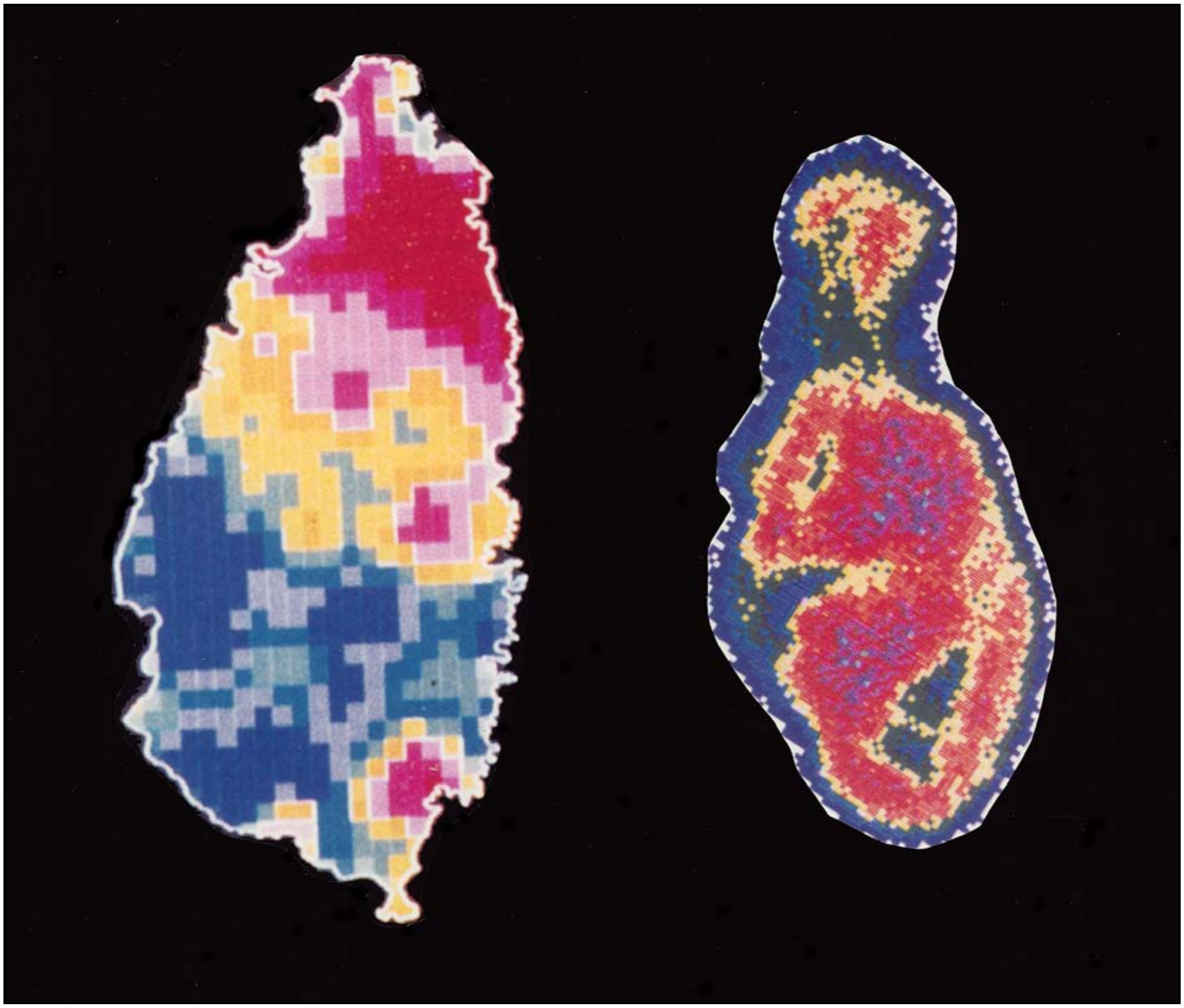


Plate 3-1 *"Patterns at all scales." On left, Cu in stream sediments, Island of St. Lucia, W. Indies. Long axis approximately 40 km. On right, Ni distribution, by microprobe, in complex Pt group mineral grain Long axis approximately 5 microns.*

from Maassen & Bolivar, 1987; Gunn et al., 1990

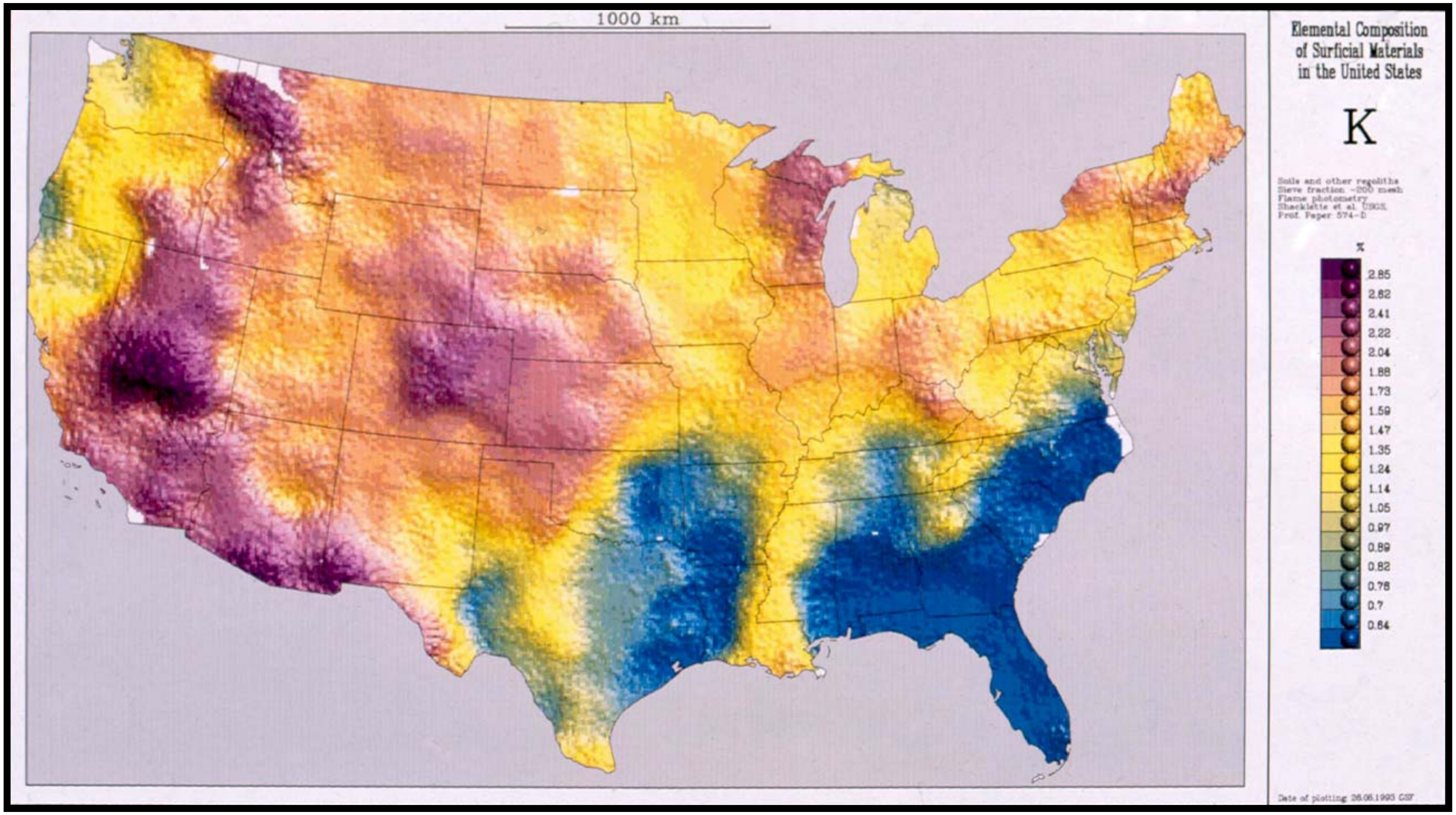


Plate 3-2 K distribution in regolith, USA. 1314 sample points.
from Gustavsson, 1994, based on Shacklette & Boerngen, 1984

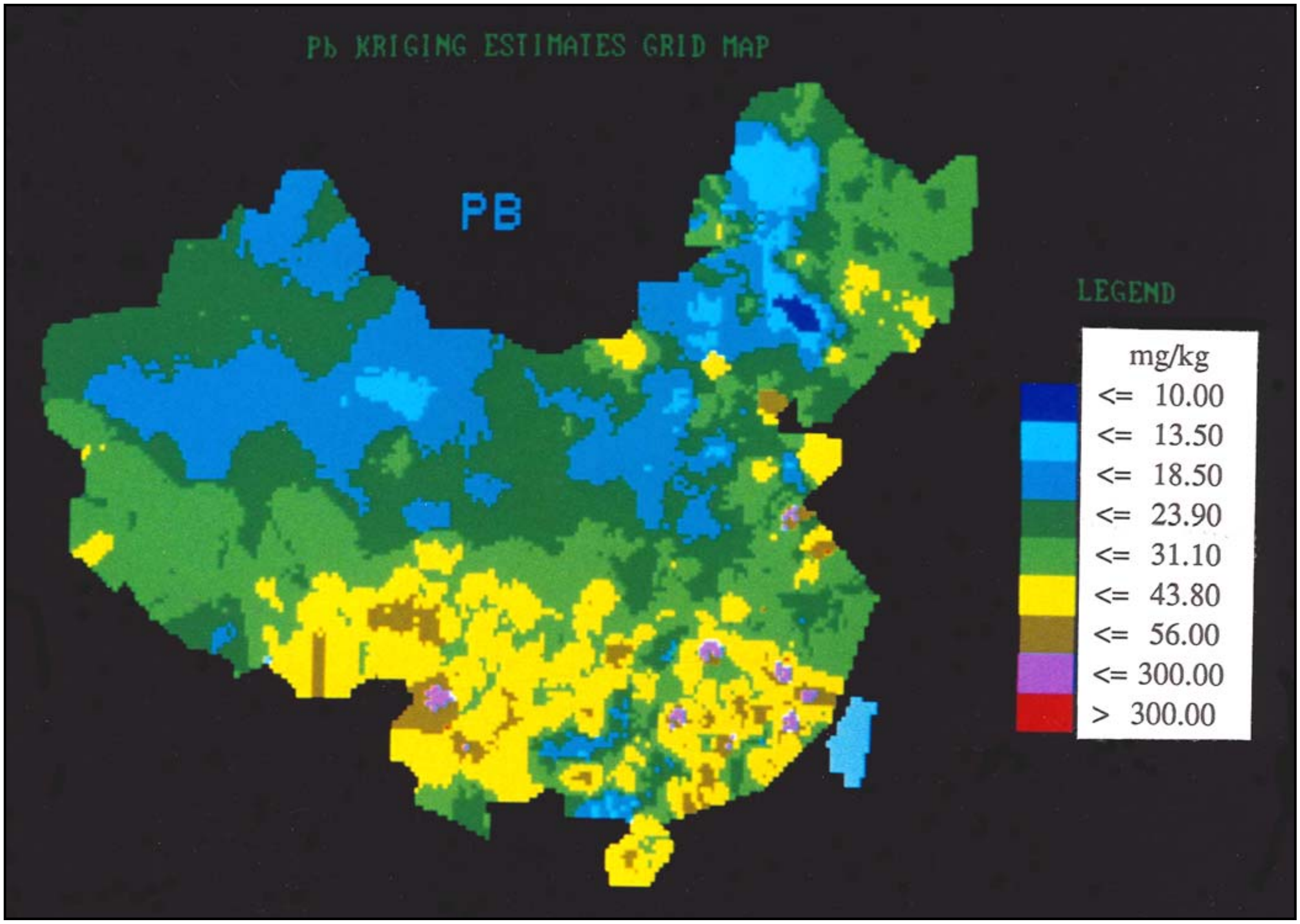


Plate 3-3 *Pb distribution in regolith, China. 4130 sample points.*
from Xie & Yin, 1993, after Zheng, 1992

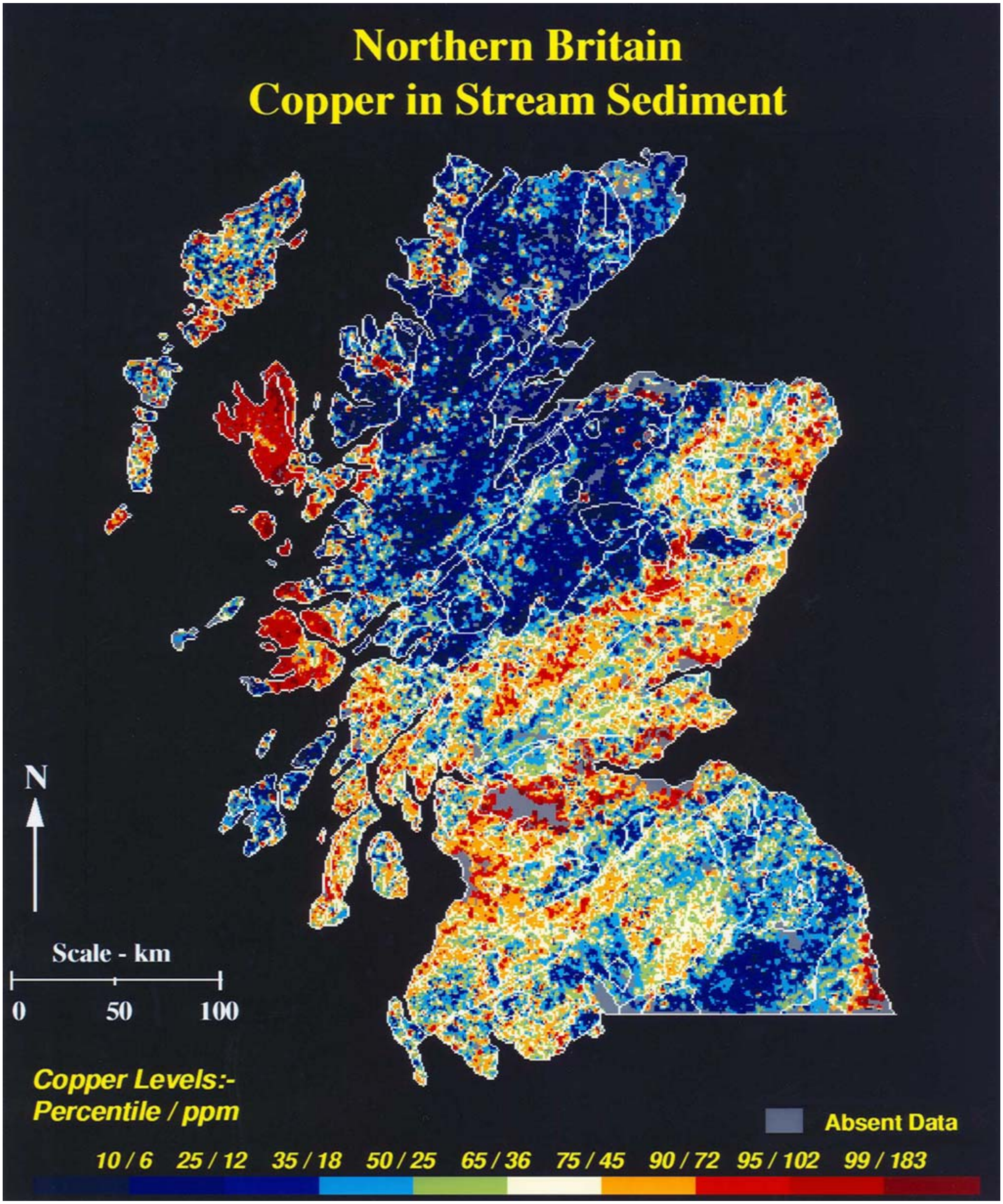


Plate 3-4 *Cu distribution in stream sediments, N. Britain. Average sampling density 1/2 km^2.*
from BGS, 1993

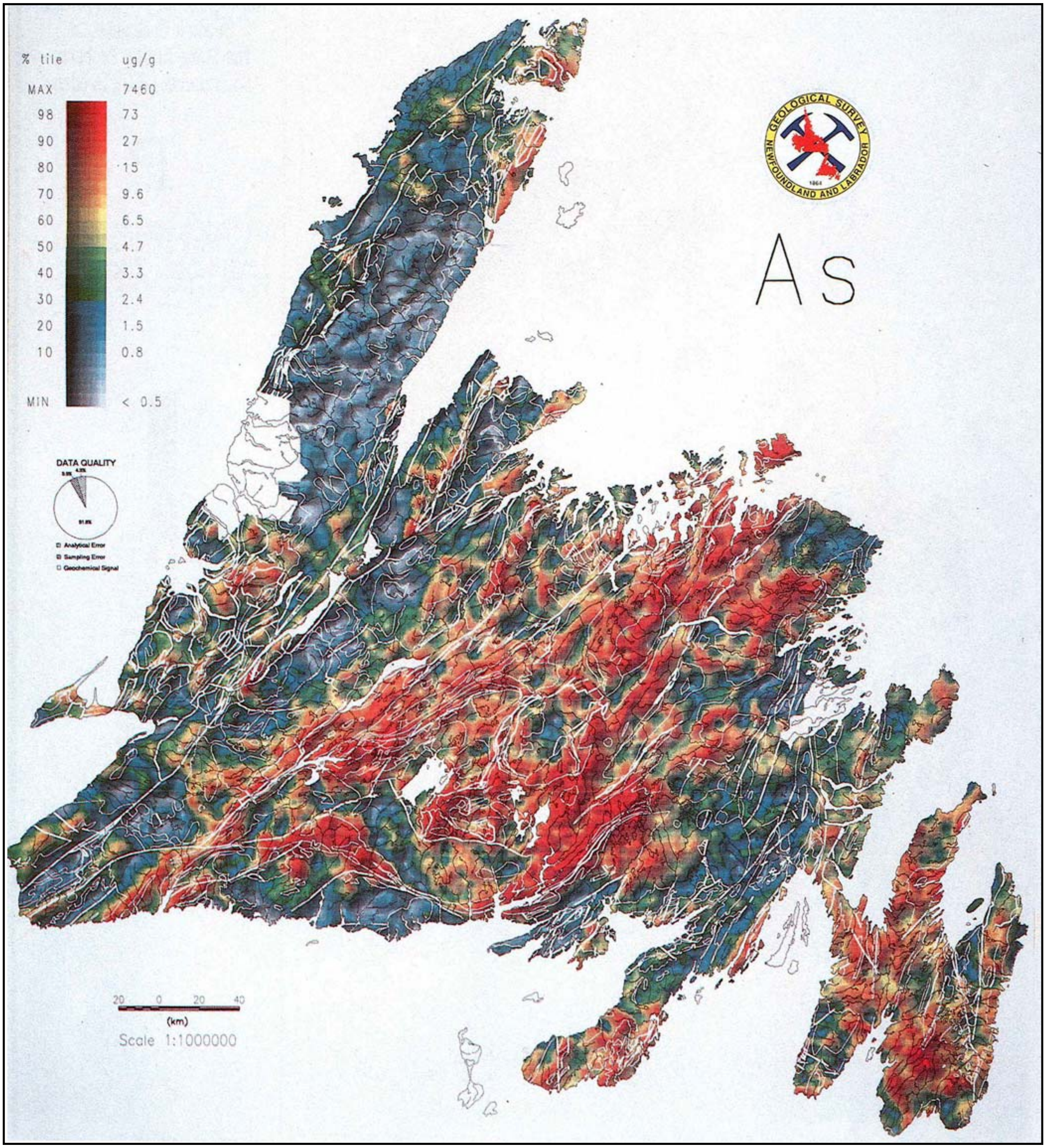


Plate 3-5 *As distribution in lake sediments, Newfoundland. Average sampling density 1/6.5 km*^{2}.
from Davenport et al., 1994

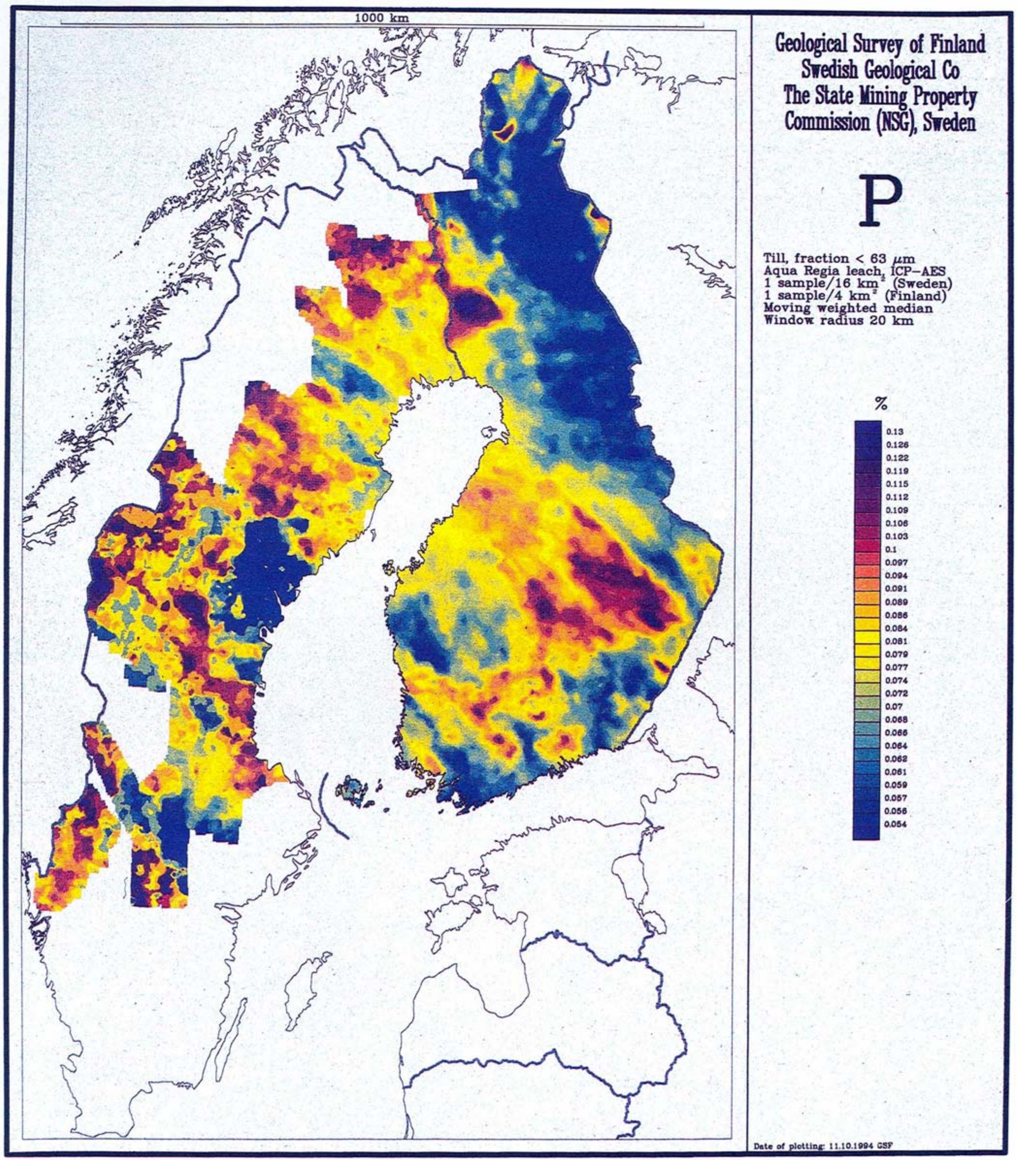


Plate 3-6 *P distribution in till, Fennoscandia. Average sampling density 1/16 km^2 in Sweeden, 1/4 km^2 in Finland.*
from Gustavsson et al., 1994

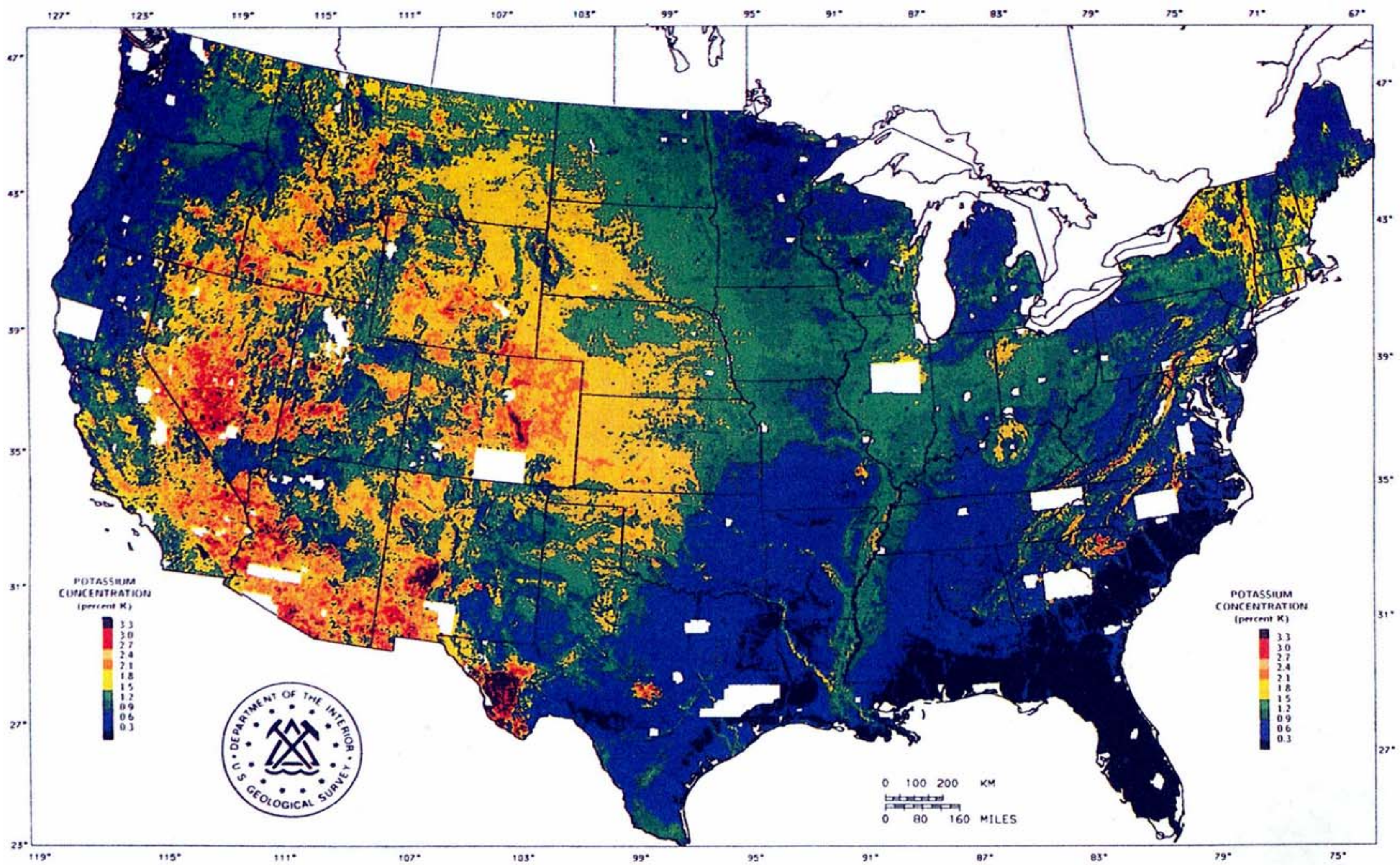


Plate 3-7 *K in regolith, USA. By airborne gamma-ray spectrometry. Line spacing mostly 10 km in E.USA 5 km in W. USA.*

from Duval, 1990

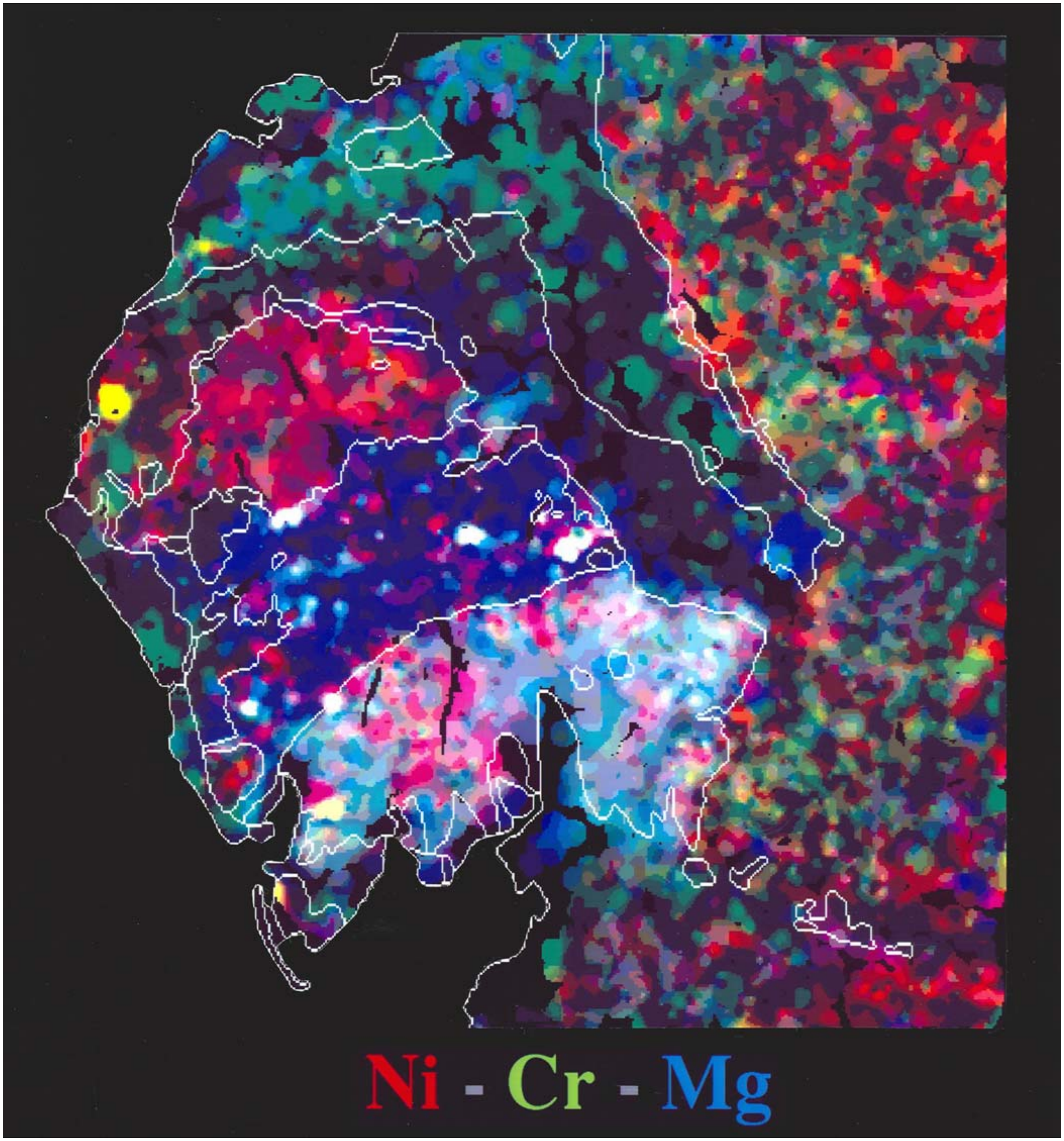


Plate 8-1 *Three component geochemical map (Ni-Cr-Mg) of the English Lake District, showing correlations between geological units and geochemistry. Based on stream sediment sampling.*

from BGS, 1994

2 General Introduction

2.1 Geochemistry and sustainable development

This report addresses the need for a coherent, systematic, worldwide geochemical database. Sustainable development requires the balancing of many factors, including the health of the environment and the utilization of natural resources. A comprehensive geochemical database is necessary for the prudent management of both.

A geochemical database contains information directly relevant to economic and environmental decisions involving mineral exploration, extraction and processing; manufacturing industries; agriculture; forestry; many aspects of human and animal health; waste disposal; and land-use planning. These are all matters of increasing public and government concern. A database showing the spatial variations in the abundance of the chemical elements over the earth's surface is a key step in constructing a comprehensive database embracing all aspects of environmental geochemistry. Environmental problems do not respect political boundaries and data from one part of the world may have important implications elsewhere.

A common database with permanent value can only be obtained by adopting standardized procedures for every step in the acquisition process. This report provides recommendations by which such a database can be achieved, through systematic geochemical mapping at the national and international level.

The earth's surface layer contains all the chemical elements involved in biological processes and all the elements exploited by man (Fig. 2-1). The biological and/or industrial importance of elements is not related to their average level of abundance in the earth's crust. The average abundance of major elements such as Na, Mg, Al, Si, K, Ca, and Fe in the earth's surface materials exceeds 1 per cent. Ti, P, S and Mn, classed as minor elements, have an average abundance in the range 1.0 to 0.01 per cent. Some trace elements with biological significance such as Be, B, As, Mo, and U have an average abundance of the order of 0.0001 per cent (1 part per million (ppm) or 1 mg/kg).

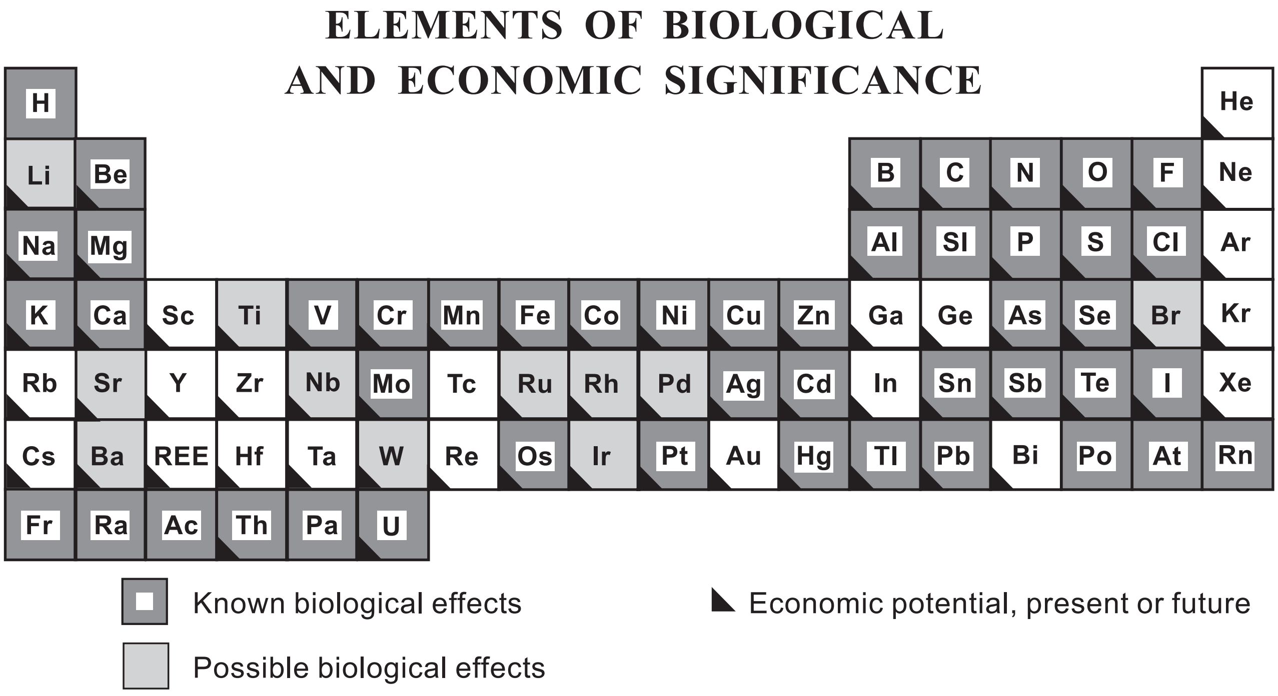


Figure 2-1 *Periodic table showing elements with known biological effects, those with possible biological effects, and those with present or future economic importance.*

Other trace elements with biological significance, such as Ag, Cd, Sb, I, Hg and Tl, have average abundances of the order of 0.1 ppm; some, such as Pt and Au, are even less abundant (see Fig. 2-2).

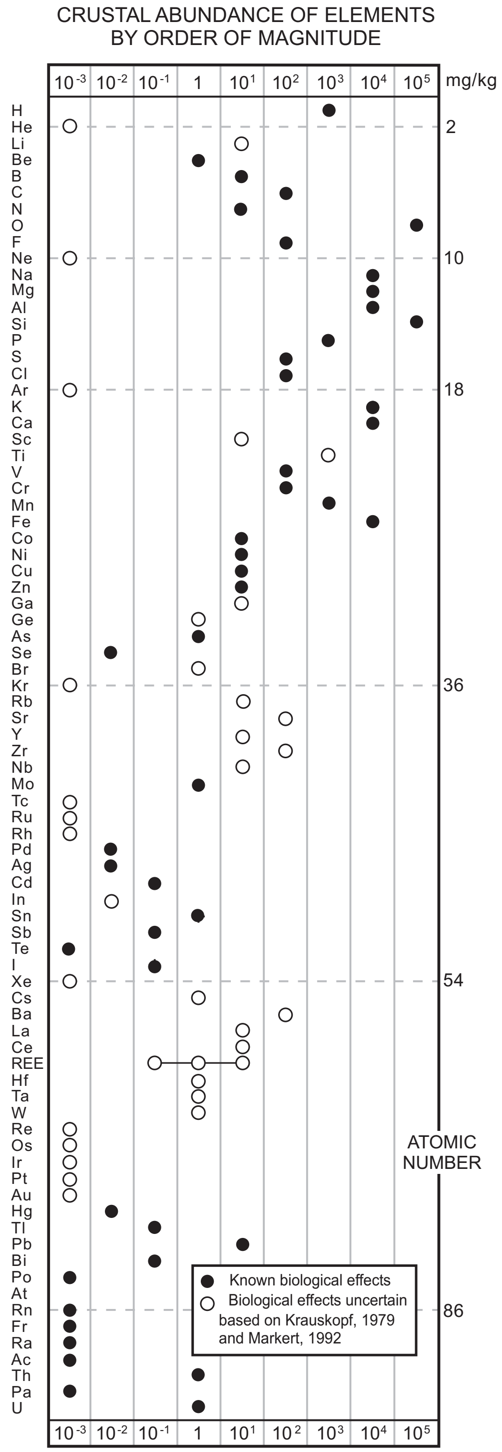


Figure 2-2 *Abundance of elements in the earth's crust, by order of magnitude.*

Geochemical mapping, initially over areas of a few tens of km^2, was originally devised as a method of mineral prospecting. During the past four decades many millions of km^2 have been explored in this way with varying degrees of thoroughness and as a result many mineral deposits, in all parts of the world, have been discovered (Thornton and Howarth, 1986). The biological applications of geochemical mapping have developed from research into the trace element composition of soils, which began during the 1920s. As geochemical maps covering large areas have become available, a variety of biochemical phenomena have been recognized through the recognition of empirical associations between trace element and morbidity patterns in plants and animals (Thornton, 1983, 1993). More recently, as the variability of the natural geochemical background has become better known, it has been recognized that in order to identify and quantify anthropogenic pollution it is necessary to have a map of the natural background.

The role played by trace elements in biological processes has only been recognized as analytical procedures have advanced. The importance of Fe in blood was first suspected about 300 years ago, but only during the past 50 years has the biological importance of, for example, Co, Mo, Cr, Se, F, Sn, V, been established (Koros in Pais, 1989). With each passing decade additional "bioactive" elements have been identified as having some specific biochemical role. Markert (1992) has pointed out how awareness of the significance of trace elements in organisms has grown as new and more sensitive analytical techniques have been introduced. It now appears that for many (possibly most) organisms there is an optimum range of concentration for particular elements, specific to the organism. Outside this range potentially harmful effects may be observed caused by either a deficiency or excess of the elements in question (see Fig. 2-3).

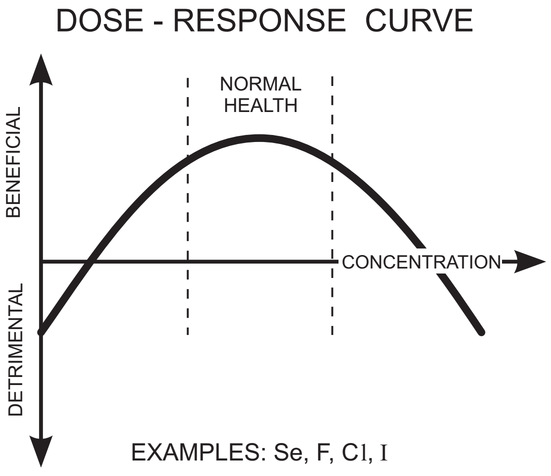


Figure 2-3 *Example of dose-response curve for some biologically active elements.*

Based on Panto et al, 1989

	Ca	Mg	P	K	Na	S	Co	Cu	Fe	Mn	Se	Zn	F	I
Antigua			-											-
Argentina	-	-	-				-	-		-	+	-	+	-
Bahamas											-			-
Bolivia	-		-		-			-			-	-		-
Brazil	-	-	-	-	-	-	-	-	-	+ -	+ -	-		-
Chile		-	-								+			-
Colombia	-	-	-		-	-	-	-			+ -	-		-
Costa Rica	-	-	-				-	-	-	+ -	-	-		-
Cuba			-				-	-						-
Dominican R.			-		-			-			-	-		-
Ecuador			-			-		-			+ -	-	+	-
El Salvador	-		-					-				-		-
Guatemala	-	-	-		-			-				-		-
Guyana	-	-	-				-	-			-	-	+	-
Haiti		-	-	-			-	-						-
Honduras		-	-					-			+ -			-
Jamaica		-	-											-
Mexico	-		-				-	-			+ -	-	+	-
Nicaragua			-				-							-
Panama	-		-	-	-			-	-	-		-		-
Paraguay			-								-			-
Peru	-	-	-				-	-		+	+ -	-		-
Puerto Rico			-								+	-		-
Surinam	-	-	-		-		-	-		+				-
Trinidad		-	-					-						-
Uruguay		-	-		-		-	-			-	-		-
Venezuela	-	-	-	-	-			-			+ -	-		-

DEFICIENCIES - TOXICITIES +

Figure 2-4 *Documented element deficiencies and toxicities for ruminants in Latin America and Caribbean. based on Appleton, 1992*

Figure 2-4, with data from Appleton (1992), lists countries in Latin America and the Caribbean where deficiencies or excesses of various major, minor and trace elements, have been identified, affecting the health of ruminant animals. In the case of homo sapiens, optimum concentration ranges apply to Na, K, Mg, Fe, F, Cl, I, P, Co, Se and there is no reason to suppose that this list is complete (see Markert, 1992). The processes involved are complex and in general poorly understood. Life on earth has evolved over a long period of time in the presence of all the elements, and it is possible that every element has some function in the biosphere.

Because of the influence of surface geochemistry upon the biosphere it is important to know where and how the elements are distributed in their natural state and where they may have been redistributed by man. On theoretical grounds it is desirable to have data about the distribution of all the elements. The natural abundance of elements in many surface sample media can vary by 2 to 3 orders of magnitude, up to 5 or 6 orders if samples from rare types of high-grade mineral deposit are included. This wide range of variation is a consequence of geological, environmental and pedological processes. Plate 2-1 illustrates the distribution of U in lake sediments in Labrador, Canada, an undeveloped region where a 10^3 range in concentration occurs. The spatial distribution patterns of trace elements are seldom obvious, hence the need for mapping.

A geochemical database and its representation in map form is directly pertinent to human occupation and exploitation of the earth's surface. The need for an adequate geochemical database increases in step with population. World population is now in excess of 5.5 billion and it is increasing at the rate of 90 million per year. All current projections of population growth, based on a variety of assumptions, show that within 50 years, unless there is some unforeseen catastrophe, world population will grow to 8 billion, approximately a 50 per cent increase on present numbers (Arizpe et al., 1992). Within 50 years world population could considerably exceed 8 billion. Population expansion will inevitably cause more intensive exploitation of minerals, agricultural land, forests, water and living space and because the great majority of people aspire to a higher standard of living than they currently have, there will be additional pressure upon these resources. Great efforts will have to be made to keep the planet habitable and recycle the resources now in use. Much more energy will be required, even assuming that usage becomes more efficient. To anticipate all these demands and react in an intelligent way it will be essential to establish a comprehensive database concerning all types of resources and all aspects of the environment. At the present time, because the world's geochemical database is incomplete and unsystematic, significant facts bearing upon environmental science as a whole may be overlooked and wrong policy decisions may ensue.

During the 6 years since the current project began (in 1987), it has become increasingly clear that standardized geochemical data are a basic requirement for administrative purposes, extending beyond the earth sciences into issues such as public health and environmental law. An increasing number of jurisdictions have been engaged in the development of quantitative criteria relating to trace constituents in soil, water and sediment. In a number of instances little attention has been paid to natural variability, in part because of the sparsity of relevant data, and in part because use of terms such as "baseline value" has often been assumed to imply that the natural background level for each element is constant. Public interest in these matters has been stimulated by the work of the World Commission on Environment and Development in the Brundtland Report of 1987, and the ASCEND 21 and Rio de Janeiro UNCED Conferences of 1991/1992. Amongst the many issues identified at these meetings, is the need for a comprehensive database describing the principal features of the global environment. Such a database is a starting point for research into complex natural processes. Both public and scientific concern relates to the consequences of "change", but there is a tendency to overlook the fact that change cannot be detected or measured if there is an incomplete description of present conditions, also that the consequences of changing conditions cannot be anticipated if all the variables have not been recognized.

2.2 The current status of geochemical mapping

Work to produce a *geological map* of the world began about 50 years ago. A first edition was published in 1989 by an IUGS Commission established for the purpose. Any study of global or continental scale processes requires systematic data for the parameters of interest. The compilation of any large scale map forces the issue of establishing the comparability

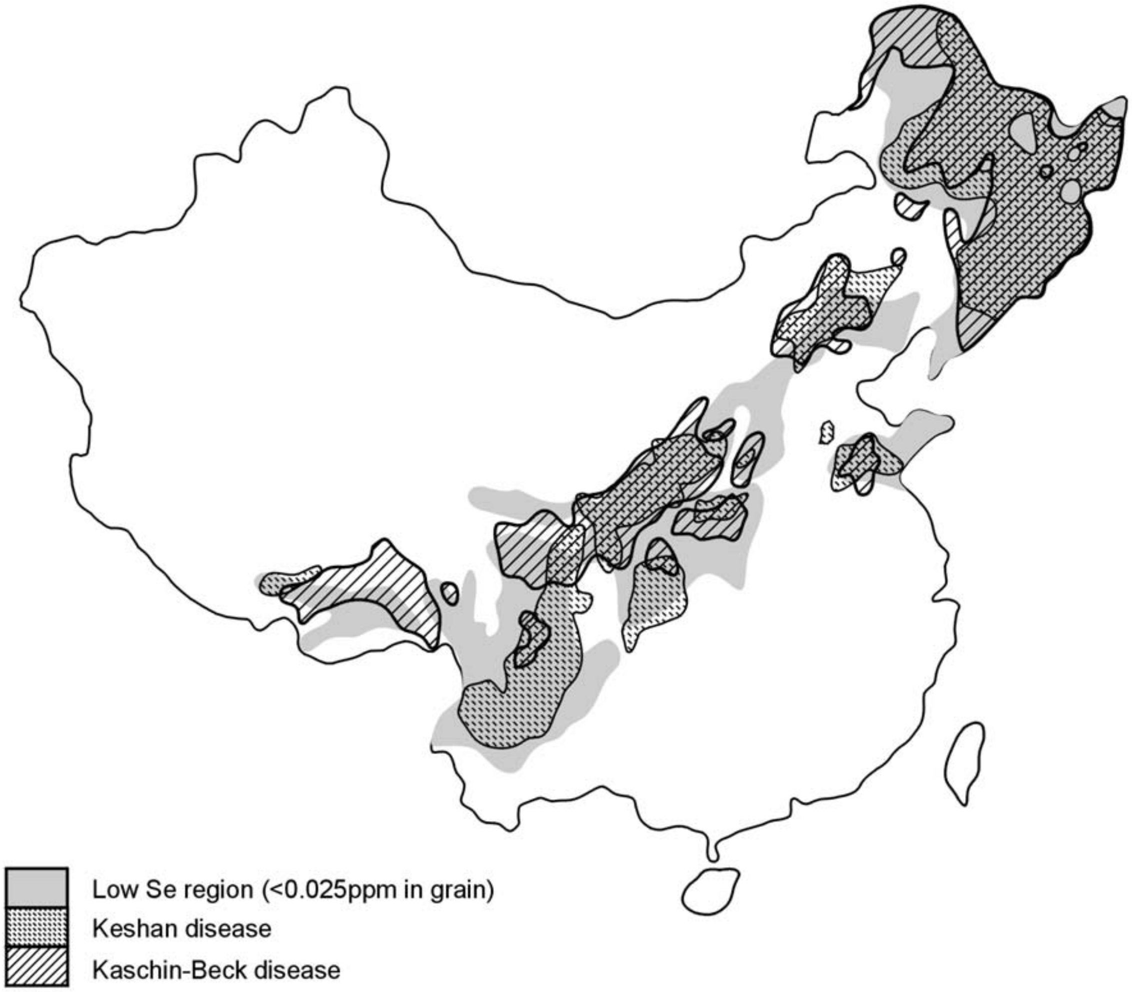


Figure 2-5 *Low Se region in China, shows areas with high incidence of Keshan and Kaschin-Beck disease. from Tan et al., 1988*

and compatibility of data between and across continents. Such compilations may provide the key to otherwise seemingly unconnected phenomena. They provide a framework within which detailed investigations can be correlated and compared.

A geological map is not a substitute for a geochemical map. Lithological information on a geological map generally indicates the probable distribution of major elements, but inferences concerning minor and (especially) trace elements may be erroneous or unknown, with important consequences. This is illustrated by the pattern of Se distribution in China, which shows a NE-SW belt of low Se values, about 2500 km long (Fig. 2-5). This does not correlate with any obvious feature on a geological map of China at the same scale, but it would be large enough to stand out on a Se map of Asia if such existed. The zone of low Se values corresponds with the occurrence of two serious, sometimes fatal diseases, Keshan (cardiomyopathy) and Kaschin-Beck (osteoarthropathy) (Tan et al., 1988). Differences in Se values between deficient and normal areas do not exceed 2 or 3 parts per million.

As of 1993 there is no geochemical map of the world because the necessary data do not exist. In Russia, during the 1920s, Vernadsky proposed the preparation of a radioactive map of the Earth's crust and in the following decade Fersman developed the idea in connection with the recognition of geochemical provinces (Burenkov et al., 1991). The development of optical emission spectroscopy during the 1930s made possible the determination of trace elements in geological materials, and from this geochemical prospecting commenced in Russia and Scandinavia. Geochemical mapping began to evolve in the 1950s, with the introduction of rapid, low cost, colorimetric methods of analysis which could be used in prospecting for base-metals. Most of the early work entailed the collection and analysis of soil samples. By the late 50s stream sediment sampling had become the most common method wherever suitable drainage patterns existed, because larger areas could be covered with fewer samples. Initially attention was limited to a few elements of immediate economic interest, such as Cu, Ni, Pb and Zn. Webb (1964) advocated the launching of national multi-purpose, multi-element, geochemical surveys, which would be applicable to agriculture and studies of human health and pollution. A few years later he was responsible for the production and publication of the first geochemical atlases (Webb et al., 1973, 1978). Uranium began to be a target for some geochemical surveys during the 1960s. In recent years, as a result of major developments in analytical techniques, as many as 50 elements have been included in the analytical list for some national surveys. Geochemical mapping methodologies have now evolved to the point where it is possible to obtain reproducible quantitative information about the chemical composition of the surface environment with whatever spatial resolution is required.

The use of radioactivity surveys to find uranium mineralization began in the late 40s, before geochemical exploration methods became established. Initially radiometric surveys only provided a method of measuring total radioactivity, caused by some combination of U, Th, and K, possibly with some contribution from radioactive fall-out. These early radiometric surveys cannot be considered as geochemical surveys. It was not until the development of high-sensitivity gamma ray spectrometry in the late 60s, which made it possible to produce quantitative radioelement maps for K, U and Th (plus specific fall-out products), that radiometric surveys became a geochemical mapping method for these elements. Because K, U and Th are large-ion lithophile elements with distinctive properties they happen to be sensitive indicators of a variety of economically significant geological and geochemical processes. For these and other reasons described in Chapter 7, airborne gamma ray spectrometry provides a valuable complement to conventional geochemical surface sampling.

Although scattered geochemical mapping programs had been started by government agencies in a few countries prior to 1970, the oil embargo of 1973 resulted in funds being made available to start national geochemical mapping programs in Canada, the USA and elsewhere. It provided an opportunity to apply newly developed methods. Nuclear energy was seen as a way of reducing dependence upon imported oil, so uranium was the prime target. However, surveys were planned so as to gather data for other elements simultaneously. In Canada and the USA a broadly similar approach was taken. It involved two components: systematic airborne gamma ray spectrometry to map eU, eTh and K; and surface sampling of stream sediment and (in Canada) lake sediment, to obtain multielement data (initially 12 to 15 elements in Canada, 30+ in the USA). Both the US and Canadian programs operated principally through private contractors, according to predefined specifications. The Canadian program required the use of approved equipment, standardized techniques, reference materials for geochemical analysis, and calibration facilities for radiometric instruments (Darnley et al., 1975). The US program allowed its larger number of contractors more flexibility in execution.

The concept of internationally approved methodology and standards for geochemical mapping evolved from the need to introduce order into gamma ray spectrometry measurements. The problem was identified at an IAEA panel meeting in Vienna in 1972 (IAEA, 1973). This led to a series of IAEA Consultants' meetings in 1973/74. An IAEA technical report with recommendations was published in 1976 (IAEA, 1976). Those recommendations, with subsequent revisions and additions, have provided the international standards for ground and airborne gamma ray surveys from that time forward (IAEA 1979, IAEA 1991). As a parallel step, during the 70s the IAEA was responsible for preparing laboratory reference materials for radiometric and chemical analyses. These activities were influential because of the IAEA's mandate, arising from its UN charter, for all matters relating to nuclear energy, including radioactive minerals.

The agency thus acts as international coordinator and facilitator for a wide range of technical activities in its field. A number of large airborne gamma ray surveys undertaken over the last 15 years, for example in Thailand, have a degree of conformity and standardization because of IAEA influence. Regrettably, neither the IAEA nor any other international agency has a mandate for sponsoring standardization for data relating to non-nuclear elements in the environment. There has been no institutional support to facilitate systematic data collection pertaining to the other elements of the periodic table, dispersed alongside radioactive elements in soil, rocks and natural waters. Consequently, on an international basis, there has been no coordination of methodology or data with respect to geochemical surveys. In general, data from neighbouring countries can only be correlated in a qualitative manner, if at all.

2.3 The deficiencies of existing multielement datasets

Although a few countries have produced geochemical atlases (see bibliography), with the first published in the 1970s, no country, or region within any country, has geochemical maps for more than a sometimes seemingly arbitrary mix of elements. The selection has commonly been determined by the capabilities and limitations of the responsible institution's analytical facilities or analytical budget. Recently published national geochemical atlases from Germany, Austria and Finland are of high quality, but, as elsewhere, they are stand-alone items with respect to their neighbours. As a result of a vigorous program throughout the past decade a large part of China has been covered with detailed systematic geochemical mapping (Xie and Ren, 1991). Each country or organization has developed its own code of practice and style of presenting data, as is readily apparent from examination of the products. Geochemical databases vary from country to country and many countries do not have any. Those which exist are incomplete, inconsistent across (often within) national boundaries, and often lack information on quality control. Different sample media, methods of sample collection and preparation, extraction and analytical techniques have been used. For a review of the variety of methods used in Western Europe, see Plant and Ridgway (1990). As a result of this diversity, numerical values can only be compared within areas where consistent methods and standards have been applied.

Table 2-1 lists countries where *some* geochemical mapping is known to have taken place, and shows the percentage of their area which has been covered by some form of conventional geochemistry (i.e. samples collected and analysed in a laboratory) or by airborne gamma ray spectrometry (AGRS). This list indicates nothing about the quality of data, the sample density, the type or variety of media, or the number of elements for which data are now available. It merely shows that expenditures have been made and work has been done. It will be noted that, according to IAEA records, a number of countries have 100% coverage by AGRS (Grasty and Tauchid, in press), whereas only 3 countries have 100% coverage by conventional geochemistry. In total, approximately 19% of the world's land surface has some multielement coverage, compared with 33% with actual or potential radioelement coverage by AGRS. The term "potential" is used because not all AGRS data has been reduced to provide radioelement concentrations (see Chapter 7 for further explanation).

Table 2-2 indicates which elements of the periodic table are included in a selection of published atlases and geochemical map sets. Results are summarized in Figure 2-6. Elements are listed in order of increasing atomic number, with biologically active (bioactive) elements in bold italics, and potentially harmful elements underlined. Twenty eight of the 29 regions listed range in area from approximately 10 000 000 km^2 (USA) to 7500 km^2 (English Lake District), on 5 different continents. Because geochemical maps of urban areas are still a rarity, data from a recently published atlas (Lis, 1992) concerning the City of Warsaw in Poland are also included. Table 2-2 includes information from some of the unpublished submissions received during the project. This allows a comparison to be made between a few developed and a few developing countries, also the extent to which analytical lists in different countries have changed over time.

The table shows that the number of elements in this selection of regional map sets ranges from 6 to 46, with a median of 22. (Note that rare earth elements, 59 to 71 inclusive are counted as one). Data are most commonly available for Cr, Mn, Co, Ni, Cu, Zn and Pb, but only 2 elements, Cu and Zn, are reported in all of these map sets. There is considerable variation between data sets with respect to the assemblage of elements, reflecting the fact that analytical suites have generally been decided according to the currently perceived mineral exploration potential of each region, coupled with a desire to minimize analytical costs. In general few elements of environmental importance have been determined in past survey work. For example, fewer than half the surveys listed in Table 2-2 have provided data on such important elements as P, S, Se, Cd, Sb, Hg and halides. None of the surveys listed include Tl. The diversity of elements included in the surveys reflects the fact that there are a variety of methods available to determine elements of prime interest, and organizations have made different choices. Depending upon the methods selected, data for other elements have been available as a by-product. It is re-emphasized that the fact that most atlases and regional map sets contain a few elements in common provides no guarantee of numerical equivalence between these particular datasets. Different sample media, different size fractions, different sample preparation methods, different dissolution and analytical methods, different levels of quality control, have been (and still are being) employed for a variety of scientific and non-scientific reasons by different countries and organizations.

COUNTRY	AREA	AGRS		CONVENTIONAL	
	Km²	Km²	%	Km²	%
Albania	28,748			6,000	21
Algeria	2,381,741				
Afghanistan	647,497				
Angola	1,246,700				
Antigua & Barbuda	440				
Argentina	2,766,889	140,000 (286,000)	5 (10)	200,000	7
Armenia	29,800	29,800	100		
Australia	7,686,848	265,000 (29,900)	3	566,000	7
Austria	83,849	8,500	10	42,000	50
Azerbaijan	86,600	86,600	100		
Bahamas	13,935				
Bahrain	622				
Bangladesh	143,998				
Barbados	431				
Belgium	30,513			12,000	39
Belize	22,963				
Belarus	207,600	207,600	100		
Benin	112,622				
Bhutan	47,000				
Bolivia	1,098,581	47,296	4	130,000	11
Bosnia & Herzegovina	51,129				
Botswana	600,372	132,250 (21,400)	22 (4)		
Brazil	8,511,965	2,037,000 (363,000)	24 (4)	2,428,343	29
Brunei Darussalam	5,765				
Bulgaria	110,912	22,000	20		
Burkina Faso	274,200				
Burma				9,430	1
Burundi	27,834	14,000	50		
Cambodia	181,035				
Cameroon	475,442	40,000 (40,000)	8 (8)		
Canada	9,976,139	2,495,000	25	2,084,000	21
Cape Verde	4,033				
Central African Republic	622,984				
Chad	1,284,000				
Chile	756,945	49,286 (44,749)	6 (6)		
China	9,596,961	1,160,000 (900,000)	12 (9)	9,500,000	95
Columbia	1,138,914	129,000	11		
Comoros	2,171				
Congo	342,000				
Costa Rica	50,700				
Cote d'Ivoire	322,463	322,463	100		
Croatia	56,538				
Cuba	114,524				
Cyprus	9,251				
Czech + Slovak Republics	127,869	76,500	60	91,000	71
Denmark	43,069	27,150	8		
Dem. Peop. Rep. of Korea	120,540				
Djbouti	22,000				
Dominica	751				
Dominican Republic	48,734				
Ecuador	283,561			6,000	2
Egypt	1,101,449	230,000	21	110,000	11
El Salvador	21,293				
Equatorial Guinea	28,051				
Estonia	45,100	45,100	100		
Ethiopia	1,221,900			96,000	8
Federated States of Micronesia					
Fiji	18,272				
Finland	337,009	337,009	100	337,030	100
France	547,026	22,430 (51,426)	4 (9)	90,000	16
French Guiana	90,909				
Gabon	267,667	267,667	100	50,000	19
Gambia	11,295				
Georgia	69,700	69,700	100		

Table 2-1 *Geochemical surveys: areas with some data.*

COUNTRY	AREA Km²	AGRS		CONVENTIONAL	
		Km²	%	Km²	%
Germany	356,749	74,440 (10,600)	21 (3)	264,000	74
Ghana	238,537	(30,000)	(13)		
Greece	131,944	99,000	75		
Greenland	342,000	175,000	51	190,000	50
Grenada	344				
Guatemala	108,889				
Guinea	248,957				
Guinea-Bissau	36,125				
Guyana	214,969	32,063 (24,000)	(15)		
Haiti	27,750				
Honduras	112,088				
Hong Kong	1,040				
Hungary	93,030	40,000	43	37,000	40
Iceland	103,000				
India	3,129,316	400,000	13		
Indonesia	2,027,087			190,000	10
Iran	1,648,000			349,500	21
Iraq	434,924				
Ireland	70,283	11,296	16		
Israel	20,700	20,700	100	15,000	71
Italy	301,225	36,623 (14,006)	12 (5)	10,000	3
Jamaica	10,962				
Japan	372,313	(61,000)	(16)	79,000	21
Jordan	97,740	97,740	100		
Kazakhstan	2,717,300	2,717,300	100		
Kenya	582,644			50,000	9
Kiribati	717				
Korea, Republic of	98,500	25,000	25		
Kuwait	17,818				
Kyrgyzstan	198,500	198,500	100		
Lao Peop. Dem. Republic	236,800				
Latvia	63,700	63,700	100		
Lebanon	10,400				
Lesotho	30,355	30,355	100		
Liberia	111,369				
Libya	1,759,540	187,500 (60,500)	11 (3)		
Liechtenstein	160				
Lithuania	65,200	65,200	100		
Luxembourg	2,586				
Madagascar	587,041	3,500 (20,000)	1 (3)		
Malawi	118,484	118,484	100		
Malaysia	329,749	31,000	9	31,000	9
Maldives	298				
Mali	1,240,000				
Malta	316				
Marshall Islands					
Mauritania	1,030,700				
Mauritius	2,045				
Mexico	1,972,546	99,000	5		
Moldova	33,700	33,700	100		
Mongolia	1,565,000	1,100,000	70		
Morocco	446,550	9,540 (4,500)	2 (1)		
Mozambique	783,030	390,000	50	306,100	38
Myanmar	676,552				
Namibia	824,296	256,948 (94,900)	31 (12)		
Nepal	140,797				
Netherlands	40,844				
Netherlands Antilles	960				
New Zealand	286,676				
Nicaragua	130,000				
Niger	1,267,000	35,000	3		
Nigeria	923,768				

Table 2-1 *Geochemical surveys: areas with some data. (continued)*

COUNTRY	AREA	AGRS		CONVENTIONAL	
	Km^2	Km^2	%	Km^2	%
Norway	324,219	12,300 (109,000)	4 (34)	324,219	100
Oman	212,457				
Pakistan	803,943			6,000	1
Panama	75,650				
Papua New Guinea	461,691				
Paraguay	406,752	220,000	54		
Peru	1,285,216	10,000 (10,900)	1 (1)	6,300	1
Philippines	300,000	2,500 (17,000)	1 (6)		
Poland	312,677	3,000	1	100,000	32
Portugal	92,082	15,000 (4,184)	16 (5)		
Qatar	11,000				
Rawanda	26,338	26,338	100		
Romania	237,500	7,600	3		
Russian Federation	17,075,400	17,075,400	100	1,000,000	4
St. Kitts & Nevis	261				
St. Lucia	616				
St. Vincent & the Grenadines	340				
San Marino	62				
Saudi Arabia (HG)	2,149,690			10,500	1
Senegal	196,192				
Seychelles	280				
Sierra Leone	71,740			40,250	56
Singapore	581				
Slovenia	20,251				
Solomon Islands	28,446			8,600	30
Somalia	637,657	53,000	8		
South Africa	1,221,037	336,467 (745,856)	28 (61)	200,000	16
Spain	504,782	45,000 (273,448)	9 (54)		
Sri Lanka	65,610				
Sudan	2,505,813				
Suriname	163,265				
Swaziland	17,363	17,363	100		
Sweden	449,964			190,000	42
Syria	185,180	40,000	22	21,000	11
Taiwan	35,980				
Tajikistan	143,100	143,100	100		
Tanzania	945,087	945,087	100	643,000	68
Thailand	514,000	514,000	100	12,000	2
Togo	56,000				
Trinidad & Tobago	5,130				
Tunisia	163,610				
Turkey	780,576	21,500 (12,000)	3 (2)		
Turkmenistan	488,100	488,100	100		
Uganda	236,036			230,000	97
Ukraine	603,700	603,700	100		
United Arab Emirates	83,600				
United Kingdom	244,046	100 (13,800)	(6)	244,820	100
United States of America	9,363,123	8,895,000	95	4,959,539	54
Uruguay	176,215	24,435	14		
Uzbekistan	447,400	447,400	100		
Vanuatu	14,763				
Venezuela	912,050			400,000	44
Vietnam	329,556				
Yemen	527,968				
Yugoslavia	127,886				
Zaire	2,345,409				
Zambia	752,614	490,000	65	207,000	27
Zimbabwe	390,580	27,000	7	13,200	3
World land surface (excluding ice-caps)	136,000,000	44,921,160	33	25,894,540	19

Table 2-1 *Geochemical surveys: areas with some data. (continued)*

As a result there are many possible intrinsic differences in datasets for any given element, which hinder or do not justify the further assembly of most existing data into broader regional compilations. To find ways of overcoming these problems, or at least to prevent their perpetuation into the future, has been a major consideration underlying the activities of the International Geochemical Mapping project.

2.4 Origin of the project

The concept of internationally standardized geochemical survey procedures was first introduced in the 1970s under the auspices of the International Atomic Energy Agency (IAEA), specifically in relation to uranium exploration. As indicated previously, while the IAEA is able to support the development of standardized geochemical methods pertaining to uranium, unfortunately it has no mandate to do the same for the non-radioactive elements, which occur alongside the radioactive elements throughout the natural environment.

This report represents a major extension of the standardization concept as developed for uranium, and stems from a discussion at an IAEA workshop held in Sweden in 1984. At that meeting the widespread gaps in the geophysical and geochemical databases available for mineral exploration and resource mapping purposes were identified as matters for concern, and questions were asked as to what actions could be taken. During 1985 a consensus was reached that the geochemical database deserved priority because its applications extend far beyond mineral exploration and geology, being relevant to many matters of day-to-day human concern such as health and the misuse of the environment.

	North America						C. & S. America				Europe									Middle East & Africa							East Asia				
Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	Σ	Element
1*H		N	U	C									E	G					P											7	1*H
2 He	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	2 He
3 Li	S	N				A				O		W	E	G				F				G						X		10	3 Li
4 Be	S	N				A				O			E		A							G	U		M		C	X	J	12	4 Be
5 B	S									O												G			M		C	X		6	5 B
6*C			U	C	N		R																							4	6*C
7 N																														0	7 N
8 O																														0	8 O
9 F	S		U	C										G														X	J	6	9 F
10 Ne	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	10 Ne
11 Na	S	N		C	N	A	R								A	S	N	F										X	J	12	11 Na
12 Mg	S	N				A	R	V			I		E		A	S	N	F				G						X	J	14	12 Mg
13 Al	S	N				A	R	V			I	W			A	S	N	F				G						X	J	14	13 Al
14 Si											I						N	F				G						X		5	14 Si
15 P	S	N													A	S	N	F				G				Z	C	X	J	11	15 P
16 S																		F												1	16 S
17 Cl							R										N													2	17 Cl
18 Ar	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	18 Ar
19 K	S	N	U	C		A	R	V			I	W	E		A	S	N	F				G						X	J	17	19 K
20 Ca	S	N				A	R	V			I	W	E		A	S	N	F				G						X	J	15	20 Ca
21 Sc	S	N	U	C	N	A	R				I	W			A		N	F							M				J	14	21 Sc
22 Ti	S	N				A	R	V					E		A	S	N	F				G				Z	C	X	J	15	22 Ti
23 V	S	N	U	C		A	R				I	W	E	G	A	S	N	F		I		G			M	Z	C	X	J	21	23 V
24 Cr	S	N	U	C	N	A	R	V	B	O	I	W	E	G	A	S	N	F	P		E	G	U	T	M	Z	C	X	J	28	24 Cr
25 Mn	S	N	U	C	N	A	R	V	B	O	I	W	E		A	S	N	F	P			G	U		M	Z	C	X	J	25	25 Mn
26 Fe	S	N	U	C	N	A	R	V	B	O	I		E		A	S	N	F	P			G				Z		X	J	21	26 Fe
27 Co	S	N	U	C	N	A	R		B	O	I	W	E	G	A	S	N	F	P	I	E	G	U	T	M	Z	C	X	J	28	27 Co
28 Ni	S	N	U	C	N	A	R	V	B	O	I	W	E	G	A	S	N	F	P			G	U	T	M	Z	C	X	J	27	28 Ni
29 Cu	S	N	U	C	N	A	R	V	B	O	I	W	E	G	A	S	N	F	P	I	E	G	U	T	M	Z	C	X	J	29	29 Cu
30 Zn	S	N	U	C	N	A	R	V	B	O	I	W	E	G	A	S	N	F	P	I	E	G	U	T	M	Z	C	X	J	29	30 Zn
31 Ga	S						R						E		A															4	31 Ga
32 Ge																														0	32 Ge
33 As	S	N	U	C	N	A	R		B	O	I	W	E		A	S	N	F	P		E		U				C	X	J	22	33 As
34 Se	S	N				A	R																						J	5	34 Se
35 Br				C	N		R										N												J	5	35 Br
36 Kr	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	36 Kr
37 Rb				C	N		R	V					E		A		N	F			E					Z			J	11	37 Rb
38 Sr	S	N				A	R	V			I	W	E		A		N	F			E	G	U			Z		X	J	17	38 Sr
39 Y	S	N						V		O			E	G	A		N	F			E	G			M	Z		X		14	39 Y
40 Zr	S					A	R	V		O			E		A		N	F			E	G				Z		X	J	14	40 Zr
41 Nb	S	N						V		O					A		N				E	G	U			Z		X		11	41 Nb
42 Mo	S	N	U	C	N		R			O	I	W	E				N	F				G	U				C		J	16	42 Mo
43 Tc																														0	43 Tc
44 Ru																													J	1	44 Ru
45 Rh																														0	45 Rh
46 Pd																S		F												2	46 Pd
47 Ag		N	U		N	A	R			O			E		A		N					G			M		C	X	J	14	47 Ag
48 Cd				C								W	E	G					P			G						X	J	8	48 Cd
49 In																														0	49 In
50 Sn		N				A		V		O		W	E	G	A		N			I	E	G	U		M	Z	C	X		17	50 Sn

Table 2-2 *Elements analysed in large surveys.*

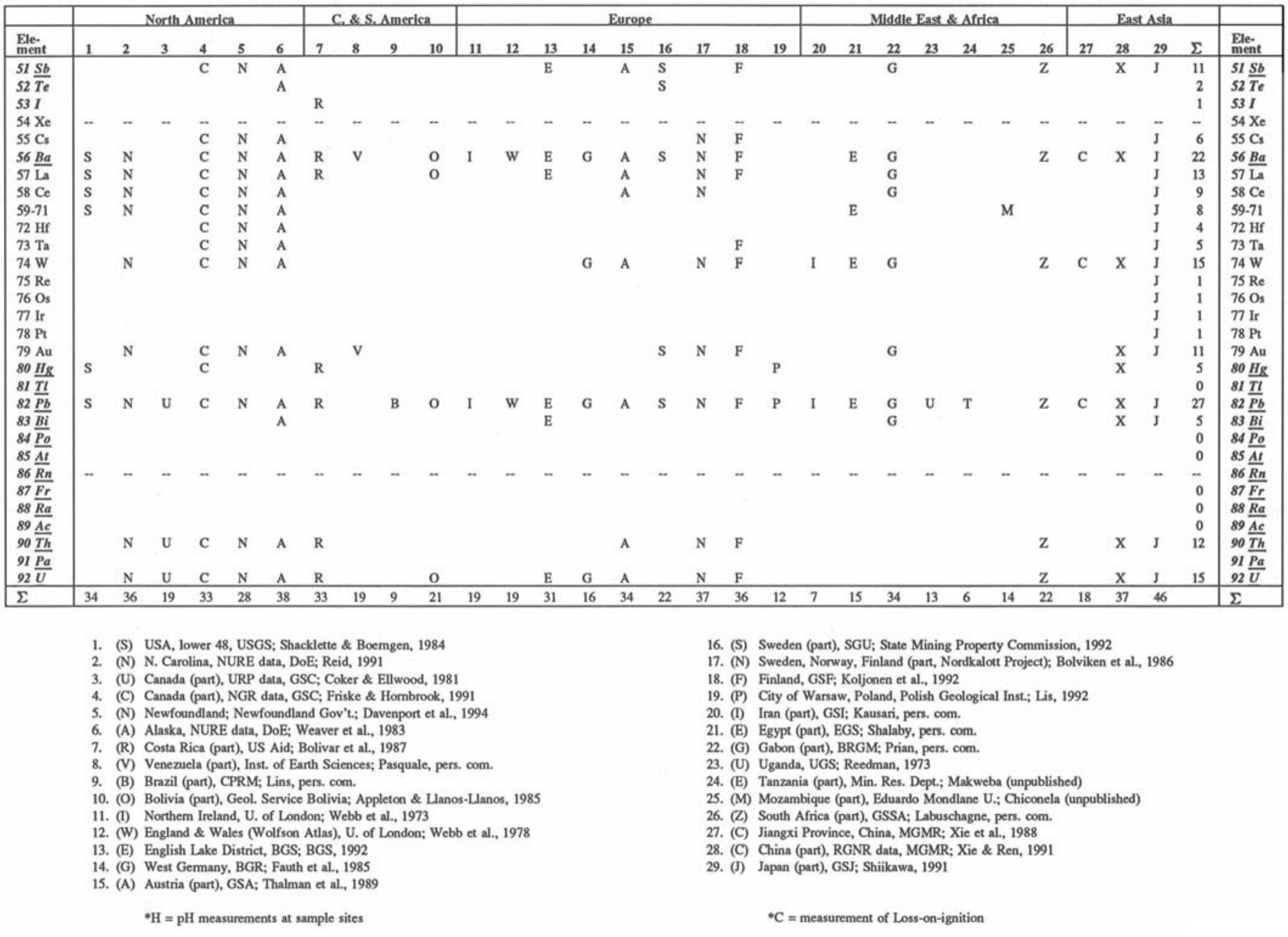
2.5 Organization of the project and authorship of the report

Support for the present project, has been obtained through the UNESCO/International Union of Geological Sciences' International Geological Correlation Program. This enabled the International Geochemical Mapping (IGM) project to commence in 1988. The outcome is contained in this report, which is the product of research and discussions amongst a group of geochemists, mostly from China, Western Europe, North America and Russia, over a 5 year period.

In order to meet the project's objectives the task was organized on the basis of scientific and technical specialization, with an overlapping regional committee structure to take into account geographic considerations. The principal contributions to the present report have been made by the former group. Five technical committees have reviewed the state-of-the-art, conducted research and prepared recommendations for the following activities:

1) Field methods;
2) Analytical methods;
3) Data management;
4) Radioelement (gamma radiation) methods; and
5) Global sampling.

Their work forms the core of this publication. The principal financial support for this project has been provided by the employers of the participants (listed in Section 12.2) who have allowed time to be spent and covered travel expenses. Research that has taken place in relation to this project has been largely undertaken as part of existing institutional programs which, outside Fennoscandia and China, have been mainly restricted to short-term national requirements. Funding from UNESCO/IUGS has enabled participants from soft-currency countries to participate in meetings, but has not supported any scientific investigations.



	North America						C. & S. America				Europe									Middle East & Africa							East Asia				
Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	Σ	Element
51 Sb				C	N	A							E		A	S		F				G				Z		X	J	11	*51 Sb*
52 Te						A										S														2	*52 Te*
53 I							R																							1	*53 I*
54 Xe	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	54 Xe
55 Cs				C	N	A											N	F											J	6	55 Cs
56 Ba	S	N		C	N	A	R	V		O	I	W	E	G	A	S	N	F			E	G				Z	C	X	J	22	*56 Ba*
57 La	S	N		C	N	A	R			O			E		A		N	F				G							J	13	57 La
58 Ce	S	N		C	N	A									A		N					G							J	9	58 Ce
59-71	S	N		C	N	A															E				M				J	8	59-71
72 Hf				C	N	A																							J	4	72 Hf
73 Ta				C	N	A												F											J	5	73 Ta
74 W		N		C	N	A								G	A		N	F		I	E	G				Z	C	X	J	15	74 W
75 Re																													J	1	75 Re
76 Os																													J	1	76 Os
77 Ir																													J	1	77 Ir
78 Pt																													J	1	78 Pt
79 Au		N		C	N	A		V								S	N	F				G						X	J	11	79 Au
80 Hg	S			C			R												P									X		5	*80 Hg*
81 Tl																														0	*81 Tl*
82 Pb	S	N	U	C	N	A	R		B	O	I	W	E	G	A	S	N	F	P	I	E	G	U	T		Z	C	X	J	27	*82 Pb*
83 Bi						A							E									G						X	J	5	*83 Bi*
84 Po																														0	*84 Po*
85 At																														0	*85 At*
86 Rn	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	*86 Rn*
87 Fr																														0	*87 Fr*
88 Ra																														0	*88 Ra*
89 Ac																														0	*89 Ac*
90 Th		N	U	C	N	A	R								A		N	F								Z		X	J	12	*90 Th*
91 Pa																															*91 Pa*
92 U		N	U	C	N	A	R			O			E	G	A		N	F								Z		X	J	15	*92 U*
Σ	34	36	19	33	28	38	33	19	9	21	19	19	31	16	34	22	37	36	12	7	15	34	13	6	14	22	18	37	46		Σ

1. (S) USA, lower 48, USGS; Shacklette & Boerngen, 1984
2. (N) N. Carolina, NURE data, DoE; Reid, 1991
3. (U) Canada (part), URP data, GSC; Coker & Ellwood, 1981
4. (C) Canada (part), NGR data, GSC; Friske & Hornbrook, 1991
5. (N) Newfoundland; Newfoundland Gov't.; Davenport et al., 1994
6. (A) Alaska, NURE data, DoE; Weaver et al., 1983
7. (R) Costa Rica (part), US Aid; Bolivar et al., 1987
8. (V) Venezuela (part), Inst. of Earth Sciences; Pasquale, pers. com.
9. (B) Brazil (part), CPRM; Lins, pers. com.
10. (O) Bolivia (part), Geol. Service Bolivia; Appleton & Llanos-Llanos, 1985
11. (I) Northern Ireland, U. of London; Webb et al., 1973
12. (W) England & Wales (Wolfson Atlas), U. of London; Webb et al., 1978
13. (E) English Lake District, BGS; BGS, 1992
14. (G) West Germany, BGR; Fauth et al., 1985
15. (A) Austria (part), GSA; Thalman et al., 1989
16. (S) Sweden (part), SGU; State Mining Property Commission, 1992
17. (N) Sweden, Norway, Finland (part, Nordkalott Project); Bolviken et al., 1986
18. (F) Finland, GSF; Koljonen et al., 1992
19. (P) City of Warsaw, Poland, Polish Geological Inst.; Lis, 1992
20. (I) Iran (part), GSI; Kausari, pers. com.
21. (E) Egypt (part), EGS; Shalaby, pers. com.
22. (G) Gabon (part), BRGM; Prian, pers. com.
23. (U) Uganda, UGS; Reedman, 1973
24. (E) Tanzania (part), Min. Res. Dept.; Makweba (unpublished)
25. (M) Mozambique (part), Eduardo Mondlane U.; Chiconela (unpublished)
26. (Z) South Africa (part), GSSA; Labuschagne, pers. com.
27. (C) Jiangxi Province, China, MGMR; Xie et al., 1988
28. (C) China (part), RGNR data, MGMR; Xie & Ren, 1991
29. (J) Japan (part), GSJ; Shiikawa, 1991

*H = pH measurements at sample sites

*C = measurement of Loss-on-ignition

Table 2-2 *Elements analysed in large surveys. (continued)*

The recommendations are the product of 15 meetings over a 5 year period involving scientists from 40 countries. They are based on discussions amongst members of the steering and five technical committees, influenced by discussions with other scientists at international meetings where IGCP 259 workshops were held. As part of the process of obtaining a consensus on the requirements for international geochemical mapping, about 100 papers and posters on matters relating to methods and applications have been presented at meetings and published as abstracts. Approximately half have been published in full, with the principal collections contained in the Journal of Geochemical Exploration, volumes 39, 44, 47 and 49, and the Transactions of the Institution of Mining and Metallurgy, vol. B100. The IAEA has published two reports relating to gamma ray methods for radioelements (IAEA 1990, 1991). Chapter 7 of this report is, in part, a condensed version of one of these. A collection of research reports centred around overbank sampling has been published by the Geological Survey of Norway on behalf of West European Geological Surveys (Bølviken et al., 1990; Demetriades et al., 1990). Brief excerpts from some of these contributions are contained in Section 12.3.

The principal contributors to this report, listed alphabetically, are: A.J. Björklund, Finland, leader Global Sampling Committee; B. Bølviken, Norway, leader Fennoscandian Regional Committee; A.G. Darnley, Canada, Project Leader and Steering Committee chairman; N. Gustavsson, Finland, leader Data Management Committee; P.V. Koval, Russia, co-leader (with E.K. Burenkov) Russian Regional Committee; J.A. Plant, UK, leader European Community Regional Committee; A. Steenfelt, Denmark, leader Field Methods Committee; M. Tauchid, IAEA, leader Radiometric Methods Committee; Xie Xuejing, China, leader Analytical Methods Committee and Chinese Regional Committee. These individuals have participated in the extended discussions held by the Steering Committee between 1988 and 1994, and in the respective Technical Committees, as indicated below. Others who have participated in the discussions of the various Technical Committees, or otherwise made valuable contributions to the preparation of this report are also listed below. First drafts of Chapters 4 to 8 of this report were prepared by the respective technical committees. The first drafts of the other chapters were prepared by the Project Leader. In order to achieve a reasonable level of consistency with respect to philosophy and methodology, all were reviewed by the full Steering Committee and subjected to iterative revision and editing over a period of 18 months. Final editing has been undertaken by the Project Leader with valuable assistance from R.G. Garrett and J.A. Plant.

Global sampling committee (Chap.4): **A. J. Björklund, Finland**; B. Bølviken, Norway; N. Gustavsson, Finland; A. Steenfelt, Denmark; Xie Xuejing, China.
Field methods committee (Chap. 5): **A. Steenfelt, Denmark**; M. Duris, Czech Republic; R. Hindel and G. Matheis, Germany; J.A. Plant, UK; R.E. Smith, Australia.

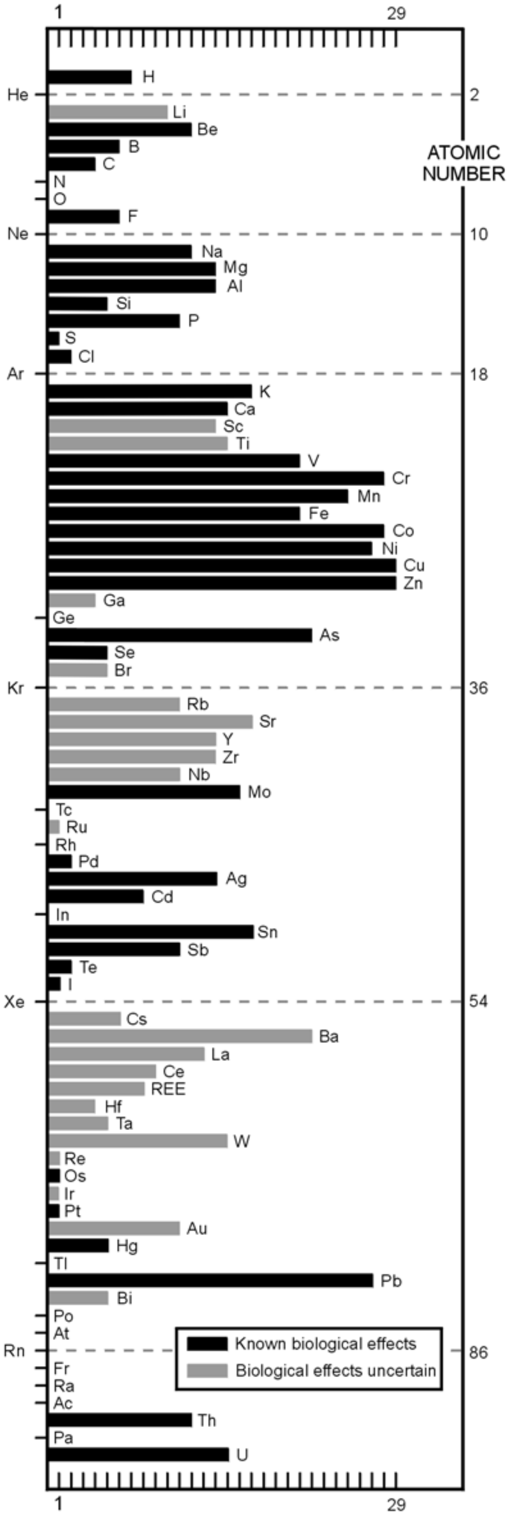


Figure 2-6 *Number of surveys in which an element has been determined. Elements identified according to biological effects.*

from Table 2-2

Analytical methods committee (Chap.6): **Xie Xuejing, China**; G.E.M. Hall, Canada; D.L. Miles, UK.
Radioactive methods committee (Chap.7): **M.Tauchid, IAEA**; A.G.Darnley, Canada; A.Y.Smith, IAEA (to 1990).
Data management committee (Chap. 8): **N. Gustavsson, Finland**; C.Y. Chork (until 1991), Australia; R.G. Garrett, Canada; E. Grunsky (since 1992), Canada; B. Kogan, Russia.

The contribution of František Mrňa (died August 1992) of Czechoslovakia, one of the project's founding participants must be acknowledged. He organized a conceptually productive symposium in Prague in 1990, with international geochemical mapping as a major theme. Valuable conceptual assistance regarding several aspects of the project has been provided by R.G. Garrett, Canada. M.J. Gallagher, UK, provided constructive criticism of the whole. G.E.M. Hall contributed the text of a comprehensive review paper. J.C. Davis, USA; J.A.C. Fortescue, Canada; D.L. Miles, UK; P. Noras, Finland; P.R. Simpson, UK and K.A. Viewing, Zimbabwe, have provided pertinent advice with respect to specific chapters. Names and addresses of supporting institutions are given in Section 12-2.

2.6 Future progress

The International Geochemical Mapping project has now entered Phase 2, entitled Global Geochemical Baselines, which is supported as IGCP project 360 until 1997. A parallel organizational structure exists through the International Association of Geochemistry and Cosmochemistry Working Group on Global Geochemical Mapping, which has an open-ended time frame, but negligible funding. Many of the recommendations contained in this report, especially those relating to standardization of field and analytical methods, data management and quality control, are designed and are suitable for early adoption by both national and international institutions. Some could be applied immediately, others might require procurement of suitable equipment. However, it must be strongly emphasized that the establishment of a global geochemical reference network cannot proceed far without:

(1) endorsement of the ensuing recommendations by the international scientific community;
(2) the availability of funding for coordination and operations.

Given sufficient priority and support, this task could be accomplished by 2005.

As with other activities relating to the global environment, which require the coordinated use of expensive laboratory facilities, ships, aircraft or satellites, with related implications for long-term data and sample storage, the establishment of a global geochemical database cannot be pursued very far by a rather informal, loosely organized, inadequately funded group of scientists, irrespective of their personal abilities, enthusiasm and dedication. These essential matters are further discussed under the heading of Implementation, in Chapter 10. Readers who are not closely concerned with the detailed scientific and technical considerations underlying this report may wish to proceed directly to that chapter.

2.7 Acknowledgments

The Royal Society of London has provided generous funding to support the publication of this report, allowing the inclusion of colour plates showing examples of recent national and international geochemical map compilations, some produced specifically because of the existence of IGCP 259.

The British Geological Survey, the Geological Survey of Canada, the Geological Survey of Finland, the Institute of Geophysics and Geochemistry (China), the Los Alamos National Laboratory (USA), the Newfoundland Geological Survey (Canada), and the United States Geological Survey are the sources of the original digital data from which the colour plates have been derived.

3 Sampling and Global Mapping: A Review

3.1 Introduction

The assembly of a global geochemical database depends upon systematic geochemical mapping, which in turn is dependant upon the integration of several specializations. Internationally, and too often nationally, there has been and still is unnecessary diversity in the various parts of the process. Many approaches have been used over the past 25 years, sometimes designed for the purpose of optimizing results for particular elements in a particular region, often determined by the limitations of available funds and facilities. Consequently there has been great diversity in the products.

Given the perceived importance of obtaining a consistent global database as rapidly as possible, the steering committee for the IGM project identified the need for much greater standardization of the geochemical mapping process as one of its primary concerns. Therefore all aspects of the activity have been reviewed, and a number of research studies undertaken, in order to reach a consensus on methodologies for multi-purpose mapping.

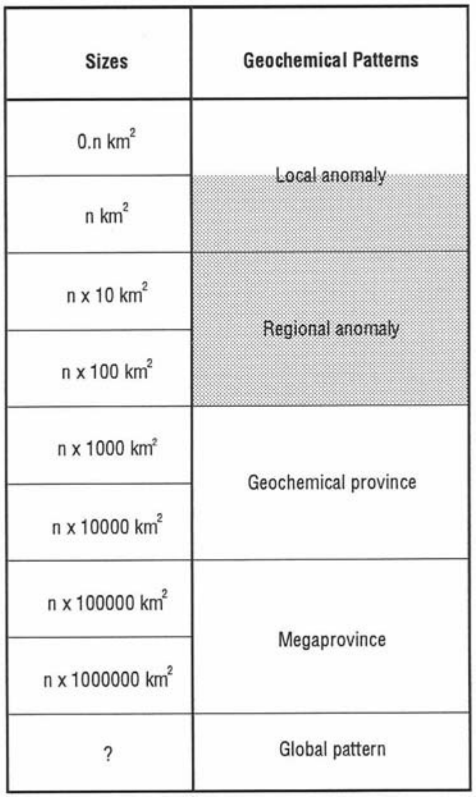
The selection of appropriate sampling media and procedures has been identified as the most crucial decision-area in the context of international geochemical mapping, and therefore it has received the most attention. In order to benefit from standardization at later stages in the mapping process, it is necessary that the various sample media collected conform to accepted specifications. Samples can be reanalysed, data recompiled and displayed in many formats (provided they are held in digital form), but it is frequently impractical to recollect samples. In most circumstances, sampling is the most expensive and time consuming part of geochemical mapping, especially in remote areas. It is also the most difficult part of the process to standardize and monitor. For these reasons this chapter focusses on aspects of sampling, namely the selection of sample media, the considerations affecting sample spacing, the need for a standardized global reference network, and the reliability and representivity of the sampling process.

In the late 1950s it would probably have been relatively simple to establish sampling methods to prepare a world geochemical atlas, since geochemical mapping was carried out almost exclusively for exploration purposes and the minus 80 BSI (177 micron) fraction of active sediment from tributary streams or surface soils was used routinely, for example, in surveys carried out in Canada (Boyle, 1967), the United States (Hawkes, 1957) and Africa (Webb and Tooms, 1959). Since that time, methods have tended to become more specialized, making the selection of appropriate sampling procedures more difficult. In exploration geochemistry a great deal of work has gone into the development of methods for particular metals in particular surface environments. For example, in the case of gold, specific sampling and analytical procedures have been developed for different types of terrain, including glaciated (Nichol, 1986; Dunn et al., 1991), arid (Fletcher, 1985; Bogoch et al., 1993), and tropical terrain (Watters et al., 1991; Andrade et al., 1991). Biogeochemical (Dunn, 1991) and other techniques such as termite-mound sampling, first applied in the early 1950s, have been reexamined and developed (Watson, 1972; Gleeson and Poulin, 1989). Such techniques generally have limited geographical range and may not be suitable for multi-element mapping. They are intended for the identification of local anomalies according to the classification of Xie and Yin (1993), and so they are not considered further in this review.

Considerable effort has been expended on the development of methods suitable for wide-spaced sampling (1/1000 km^2 to 1/25 000 km^2), primarily to accelerate the rate at which reconnaissance coverage can be obtained over large regions. Some of the earliest work investigating the utility of relatively wide-spaced sampling was undertaken in the 1960s, by Garrett and Nichol (1967) in West Africa and Armour-Brown and Nichol (1970) in Central Africa. During the life of the current project studies on this topic have been reported by Bølviken et al., 1990; Björklund, 1992; Xie, 1990; and Garrett, 1994. The resulting availability of geochemical data over large regions has demonstrated the existence of large-scale geochemical provinces and patterns, (see Plates 3-2, 3-3, 3-6 and 3-7). Although these were anticipated, given the large, continental-scale, geophysical patterns that can be seen in aeromagnetic and gravity map compilations from, for example, N.America (GSA, 1987a, b), they confirm that the dimensions of geochemical phenomena are an important consideration with respect to:

(1) the amount of on-the-ground-data, i.e. sampling density, required to recognize them;
(2) the scale at which useful geochemical information can be displayed.

It has been known since the 19th century that the major element composition of the continents is different from the major element composition of the ocean floor, but it is only within the last decade that data have been compiled over sufficiently large continental areas to demonstrate that both major and trace element distribution exhibit large as well as small-dimension patterns (see Fig.3-1, from Xie and Yin). For a recent discussion on the fractal nature of geochemical landscapes, see Bølviken at al., (1992). Examples of large-dimension geochemical features, (extending hundreds or even thousands of km) have been found in China (Xie and Yin, 1993), Fennoscandia (Gustavsson et al., 1994; Edén and Björklund, 1993, 1994), Canada (Garrett et al., 1990) and the USA (Duval, 1991; also Gustavsson, 1994, based on Shacklette and Boerngen, 1984). Unfortunately, because in many regions data are limited to scattered small areas (and the data are often incompatible) there is insufficient information over most of the world to permit large features to be recognized or their continuity to be traced.



Sizes	Geochemical Patterns
$0.n\ km^2$	Local anomaly
$n\ km^2$	
$n \times 10\ km^2$	Regional anomaly
$n \times 100\ km^2$	
$n \times 1000\ km^2$	Geochemical province
$n \times 10000\ km^2$	
$n \times 100000\ km^2$	Megaprovince
$n \times 1000000\ km^2$	
?	Global pattern

Figure 3-1 *Classification of geochemical patterns according to size of feature. Shaded region relates to scales discussed in Chapter 5.*

from Xie and Yin, 1993

Wide-spaced sampling has caused some controversy, since misinterpretations of the significance of the resulting patterns have been made. In the UK, for example, a “high heat flow province” in northern Britain proposed by Richardson and Oxburgh (1978) was found to be related to the spurious linking of isolated anomalies relating to two or three granites (Brown et al., 1987). Simulations such as those of Ridgway et al. (1991) and Fordyce et al. (1993) also indicate that whereas stable large-scale patterns can be generated by progressively averaging high-density geochemical data, low-density sampling of high-density data representing small areas can generate misleading patterns when employed at broader scales. However, the fact that there are geochemical patterns at many scales is illustrated by Plate 3-1, which shows the distribution of a heavy metal (Ni) in a mineral grain a few a microns across, alongside the distribution of another heavy metal (Cu), in a volcanic island 25 km across. In the absence of a scale, these subjects which are 10 orders of magnitude apart in size, could easily be confused! (Different metals are displayed in this illustration to take advantage of good images; other elements exhibit similar patterns). Thus, sample spacings should be related to the size of object that is to be studied. Provided that wide-spaced data representing appropriately sized areas are used primarily for reconnaissance purposes, to indicate where more detailed investigations are required, such surveys have a critical role in providing a continental or global scale geochemical overview, and in providing a reference framework for regional surveys (see Chapter 4). The remainder of this chapter is concerned with sample media and sample spacing in this context. Chapter 5 also covers many of the same topics, but from the perspective of more detailed national and regional surveys.

3.2 Sample media

In order to be useful, a global database must describe readily obtainable sample media with broad significance. It is important to point out a distinction between multi-purpose geochemical mapping, which is the objective of this international project, and geochemical mapping undertaken for a specific purpose such as mineral exploration. In the latter application deliberate efforts are often made to select a sample medium (e.g., the B horizon in soil), or a size or density fraction in a stream sediment, in which elements of economic interest will show the greatest contrast between mineralized and unmineralized areas, in order to maximize the probability of finding a particular type of mineral deposit. The medium or fraction thus selected may under-represent other elements present in the vicinity.

For general reference purposes, comparable, representative data are needed from all parts of the world. With this in mind the following sample media have been considered, listing first those which have the most widespread application.

(1) Regolith materials. The regolith, including all soils, *sensu lato*, both residual and transported, is the surface sampling media which is most readily available. Because vegetation is rooted in it, and groundwater drains through it, this medium has great significance to all life on this planet (Fyfe, 1989). The most areally extensive geochemical surveys in existence are based on regolith sampling, using either conventional laboratory analysis, e.g., Shacklette et al., 1971, 1984 (see Plate 3-2); Tidball and Severson, 1976; Garrett, 1994, or airborne gamma ray spectrometry as the analytical technique. Airborne gamma ray spectrometry, has provided detailed coherent data over large areas, from Greenland and North America to the equatorial regions of S.America, Africa and S.E.Asia (Darnley and Ford, 1989; Darnley, 1993). Residual soils provided some of the earliest successes for mineral exploration geochemistry and there is much literature on the subject. Recent textbooks reviewing the use of regolith materials for exploration geochemistry in all climatic zones are Kauranne et al., (1992) and Butt and Zeegers (1992).

Regolith materials which have been transported include alluvial soils in the form of overbank and floodplain sediments and also glacial till. These are considered under separate headings.

(2) Overbank and floodplain sediments are a category of regolith materials which have received special attention during the project, stimulated by studies in Norway (Ottesen et al., 1989). Valley alluvium has been employed as a sample medium for detailed exploration work in France for some years (Roquin and Zeegers, 1987; Zeegers, pers. com.). In China a regolith survey, with many sampling sites located on alluvial floodplains, has been used to produce a geochemical overview of China (see Plate 3-3; Xie and Yin, 1993). Overbank sampling has been the subject of considerable research in Europe under the West European Geological Surveys (WEGS) Working Group on Regional Geochemical Mapping (Bølviken et al., 1990; Edén and Björklund, 1994). This sampling medium, as with lake sediments, can provide a time-section with depth but research has indicated that the history of overbank material may be complex and considerable work may be required to determine the detailed chronology of events at each site.

It should be noted that for the purpose of this report it is deemed advantageous to make a distinction between overbank and floodplain sediments. Both are alluvial sediments, but it is consistent with definitions in the Glossary of Geology (Bates and Jackson, 1980) to employ the term overbank sediment for alluvium accumulated adjacent to low-order streams (where stream sediment samples may be collected) and floodplain sediment to alluvium adjoining high-order drainage channels, typically large rivers. *The significance of this distinction from a geochemical mapping viewpoint is that overbank samples represent small drainage basins, whereas floodplain samples represent much larger basins. The former are relevant to national mapping programs, the latter are significant at a continental or global scale, where it is preferable that samples are geochemically representative of a large proportion of the surface.*

(3) Water, which because of the expanding world population is an increasingly valuable natural resource, is essential to all life and a key component of any geochemical database concerned with surface materials. For a recent pilot study concerned with hydrogeochemistry see Simpson et al. (1993) and Edén and Björklund (1993).

(4) Stream sediments. Wherever the landscape permits, stream sediments have been the preferred sampling medium for reconnaissance geochemical surveys concerned with mineral exploration. The samples, if properly collected, represent a composite of materials from the drainage basin upstream of the collection site. Government-sponsored reconnaissance surveys covering, for example, large parts of Austria, the Canadian Cordillera, China, Germany, South Africa, UK, and USA have been based on stream sediments. Stream sediments provide good sensitivity for many heavy metal trace elements, but the medium has been relatively neglected by scientists concerned primarily with environmental questions. Plate 3-4 is a compilation for Northern Britain showing Cu in stream sediments, obtained from detailed survey data (1 sample/2 km^2). Copious documentation and numerous scientific publications relate to the use of stream sediments in exploration geochemistry. For a review of stream sediment methods see Plant and Hale, (1994).

(5) Lake sediments can be substituted for stream sediments in recently glaciated areas with poorly developed drainage, for example the Canadian Shield. Lake sediments have the advantage that, using suitable core samplers, long-term changes in sediment composition can be detected. However, as with till, which is discussed in the following paragraph, lake sediment sampling is effectively confined to (some, not all) parts of the world covered by the Pleistocene glaciation. Elsewhere lakes are not sufficiently numerous to allow for representative regional coverage. Plate 3-5 is a map showing As in lake sediments from the Island of Newfoundland (1 sample/6.5 km^2; Davenport et al., 1994). For a recent review of methods see Davenport et al. (1993).

(6) Till. Till is a regolithic material. Till sampling has been used very effectively for geochemical mapping in Finland and Sweden. It has been used to produce a geochemical atlas of Finland, and also geochemical compilations covering Finland and large parts of Sweden. However, till, being the product of geologically recent glacial erosion, is geographically restricted in its extent and so, as with lake sediments, can only be used in certain regions. Plate 3-6 is a map showing P distribution in till, across Finland and adjoining parts of Sweden (Gustavsson et al., 1994). For a comparison of results obtained in the Fennoscandian Nordkalotte project, which employed till and other media, see Steenfelt (1993a).

(7) Biogeochemical sampling. The possibility of using specific botanical species has received careful consideration over the duration of the project. For a recent review in the context of the project see Dunn (1991). Based on the present evidence that:

- individual plant species are selective in their uptake of elements;
- only a small number of species have a wide regional distribution;
- there is seasonal variability in trace element content;
- sample collectors require botanical training:

biogeochemical sampling based on selected species is considered unsuitable as a general-purpose global multi-element mapping method despite its effectiveness in some exploration situations. However, collection and analysis of surface humus derived from an assemblage of vegetation provides a pointer to bioavailability of elements at each sampling site and this is considered to be useful information.

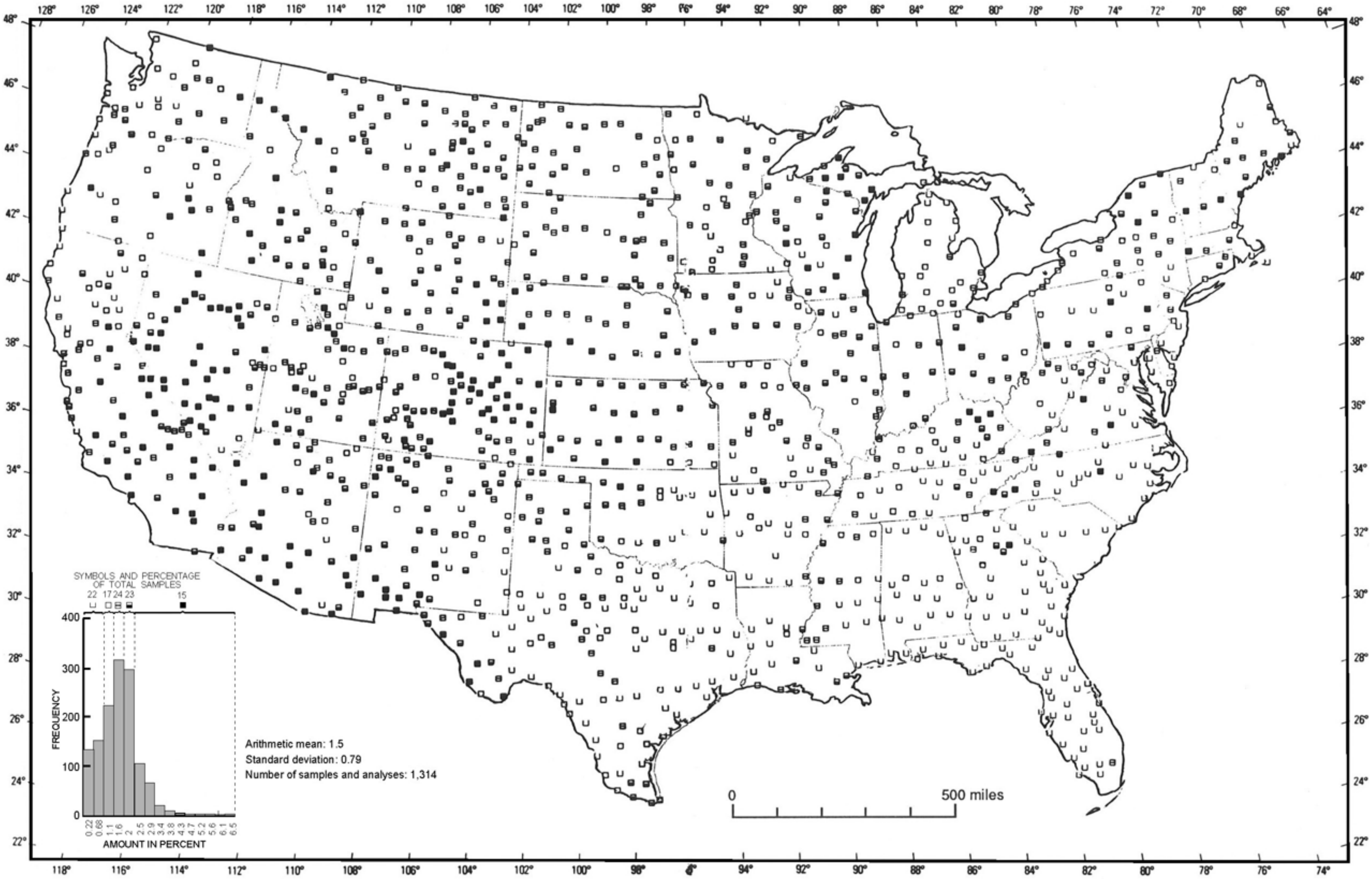


Figure 3-2 *Shacklette's sampling pattern for the regolith of the USA. This map shows 1314 sites sampled for potassium analysis. The analytical data were used to produce Plate 3-2.*

from Shacklette and Boerngen, 1984

It should be noted that gamma ray methods are important in the context of regolith sampling because they possess some unique advantages, namely the ability to monitor radioactivity and provide data immediately from *in situ* or mobile measurements. Gamma-ray spectrometry is a method which identifies and quantifies radioactive elements (natural and man-made) in (or on) the surface layer of the ground. The radioelement content of the regolith can be sampled effectively from a moving vehicle. Airborne gamma ray spectrometry is applicable over any type of land surface however difficult the ground access (see Plate 3-7). It can provide a continuous quantitative profile across any sequence of surfaces, whatever their composition (residual or transported soil, sand, rock, etc). The method can thus generate inter-regional and intercontinental reference datums based on the natural radioactivity of Th and/or K (see Chapter 7). Equipment is readily standardized and can provide a quantitative estimate of the radioelement abundances within (approximately) the upper 25cm of the land surface. To relate to other soil profile descriptions, this is identified as the A_{25} layer.

Many countries which have already undertaken regional geochemical surveys have selected stream sediments as their preferred medium and so it is important to be able to relate their data to a global database which, where possible, holds data for the same medium. However, for the purpose of interlinking national, regional and local detailed surveys, where different media may be selected in order to optimize results, it is important to obtain comparable analytical data from each media in use, at common (or adjacent) sites. A statistically adequate zone of overlap is required. These matters are further discussed in the following sections.

Figure 3-3 *Sampling site locations for wide-spaced survey of China. Inset shows centres of nominal 160 x 160 km cell pattern over E. Asia. This pattern has been superseded by that shown in Figure 4-1.*

3.3 Sample spacing

Sample media and sample spacing are interrelated issues. Sample spacing is a critical consideration from both theoretical and practical points of view. From a theoretical point of view, the delineation of coarse regional patterns contributes to the understanding of large scale processes and the identification of areas deserving more detailed attention. In practical terms, wide-spaced sampling is a key factor in the attainment of international geochemical mapping because, since there are no multi-element airborne or satellite techniques, it provides the only practical way to obtain a controlled, systematic and potentially rapid overview of global geochemistry. It allows speed, economy and relative simplicity in execution, which are necessary ingredients in quality control.

It has been one of the tasks of IGCP 259 to gather evidence that wide-spaced sampling is valid and useful. Xie and Yin (1993) have pointed out that the history of geochemical exploration has been marked by a progressive expansion of the area of search and an increase in sampling interval. One consequence has been the recognition of a hierarchy of geochemical patterns, which they describe as “local to global” (Fig.3-1). Evidence that very wide-spaced sampling can provide significant data with respect to large geochemical patterns has accumulated almost accidentally, from unconnected investigations in the USA and China, which were not designed to find such features. Shacklette et al. (1971, 1984) conducted very wide-spaced sampling of the regolith of the conterminous USA for the purpose of obtaining data on mean element abundances. Data were plotted as maps, with symbols marking the point of collection (see Fig.3-2). In 1993, as a contribution to IGCP 259 by the Geological Survey of Finland, these data were gridded, contoured and colour plotted in order to examine their coherence and allow comparison with other known features (Gustavsson, 1994, see Plate 3-2). Recently one component in this dataset (K) has been compared with independently derived and much more detailed airborne gamma ray spectrometry data (see Plate 3-7, Duval, 1990). Considering the methodological differences, and vast difference in the number of data points, the results are in good numerical agreement, with similar gross patterns (Darnley, 1993).

At the end of 1990, maps showing the variation of 49 elements in soil, *sensu latu*, (i.e. regolith) over the whole of China (9 600 000 km^2) were compiled as the result of cooperative research by several Chinese institutions (Xie and Yin 1993, Zheng 1992, see Plate 3-3). The average sampling density over all of China was 1 site per 2300 km^2 ranging from 1/1600 km^2 in the densely populated east to an average of 1/6400 km^2 in remote areas (see Fig. 3-3). Coherent patterns were revealed by this wide-spaced sampling (see Plate 3-3), which appear to be explicable in terms of the more detailed information that is available for selected regions (Xie and Yin, 1993).

Research undertaken as part of IGCP 259 by Bølviken, Garrett, Xie, Eden and Björklund, and others (see references) leads to the conclusion that for the purpose of obtaining representivity in the sampling of large areas, there are two choices. The first is to use materials (e.g. floodplain sediment) which provide a natural composite sample from large source areas, and the second is to use materials (e.g. low-order stream sediments, or residual soil) from smaller source areas, where the sampling pattern is either very dense or must be statistically designed to provide a result approximating to a large composite sample. A radiometric (e.g., gamma ray) profile is a variant of the dense sampling approach, with successive overlapping regolith samples along the line of traverse. Till and lake sediment samples are typically intermediate in the size of source area they represent.

The following table summarizes experiments and surveys relating to wide-spaced sampling which have been conducted over large areas, in some instances by collecting few samples, (Shacklette et al., 1984; Xie and Yin, 1993; Garrett, 1994) in others by manipulating existing data sets (Garrett et al., 1990; Davenport and Nolan, 1991; Fordyce et al., 1993). This work has shown that large and sometimes unanticipated geochemical features can be delineated by sampling at the following densities:

1 per 23 000 km^2 (water and overbank sediments, Fennoscandia; Edén and Björklund, 1993, 1994);
1 per 6000 km^2 (regolith, USA; Shacklette and Boerngen, 1984);
1 per 1600 km^2 (regolith, China; Xie and Yin,1993);
1 per 800 km^2 (regolith, N.American prairies; Garrett, 1994);
1 per 625 km^2 (lake sediments, Labrador/Quebec; Garrett et al., 1991);
1 per 400 km^2 (lake sediments, Newfoundland; Davenport and Nolan, 1991);
1 per 300 km^2 (till sampling, Finland; Koljonen, 1992).

The fact that these sample densities have produced intelligible information should not be construed as indicating that it would not be advantageous in every instance to employ a considerably higher sampling density. More detailed information at a reconnaissance stage facilitates the planning of follow-up investigations, can eliminate some false trails and identify some small features that might otherwise be overlooked. Decisions as to sample density need to be made in relation to the level of information required.

In addition to the above, several publications from the 1970s and subsequently (Darnley et al., 1975; Cameron et al., 1976; Mellander, 1989) have illustrated the resolution provided by airborne radiometric surveys at different line spacings. Useful results have been demonstrated for regional reconnaissance purposes at up to 30 km line spacing (Hetu, 1992). In the absence of other information, single profiles have revealed the

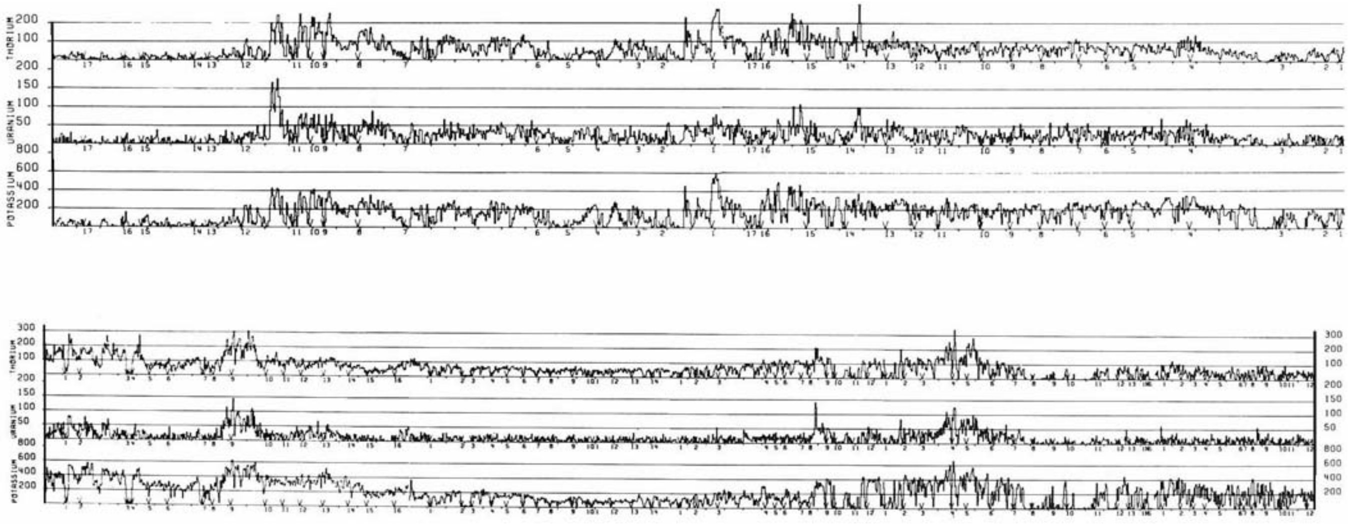


Figure 3-4 *Examples of regolith profiles across the Canadian Precambrian Shield by airborne gamma ray spectrometry; corrected data.*

upper: 450 km along 94°W meridian from (left hand end) Gods River, Manitoba (Lat. 55°N) to Red Lake, Ontario (Lat. 51°N).

lower: 570 km from Uranium City, Saskatchewan (left hand end) (59.5°N, 108.5°W) to Lynn Lake, Manitoba (57°N, 101°W).

Count Rates, shown in margin can be converted to element concentrations as follows:

potassium channel, 125 counts = 1 per cent K

uranium channel, 20 counts = 1ppm eU

thorium channel, 8 counts = 1ppm eTh

from Darnley et al., 1971

presence of unexpected large anomalies, many tens of km across, as shown in Fig. 3-4, from Darnley et al. (1971). For later commentary on these features see Darnley (1981,1988). It should be noted that airborne measurements always provide a continuous profile along the line of flight; as line spacings are increased the continuity of particular features from line to line becomes less certain. As with any method, increasing the sampling interval results in failure to detect small features, combines and distorts the shape of large ones and renders interpretation more tenuous. As previously noted, Fordyce et al.(1993) have experimented with detailed geochemical mapping data from N. Britain and illustrated the non-representivity that is the consequence of increasing sample spacing between samples which represent only a very small proportion of the total area surveyed. However, in many parts of the world, the alternative to wide-spaced (and spatially poorly resolved) data is no data at all, possibly for a long time into the future. In this situation, the IGCP 259 Steering Committee is of the opinion that sparse but reliable and representative data are a significant advance on zero information, and are valuable in identifying regions which require closer attention. Sparse but reliable data will also assist in normalizing data from regions which have already been partially mapped by a variety of methods. Given the accumulating evidence that, as with geophysical phenomena, there are geochemical patterns with a wide range of dimensions, it is logical, practical and practicable to commence international geochemical mapping with the delineation of the larger patterns, for example, linear features longer than 500 km, or area features exceeding 100 000 km^2.

3.4 A standardized global reference network

As outlined in the previous section, there is empirical evidence that geochemical patterns can be of any size, from 10^{-n} m to 10^{n} m. Geochemical mapping is concerned with the upper part of this range. Bølviken et al. (1992) have carried out an analytical study of an area in northern Fennoscandia and concluded there is some evidence for a fractal dimension for geochemical patterns between distances of 5 km to 150 km. In the past, apart from a few experimental studies referred to in the preceding section, there has been little or no coordination of geochemical mapping at various scales. Each project has been conducted independently. One of the objectives of the IGM project is to provide a means of overcoming this problem.

It is proposed to link national and international surveys by means of a hierarchial sampling pattern based on multiples or subdivisions of a 10 × 10 km cell.

National surveys can subdivide the 10 km cell,e.g., 1, 2, or 5 km, to provide higher definition of local geochemical patterns in economically important and populated areas. For international correlation and initial reconnaissance of large areas, also for the preparation of a world atlas, a larger cell is advocated, e.g., 20, 40, 80 or 160 km (see Table 9-1 for an illustration of the relationship between sampling density and map scale).

Just as the foundation for detailed topographic surveys is provided by a primary 3-dimensional geodetic network, a comparable reference network is required for geochemical surveys. It is proposed that the highest order cell in the geochemical mapping hierarchy should be 160 × 160 km, an area of 25 600 km^2. A collection of standard reference materials is required from these cells over the entire land surface of the world as the first step in the technical implementation of the IGM project. This geochemical global reference network (GRN), based on carefully controlled sampling needs to be established to provide an inter-regional (and intercontinental) framework to which more detailed or more specialized local surveys can be related.

3.5 Reliability of the sampling process

The principal reasons for acquiring a global geochemical database is to describe the geochemical variability of the surface of the earth, both spatially and statistically. With the exception of the radioactive elements, which can be determined *in situ* by gamma ray spectrometry, sample material must be removed to a laboratory for analysis in order to ensure adequate sensitivity. It is scientifically, economically and logistically impossible, as has been stressed elsewhere in this report, to undertake more than restricted and selective sampling of the earth's surface. Therefore it is very important to establish the reliability and representivity of what is done. This particularly applies to the wide-spaced sampling implicit in the geochemical global reference network. The most widely used technique that has been employed to aid sampling design and evaluate survey data is analysis of variance (ANOVA). This technique was first applied in a geochemical context by Miesch (1964, 1967), and subsequently used by other workers (for a review see Garrett, 1983).

Analysis of variance is well suited to testing the reliability of apparent regional variations in geochemistry across a survey area by collecting samples in a random unbiased fashion. It allows the variation at different levels in the mapping process to be estimated, beginning with analytical and site replicability. If laboratory and local variability are not sufficiently small, clearly, all spatial variations over larger areas are in doubt. Analysis of variance in geochemical mapping is based on random sampling design. Commonly, stratified designs are employed, whereby the survey area is divided into cells of a pre-determined size and one or more geochemical samples are drawn from within selected cells. If the sample medium is regolith material this will normally present few problems (except in built-up areas). In the case of stream sediment or lake sampling, for example, sample site selection may not be a random operational procedure as the desired medium may be present at only one (or no) location within a cell. However, if the areal distribution of the desired sample media is random, the grid delineating the cells can be placed over the entire survey area such that there can be a haphazard, i.e., random, selection of sites containing the desired media.

The most efficient form of random stratified sampling entails what is known as an unbalanced design. This substantially reduces the number of geochemical samples to be collected and analysed. It was first applied to geochemical studies by Tidball and Severson (1976) and Ebens and McNeal (1976) in the United States. An unbalanced stratified random design has been used for sampling lake sediments in 13 km^2 cells as part of the Canadian National Geochemical Reconnaissance program. This design, which has been applied over 2 000 000 km^2 allows the components of variance at regional, 13 km^2 cell, lake and analytical levels to be monitored continuously

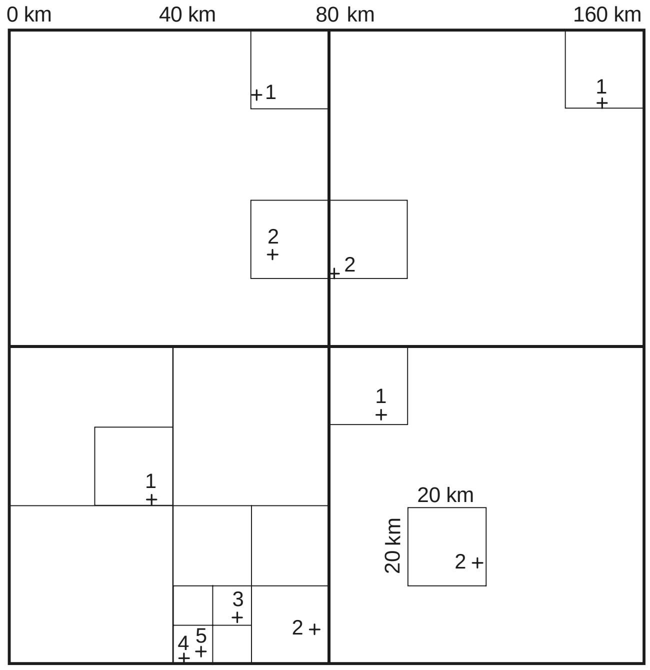


Figure 3-5 *Random sampling design for regions with easy access; unbalanced stratified design for a 2-dimensional pattern.*

Garrett, pers. com.

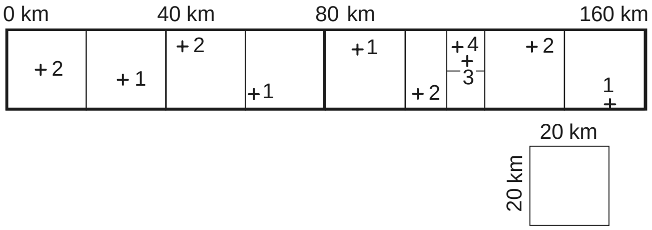


Figure 3-6 *Random sampling design for regions with difficult access; unbalanced stratified design for a corridor or profile.*

Garrett, pers. com.

(Garrett and Goss, 1979). An unbalanced stratified random sampling design has recently been employed in a soil and till survey covering 850 000 km^2 of North American prairies (Garrett, 1994). Ideally, random site-selection should be applied 2-dimensionally over an area (see Fig 3-5), but if operationally necessary it can be applied within a corridor or along a profile (see Fig. 3-6). It is anticipated that in different parts of the world both approaches will be employed.

It should be noted that in the case of gamma ray spectrometry profiles, obtained from an aircraft or vehicle, successive readings have overlapping sampling areas with centres a few tens or hundreds of metres apart, depending upon the operational parameters, along each line of traverse. As a result the reliability of individual measurements is much less critical than for conventional geochemical sampling where single samples, of necessity, have much more significance. In vehicle-mounted gamma ray spectrometry the reliability issue generally relates to the calibration of a whole profile, or a segment of a profile. Sources of uncertainty in gamma ray spectrometry are discussed in Chapter 7.

The following chapters in this report provide specific recommendations concerning the essential features of the reference network, how it should be linked into national mapping programs, and the related analytical and data management requirements to ensure consistency and quality in geochemical mapping at all scales.

4 A Global Geochemical Reference Network

4.1 Introduction

In order to produce coherent, quantitative, geochemical maps to portray the composition of the world's land surface it is necessary to establish a suitable frame of reference. Before the advent of satellites, accurate topographic mapping required the creation of a geodetic network for control purposes. A geochemical reference network (GRN) is required in order to fulfil a comparable function for geochemical mapping. As with a geodetic network, a geochemical reference network is not concerned with local detail, but the latter, as it is acquired, should be tied in to the fixed points of the network.

The geochemical reference network and the ensuing database are intended to serve several purposes:
(1) provide authoritative documentation concerning the composition of a variety of surficial materials at locations evenly spaced over the land surface of the globe;
(2) provide a supply of locally relevant standard reference materials for on-going use in the region of origin;
(3) provide reference points for normalizing national geochemical databases;
(4) provide a framework of systematic baseline data which will make possible the preparation of a WorldGeochemical Atlas;
(5) provide samples on which further work can be undertaken, e.g., to undertake isotopic analysis, speciation studies, determine organic pollutants, etc.; and
(6) provide sites for recurrent monitoring in the future, to facilitate the recognition and measurement of "change", from whatever cause.

It is self evident that all aspects of work relating to the creation and maintenance of a global reference network must be of the highest quality and consistency. Given the large number of variables entailed in geochemical mapping as currently practised in different countries and organizations, it is a matter of major concern how best to ensure the adoption and maintenance of standard specifications. Sample collection is the most critical issue. It has been identified as the most expensive, most difficult to standardize and monitor, and, once completed, most unamendable part of the geochemical mapping process. Provided that specified sample material has been collected from an appropriate location in sufficient quantity, it can be prepared, analysed and reanalysed, and the resulting data treated and compiled in many different ways.

The project will require both national and international regional co-ordinators, to make plans and provide advice and quality control for the execution of the work. Prior to sampling in any region, detailed discussions with regard to location of sample sites in the context of the required sample types must be held, making full use of local knowledge and experience. Detailed plans, including maps indicating cells and sampling sites, sample handling and storage arrangements, must be jointly discussed between national and international coordinators and the team which will carry out the work before sampling is initiated. It is logical for sampling to commence in regions where there are already reconnaissance data and extend into regions where there is no information. For further discussion of matters relating to the implementation of the recommendations, see Chapter 10.

To obtain a satisfactory global reference network it is necessary to establish procedures which can be clearly defined, are simple to follow and involve a relatively small number of people and laboratories for their execution. It is logistically necessary to adopt widespaced sampling to reduce to manageable proportions the practical problems which would be created by many field parties collecting a large number of samples over a period of many years. Wide-spaced sampling, combined with compositing of samples, allows speed, economy and relative simplicity in execution. As discussed in Chapter 3, research has shown that wide-spaced sampling can produce geochemical maps which outline the large geochemical features of countries and continents.

To commence international geochemical mapping it has been proposed in Chapter 3 that a variety of standard reference materials should be collected from some 5000 cells, each 160 x 160 km (area 25 600 km^2), over the entire land surface of the world. A grid network will be provided by the organizers of the Global Geochemical Baselines project for planning purposes within each region and country. Figure 4-1 shows a proposed cell pattern with respect to Africa. The cells (for the entire world) have their origin on the equator at the 0^o (Greenwich) meridian and they are symmetrical N and S of the equator. For practical convenience the cells are bounded by lines of latitude 1½^o apart (approximately 166 km). To retain a constant area of 25 600 km^2 the meridians defining E and W boundaries are systematically displaced in longitude E and W in successive latitudinal bands. Overlap in the vicinity of the international dateline is ignored because it occurs over the Pacific Ocean.

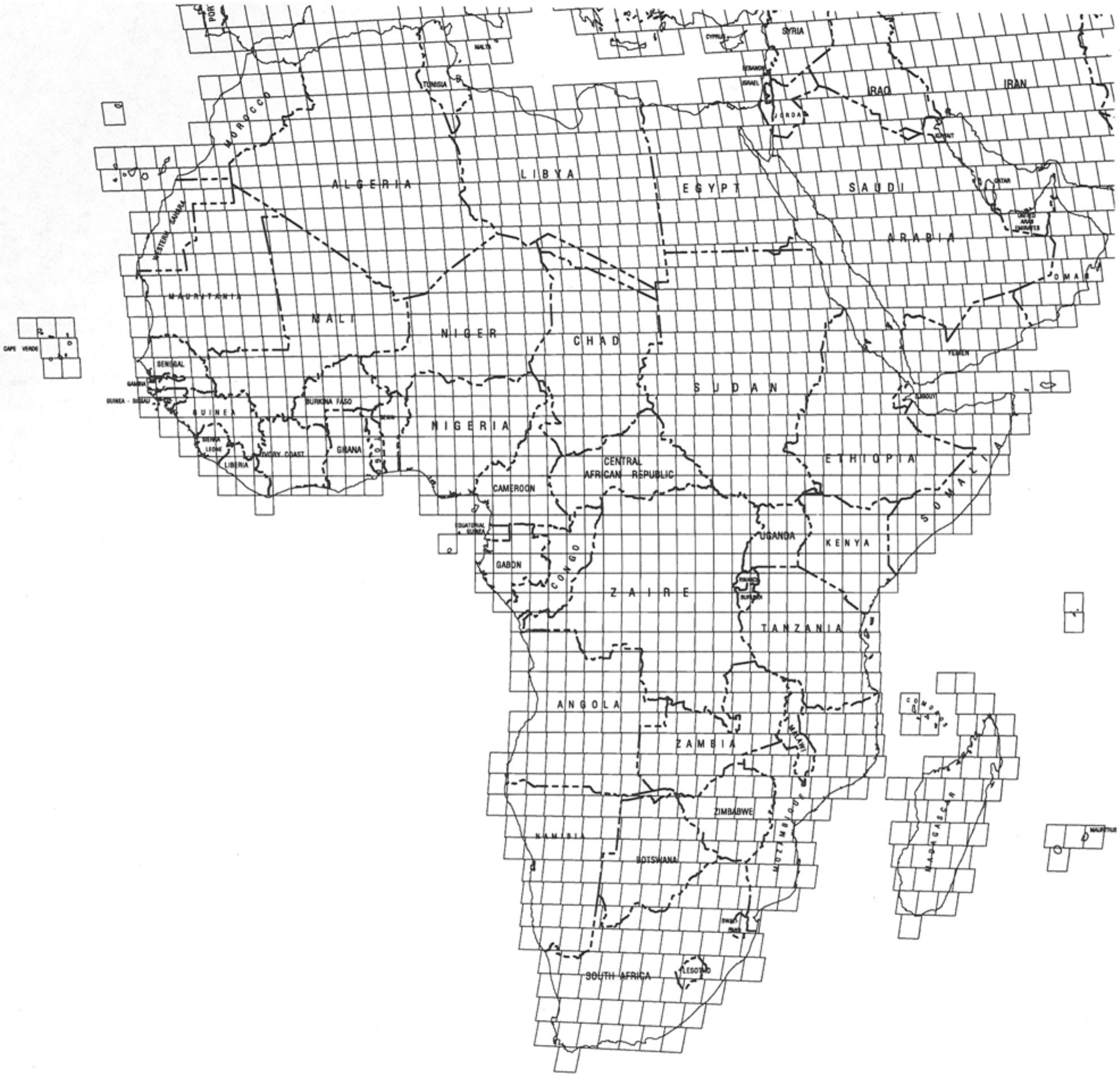


Figure 4-1 *Global geochemical reference network; nominal 160 x 160 km cells defined by two parallels of latitude 1 1/2° (approx. 166 km) apart, and two meridians. In order to retain a constant area, the cells are systematically displaced in longitude E and W in successive latitudinal bands.*

4.2 Sample media for a global network

As indicated above, the whole project depends upon the suitability, representivity and consistency of the samples collected. The correlation of regional geochemical data based on different media is difficult (Davenport, 1990; Steenfelt, 1993a), therefore it is recommended that the initial stage of world-wide geochemical coverage be based on as few sample media as possible. Following from the discussion in Chapter 3, in order to meet the global objectives of the project and establish systematic baseline data, emphasis must be placed on media which are relatively easy to collect and available over a large area. Since a primary objective is to document the present geochemical state of the world's exogene environment and not specifically focus on mineral resources or pollution problems *per se*, the following materials are recommended, based on the discussion in Section 3.2:

(a) **regolith** (residual/non-alluvial and alluvial)
- selected because regolith material occurs almost everywhere;
(b) **drainage system sediments (stream or lake)**
- selected because they are used by most national surveys;
(c) **surface humus and surface water, where present**
- selected because of their biological significance.

Provided the minimum sampling requirements for international correlation are met, it may be convenient to collect additional materials from the same sites for national or regional investigations. Also, in order to gather additional data for national requirements it may be decided to sample more sites, conforming with the international procedures. These are national decisions which are encouraged provided the international requirement to establish a global reference network is not delayed as a consequence. It is important that in any region, professional geochemists familiar with local conditions are consulted prior to the preparation of an operational plan.

It should be noted that during the preparation of this report another scenario has also been considered. In the interests of expediting the production of a global map, the consequences of restricting sample collection to a single sample medium have been assessed, for example by using *only* regolith materials, or *only* floodplain sediments. Such an approach would be cheaper and faster than the multi-media path which is recommended. However, the data obtained would have limited value because they could not be closely correlated with, nor provide reference materials for, the media commonly selected for detailed regional and national surveys, as discussed in Chapter 5. The purpose of the proposed global geochemical reference network is to provide sufficient data to link mapping at all scales, so several sample media must be collected.

The sampling instructions for the various media overlap those recommended by the Technical Committee for Field Methods, for use in national surveys. Procedural details and cautionary notes are provided in Section 12.4 and 12.5.

4.3 Sampling logistics

The selection of sample sites within the cells requires careful consideration from both theoretical and practical points of view. It is important not to bias a sampling pattern in such a way as to confirm the presence of some already known feature, and unwittingly miss the discovery of features presently unknown. The desired sampling pattern must be achievable within the practical constraints of funds, ease of access, and safety and security considerations. Nevertheless, there may be substantial costs involved in obtaining satisfactory random samples in areas of the world with poor physical access. In order to provide independent data for correlating the global reference network with regional surveys, it is important to collect samples of floodplain sediment, representative of large areas, in addition to the various sample media from small basins (which are preferred for most detailed regional surveys). This increases the number of sites to be visited and samples to be collected, but the additional data justify the costs involved.

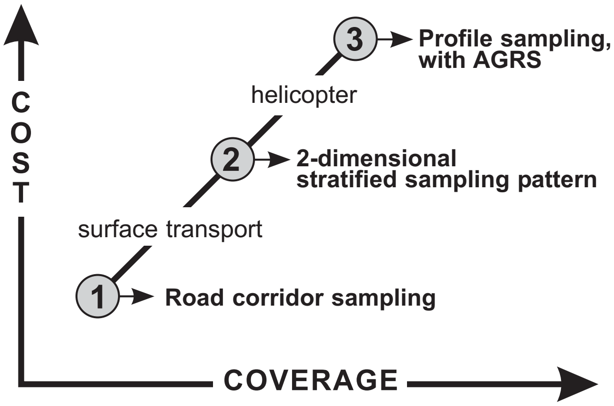


Figure 4-2 *Sampling logistics: options and constraints.*

If a region lacks roads, then helicopters or (in a few suitable situations) boats must be employed. Before entering into the details of what should be collected and the number of sites to be visited, it is necessary to consider the logistical options that are available for different regions of the world. Figure 4-2 identifies three approaches (options) to sampling in terms of Relative Cost versus Coverage Obtained. Options 1 and 2 have been used as indicated below, and results published. Option 3 has been used, and results published (see below), but without *en route* gamma ray spectrometry. The advantages and disadvantages of these approaches are as follows:

In ***Option 1*** the sampling pattern is determined by the available roads, which provide sampling corridors. Samples are collected adjacent to roads, the position and direction of which are influenced by the terrain. Shacklette's pioneering work to obtain a rapid overview of the composition of surficial materials across the USA was based on samples collected adjacent to highways, in uncultivated land wherever possible, at approximately 80 km intervals. Over much of the country the highways selected were approximately 100 to 200 km apart (see Fig. 3-2). A similar approach has recently been adopted in China to prepare an atlas of soil geochemistry (Zheng, 1992). In central and western China there are wide gaps in the road network (see Fig. 3-3). Option 1 provides a comparatively speedy and economical approach, but the sampling pattern is inevitably biassed to a greater or lesser extent. In so far as road network density generally correlates with population density there should be no difficulty in locating samples in populated regions. Data gaps will be present in remote areas. Major traffic arteries should be avoided where possible and sampling should take place on the prevailing up-wind side to minimize anthropogenic contamination.

Option 2 involves a deliberate effort to obtain representative 2-dimensional sampling. It is designed with the objective of being able to employ analysis of variance techniques to estimate the relative spatial variability within the GRN cells. If there is an adequate road network (as in the North American prairies), or it is possible to use cross-country vehicles, sampling is a simple operation (Garrett, 1994). Where there is no surface access, as for lake sediment sampling in the Canadian Shield (Friske and Hornbrook, 1991), it is necessary to employ a helicopter. Use of road vehicles entails low costs, but because of the need to zig-zag from site to site, sampling is slower and therefore more expensive than under Option 1. Where helicopters are used the transportation is much more expensive, but work is completed far more quickly and the sampling pattern is not biassed by access problems. Helicopters have been used for stream sediment sampling in Canada and South Africa.

Option 3 is a combination of surface geochemical sampling along a profile with an airborne gamma ray spectrometer survey to provide continuity from site to site (see Chapter 7). This approach, which is particularly suited to otherwise inaccessible terrain, is the most costly, but has both scientific and logistical advantages. It facilitates correlation of geochemical with geophysical, remote sensing and geological data. Earth scientists are accustomed to making interpretations of data in relation to cross-sections. Sampling at intervals along predetermined straight lines is a standard geophysical procedure. In geochemistry straight-line sampling is normally restricted to detailed surveys requiring regolith sampling over small areas. A profile approach to sampling does not preclude the application of analysis of variance procedures. Line spacing can be selected according to funds available and additional lines can be added at a later date.

Fortescue and Dyer (1994) have used a profile approach in Ontario, Canada, for lake and stream sediment sampling along two meridians (Long. 80°W and 90°W), using a helicopter for most of the work and a road vehicle in the populated southern portion of the Longitude 80°W transect. Lines of traverse were divided into 10 km cells, collecting 4 subsamples in every 10 km cell. Figure 4-3, taken from Fortescue and Dyer (1994), shows the abundances of six elements, collected along the 80°W profile, which is 930 km in length. Examples of long regolith profiles obtained by airborne gamma ray spectrometry are shown in Fig. 3-4.

To summarize, *Option 1* is the cheapest, but it can only be used where there are suitable roads and in general the results will be spatially biassed. *Option 2* reduces the spatial bias, but unless a helicopter is used it is limited to those parts of the world with a dense road network. *Option 3* is the preferred general approach to geochemical data acquisition for less-developed parts of the world. It is unsuitable for use in urban and semi-urban areas, but if funding permits it should be used wherever possible. It offers more coherent scientific data and, because of the rate of coverage, it facilitates standardization and quality control. It is the most expensive option, but more useful data are obtained.

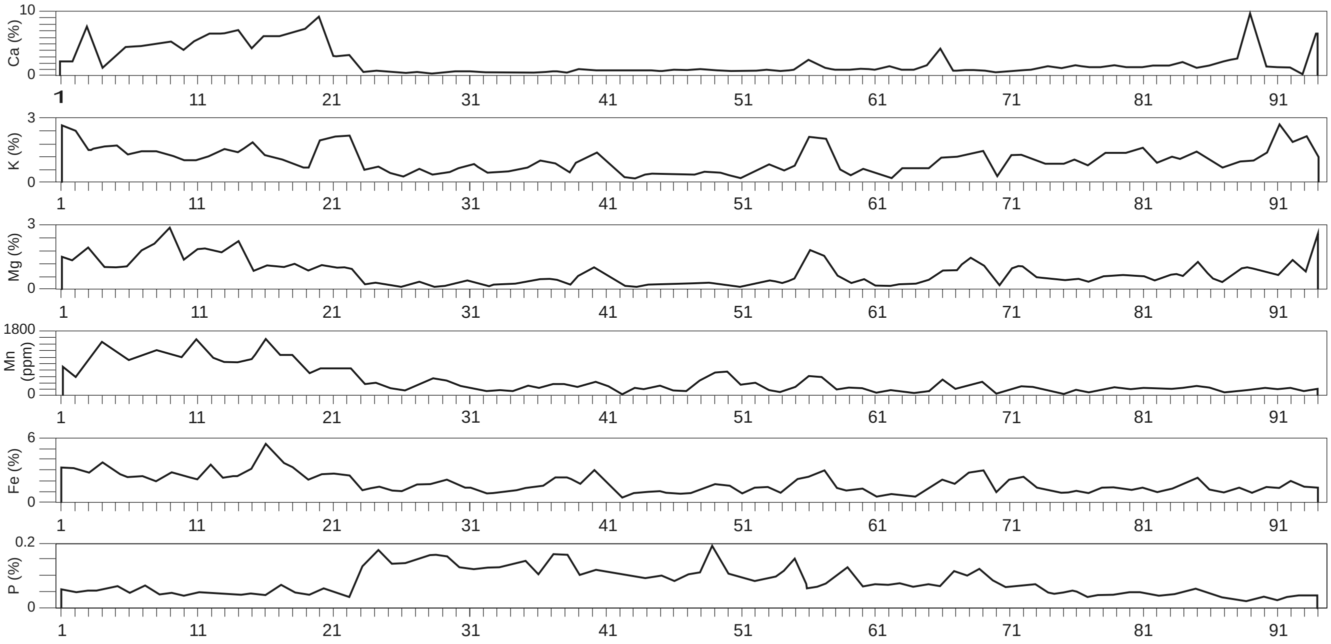


Figure 4-3 *930 km multi-element profile along 80°W meridian based on drainage sediments. The Precambrian Shield extends from cells 23 to 93. Four sub samples taken from each 10 km cell.*

from Fortescue and Dyer, 1994

The road pattern, population density and land use, topographic relief and density of vegetation cover, and also security considerations in some regions, will determine which of the above logistical options are capable of meeting the requirements of the project in any given region of the world. These matters must be considered on a national and regional basis.

4.4 Site location and the number of sites sampled

Global geochemical reference network samples (of each media type) must be collected from several sites within each 160 km cell. It is highly desirable for reasons of subsequent data evaluation, as discussed in Section 3.5, that there should be a sampling design which will permit the application of multi-level analysis of variance (ANOVA) procedures, irrespective of the sample collection logistics. This requires the collection of a sufficient number of appropriately located subsamples of each sample media from each 160 km cell. The GRN composite sample should be prepared from these individual samples, and the remaining original sample material carefully stored pending further studies. For cost or other reasons it may not be possible to arrange for the immediate analysis of all the individual samples collected within each cell, but it is desirable that this should be commenced without long delay in order to establish the magnitude and significance of geochemical variability between and within the GRN cells using ANOVA procedures. It is desirable that all samples should be collected by one team during the same time-period to ensure consistency of procedures.

Following from the sampling strategy options listed in Section 4.3, the different sampling situations entail the following considerations. Note that if funding permits, *Option 3* is preferred.

Corridor or profile sampling: Options 1 and 3
Where highway transects are adopted (*Option 1*), and where any choice exists, it is desirable to select highways not more than 160 km apart which cross the regional geological strike. If, for example, two highways cross a cell, both should be used for sampling. If there is a single highway across the cell, it should be divided into 20 km subcells and a sample of each media (if available) should be taken from each 20 km subcell. If two highways cross the 160 km cell, then 40 km subcells should be distributed along each. In cells where there are large tracts of apparently similar regolithic materials sample material may be collected in small amounts at fixed intervals to obtain the required subcell composites. In one of the subcells, chosen at random, each type of sample media should be sampled twice, in different locations, to provide a cell duplicate, and one site should be sampled twice to monitor site replication (see Fig. 3-6).

If *Option 3* can be adopted, a minimum of 2 profiles (80 km apart) should be flown across each cell, collecting samples of each media type, as available, within 40 km subcells.

Collection of regolith (floodplain sediment and/or residual soil) samples will be possible in each 20 or 40 km cell along every sampling corridor or profile. If present, stream (or lake) sediment, overbank sediment, humus and water, should be sampled from within each cell where they are first intersected by the corridor or profile, provided they meet the requirements of Section 4.5.

Two-dimensional sampling: Option 2
Where *Option 2* is followed, a sampling strategy similar to the one illustrated in Fig. 3-5 should be adopted. For example, two randomly selected sample sites, within 20 km subcells, in each quarter of each 160 × 160 km cell, result in 8 different sites per 160 km cell, plus one subcell and one site duplicate, making a total of 11 samples from the cell (see Fig. 3-5). Individual site locations are identified within the randomly selected 20 km subcells according to the requirements of Section 4.5.

4.5 Sampling details

A schematic outline of possible sampling patterns, and a sample pit, is provided in Figure 4-4. Note that the site distribution in (a) is greatly preferable to (b).

4.5.1 Regolith sampling

4.5.1.1 Alluvial regolith (overbank and floodplain sediments)

In Section 3.2 (2) a distinction has been made between overbank and floodplain sediment, the former term applying to alluvium adjacent to low-order streams which may be suitable for stream sediment sampling, the latter to alluvium in wide river valleys. Accordingly, overbank sediments should be collected adjacent to stream sediment collection sites. Floodplain sediments should be collected at other sites in the vicinity of large rivers or, in arid areas, large drainage channels. *Overbank and floodplain sediment samples, as defined, should be collected independently, because of the large contrast in their areas of provenance.* Floodplain sediments should be collected from large basins, not less than 1000 km^2, preferably larger, up to 6000 km^2 in area. Conventional soil profiles will not be present in alluvial materials. As indicated in Section 3.2 (2), samples taken some distance below the surface of alluvium are older and therefore may provide useful data relevant to temporal change, including anthropogenic effects (see Fig. 4-4). To minimize collection and analytical costs national authorities should decide whether or not such data are useful and decide accordingly whether to collect samples. Each pit profile should be photographed and described.

To summarize:

Upper horizon: 0 - 25 cm (A_{25}) surface layer (**excluding** humus where present)

Lower horizon: a 25 cm interval at deepest accessible depth **(optional sample)**

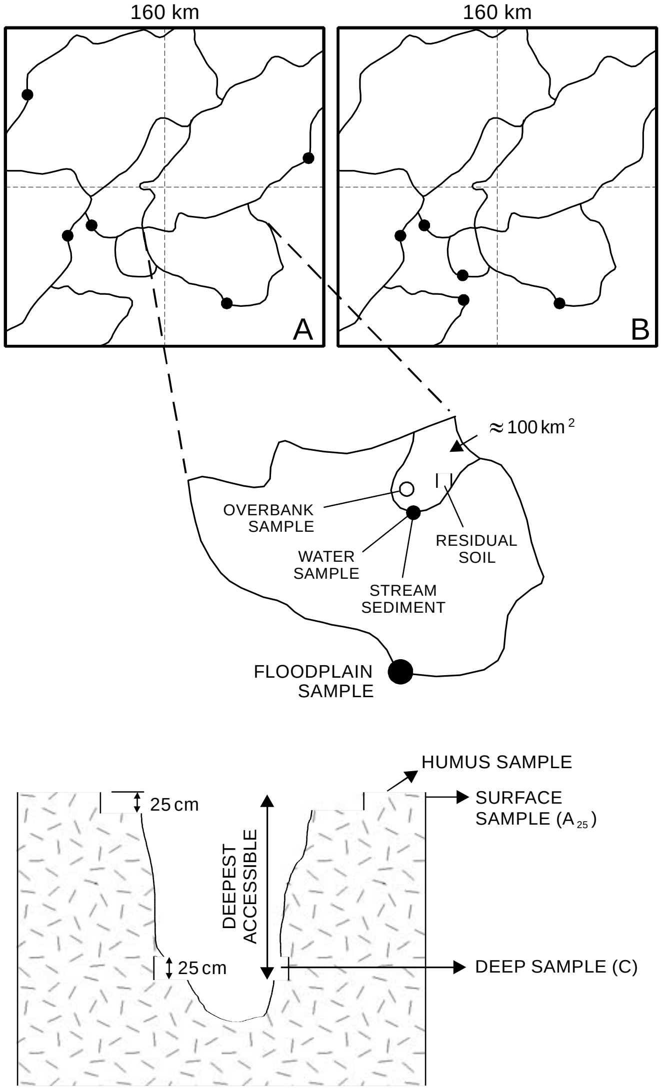


Figure 4-4 *Schematic outline of sampling pattern and sampling pit for Geochemical Reference Network. The site distribution in A is greatly preferable to B. The sample pit applies to all residual soil locations. Collection of the lower sample is optional in overbank and floodplain situations.*

4.5.1.2 Nonalluvial regolith (residual soil)

This should be sampled, if present, in the vicinity of the drainage system which has been sampled. Two sample types should be collected (Fig. 4-4). The soil profile in each pit should be photographed and described.

To summarize:

A horizon: 0 - 25 cm (A_{25}) surface layer (**excluding** humus where present)

C horizon: a 25 cm thick interval at the deepest accessible depth.

Note that in some tropical locations this horizon may be inaccessible unless a power-auger is employed.

As recommended in Chapter 7, gamma ray spectrometer measurements should be taken at each site. As part of establishing a true network, it is desirable that measurements should be made in transit between sites.

4.5.1.3 Humus sampling

If there is a well developed surface humus layer overlying the regolith material which has been sampled, 10 litres of compacted material should be collected.

4.5.2 Drainage system sampling

4.5.2.1 Stream sediment

Samples should be collected at the outflow of basins, preferably not exceeding 100 km² in area. Basin size is the prime consideration in site selection for drainage samples and all types of sample should be collected in the same vicinity. The basins to be sampled will be from within the 20 (or 40) km sub-cells selected as indicated in Section 4.4 above. It is acceptable to sample basins which extend into adjoining subcells.

Samples should be collected from the inorganic fine-grained silt and clay fraction of the stream bed load. *In situ* precipitates should be avoided. Active sediment is the preferred material. A minimum of 10 grab samples should be collected in each stream from different parts of the stream bed over a minimum distance of 500 m. Collectively these constitute one site.

4.5.2.2 Water

Stream (or lake) water is sampled at each locality where stream (or lake) sediments, are collected, following procedures given in Chapter 5 (Field methods).

4.5.2.3 Lake sediment

Lake sediment is an alternative medium to stream sediment only in regions where stream drainage is poorly developed. Lakes should be sampled according to the method described by Friske and Hornbrook (1991).

4.5.3 Sample quantities, preparation and storage

For each reference cell the total weight of each stream sediment sample collected must be such that a minimum of 5 kg with an upper size limit in the range 0.10 mm to 0.18 mm can be retained. Samples may be sieved at site, as far as possible avoiding the loss of fines. Each regolith sample should be sufficient to permit preparation of a 5 kg subsample in the range of 0.10 to 0.18 mm and have a reserve of 2 kg of < 2mm material. Three separate hundred millilitre containers of water and 10 litres (tightly packed) of the humus layer is required from sites where these media are collected. Each agency participating in the sampling must ensure proper control and management of samples at all stages from collection to analysis to archival storage. Samples must be dried at a temperature not exceeding 40^{o}C, and sieved to the appropriate grain size. In preparing the GRN composites, the samples should be homogenized and divided as required to provide an equal weight of each to the composite. Uncomposited material from each original sample should be retained and clearly identified in case it becomes possible, or necessary, to analyse this material at a later date. It is proposed that all but 50 g of the prepared GRN composite should be retained in the country of origin for on-going reference purposes. Again, care must be taken in preparing the 50 g split which is to be forwarded to the GRN laboratories to ensure that it is representative of the GRN composite. Proper storage facilities must be available. For detailed recommendations on sample, site, and storage documentation see Section 12.4.

4.5.4 Other important considerations

4.5.4.1 Regional coordination

Because cells will overlap national boundaries it is highly desirable for countries with common borders to discuss and agree on sample locations in conjunction with international project coordinators. For this reason it is recommended that regional workshops should be held prior to the commencement of work (see Chapter 10).

4.5.4.2 Quality control of sampling

In order to provide quality control for the composites of the GRN, 3% of the network cells should be resampled, quite independently of the initial sampling pattern, duplicating all media. Duplicates should be labelled “D” in addition to the sample number. Duplicate analyses should be undertaken, to determine objectively the analytical variance. All samples, including the duplicates, will be renumbered in a random order prior to analysis (see Chapter 8).

4.5.4.3 Analysis of samples

Samples will be analysed according to the recommendations in Chapter 6 (Geoanalytical Requirements). The 50 g sub-sample of the prepared GRN composite for each media will be forwarded to the designated GRN laboratory responsible for coordinating all the analytical work on that particular media.

4.5.4.4 Availability of samples and data

To collect, prepare and analyse well-controlled samples, considerable effort and costs will be expended. It is important to recognize the long-term reference value of the samples and the data. The splits of the GRN samples retained in the countries of origin are intended to be used as national SRMs to facilitate international and national calibration. (Note previous comments on the compositing of samples). Excess sample material should be available to *bona fide* researchers for approved investigations, but sufficient material to permit nondestructive analysis should be retained indefinitely. The data obtained through the project should be available for public reference.

4.6 Production of a world map, based on GRN data

Table 9-1 shows the sampling density that is considered necessary to provide coherent, visually acceptable maps, at different scales, from evenly distributed data. Regolith data (A_{25} horizon) should be available from all cells in all parts of the world and is therefore the media capable of providing a complete map. Other media (stream sediment, water, humus) will be sparse or absent from some parts of the world and will provide a less complete picture. Composite analytical data from 160 × 160 km cells could be used to produce a map at 1:80 million scale. Somewhat improved definition, although noisier, is available by plotting analytical data from each sampling site separately when these individual analyses are available. In addition, those individual data would permit a more detailed study of spatial variability if the field sampling has been carried out appropriately.

Further subdivision of the basic sampling blocks would increase time and costs required to do the work, but produce correspondingly higher resolution data. Closer spacing should be considered for the purpose of establishing national baseline data in heavily populated areas, or in small countries. Individual countries are encouraged to undertake more detailed sampling at an early stage if they can afford to do so, but it is important that this should not delay the acquisition of regional and global network samples over the whole area within their jurisdiction.

Airborne gamma ray spectrometry, which samples the regolith and provides linear continuity, complements the data obtained from surface sampling at discrete sites. A world map of radioelement distribution can be produced as a product of reference network data collection. An 80 km line-spacing can provide radioelement maps with spatial resolution equivalent to that provided by 8 surface sites per 160 km cell. This is further discussed in Chapter 7.

SUMMARY OF SAMPLE TYPES AND REQUIREMENTS

Sample Media	Sub-Type / Location			Fractions / Amounts
Humus	(no subdivision)			10 litres
A_{25} surface regolith	Residual soil	Overbank	Floodplain	Bulk / 2 kg: < 2 mm / 2 kg: < 0.18 mm / 5 kg:
Deep regolith	C horizon	*Overbank	*Floodplain	< 0.18 mm / 5 kg:

Surface Water	stream	▲lake	Untreated; acidified; filtered & acidified 100 ml each
Drainage Sediment	stream	▲lake	< 0.18 mm / 5 kg:

* Collection of **deep** overbank and floodplain samples is optional
▲ In specific regions only

Table 4-1 *A summary of the sample types and requirements for the Global Reference Network.*

4.7 Summary of Recommendations

In order to begin systematic international geochemical mapping it is necessary to establish a primary global geochemical reference network (GRN), analogous to a geodetic grid. Wide-spaced sampling is required everywhere, including regions already surveyed and regions where there is low probability of any geochemical mapping being carried out in the near future. The samples collected will serve as analytical reference materials, so strict procedures must be followed, and adequate quantities must be obtained and retained. Table 4-1 summarises the sample collection requirements. *In situ* gamma ray measurements should be undertaken as a complementary parallel activity, as indicated.

Sampling details

(1) the primary reference network will be based on approximately 5000 160 × 160 km grid cells distributed over the land surface (key maps will be supplied by the international coordinators);

(2) sample sites should be located in several (minimum of 5, 8 preferred) 20 × 20 or 40 × 40 km subcells within each 160 km cell to permit the application of ANOVA statistical techniques; access and cost considerations will determine whether the subcells are randomly selected along one or two sampling profiles or road corridors, or randomly distributed in any part of a 160 km cell; in undeveloped regions helicopter-borne profiles are recommended;

(3) materials to be sampled from within each cell are:
- A_{25} regolith on residual and alluvial surfaces (overbank and floodplain sediments should be collected separately, see Sections 3.2 and 4.5.1 for discussion)
- stream or lake sediment
- C horizon; collection of deep alluvial sediment is **optional**
- surface humus, if present
- water, if present

(4) stream sediment samples should be from drainage basins not exceeding 100 km^2; overbank sediment should be taken from an adjacent site;

(5) each sample of each medium at each of the subcell sites should be a composite of a minimum of 5 subsamples; this composite material must be thoroughly homogenized;

(6) floodplain sediment should be taken from large basins, between 1000 km^2 and 6000 km^2 in area; and

(7) gamma ray spectrometer readings should be taken at each site for *in situ* radioelement determination the acquisition of carborne or airborne gamma ray spectrometry in transit between sample collection sites is recommended to establish a linked data network (see Chapter 7).

Sample quantities

(8) sufficient material should be collected to provide, from each cell, 10 l of humus (where present) and 5 kg of < 0.1 to 0.18 mm fraction of sediment and each type of regolith sample;

(9) a bulk A_{25} regolith sample and < 2 mm regolith size fraction should be retained separately (2 kg each) for radiometric and agricultural reference respectively;

(10) three separate water samples are required (where present), about 300 ml in total,

- unacidified, unfiltered, for anion determination
- unfiltered, acid digested for total cations
- filtered (45 micron), acidified, to provide “dissolved” cations.

Analytical arrangements

(11) Instructions will be provided by the project co-ordinators concerning which international reference analysis laboratories will receive the samples. A cell-composite sample must be prepared (with equal weights from each subcell site) for each media type within each cell, retaining a minimum of 50 g of each individual subcell sample for separate analysis at a later date. Fifty grams of each cell-composite should be sent immediately to the participating international reference laboratories. The bulk of each composite sample should be retained in the country or region of origin in order to provide a range of secondary SRMs to standardize future geochemical work in the area. Individual samples from within each cell of the reference network should be analysed at the earliest opportunity.

5 Field Methods for Regional Surveys

5.1 Introduction

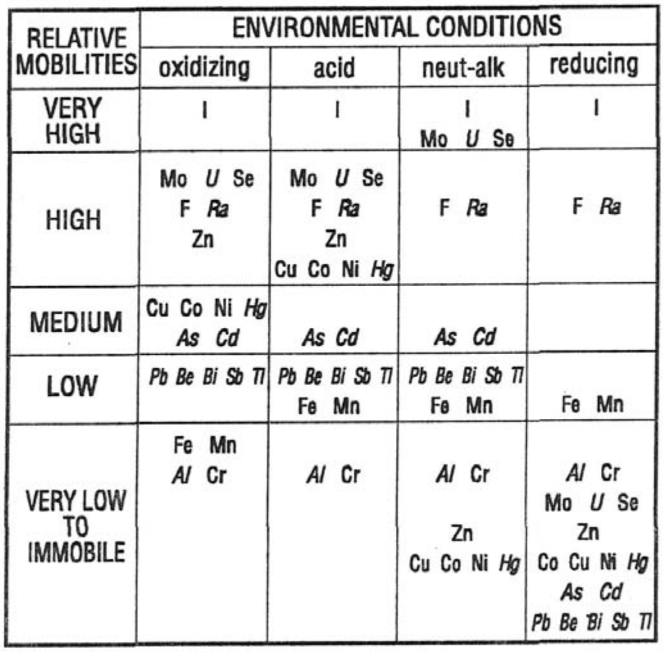
In order to obtain a global geochemical database which extends correlation beyond the very coarse scale provided by the global reference network, it is essential that national and regional geochemical surveys should be tied into the GRN, and as far as possible be compatible, one with another. This chapter is concerned with regional geochemical surveys normally involving sampling densities in the range 1/1 km^2 -1/100 km^2 (see Fig. 3-1). This is the scale at which multi-purpose multi-element geochemical maps are most frequently prepared by national mapping organizations (Plant and Ridgway, 1990; see also Chapter 2). This chapter was prepared by the Technical Committee on Field Methods (for a list of members see Section 2.5) to provide a basis for integrating national and international mapping through the standardization of regional geochemical surveys. Attention is focussed on the desirability of using standard procedures, especially common sample media, as already reviewed in Chapters 3 and 4. The sample media are discussed again here, this time from the perspective of regional surveys. The Committee was concerned with:

(a) reviewing information on available field methods for multi-purpose multielement regional geochemical mapping;
(b) selecting sample media and procedures suitable for particular physiographic environments; and
(c) preparing sampling instructions for use in different physiographic environments.

In this chapter recommendations on the selection of appropriate sample media, spacing and documentation are described on the basis of terrain morphology and global climatic zones. Detailed sampling instructions for four main terrain types are given in the appendix (Section 12.5). No attempt is made to review the literature comprehensively, but references throughout the chapter provide a basis for further reading. All of the recommended procedures have been designed so that the quality and amount of sample material permits:

(1) several analytical treatments to be carried out;
(2) a reference subsample to be retained; and
(3) data from national surveys to be used to prepare a world geochemical atlas using the procedures described in Chapter 4.

Although it was the aim of the Committee to assist in implementing methods to standardize new and existing national multi-purpose multi-element geochemical data, certain problems cannot be overcome by the development of sampling or analytical methods but must be considered at the stage of data interpretation. Hence, in polar and temperate regions, where there is relatively little chemical weathering, stream sediment or soil samples frequently provide data on a wide range of chemical elements for purposes ranging from geological mapping, mineral exploration and metallogenesis to environmental studies (e.g., Thornton and Howarth, 1986). However, in tropical and equatorial regions where there is deep weathering and marked chemical differentiation of the weathering profile the relationship between bedrock and stream sediment or surface soil may become obscured (Butt and Zeegers, 1992). Some elements may be intensely leached (Fig. 5-1) while others may be concentrated. In these circumstances the data obtained will be of value generally in documenting the chemistry of the surface environments, but only a limited range of elements, for example the high-field-strength elements such as the Ti, Y, Zr and REE, may provide data on bedrock at depth.



RELATIVE MOBILITIES	ENVIRONMENTAL CONDITIONS			
	oxidizing	acid	neut-alk	reducing
VERY HIGH	I	I	I Mo *U* Se	I
HIGH	Mo *U* Se F *Ra* Zn	Mo *U* Se F *Ra* Zn Cu Co Ni *Hg*	F *Ra*	F *Ra*
MEDIUM	Cu Co Ni *Hg* *As Cd*	*As Cd*	*As Cd*	
LOW	*Pb Be Bi Sb Tl*	*Pb Be Bi Sb Tl* Fe Mn	*Pb Be Bi Sb Tl* Fe Mn	Fe Mn
VERY LOW TO IMMOBILE	Fe Mn *Al* Cr	*Al* Cr	*Al* Cr Zn Cu Co Ni *Hg*	*Al* Cr Mo *U* Se Zn Co Cu Ni *Hg* *As Cd* *Pb Be Bi Sb Tl*

Figure 5-1 *Relative mobilities of some essential and potentially toxic elements (based on Andrews-Jones, 1968). Normal typescript indicates essential trace elements; italics indicate potentially toxic elements.*

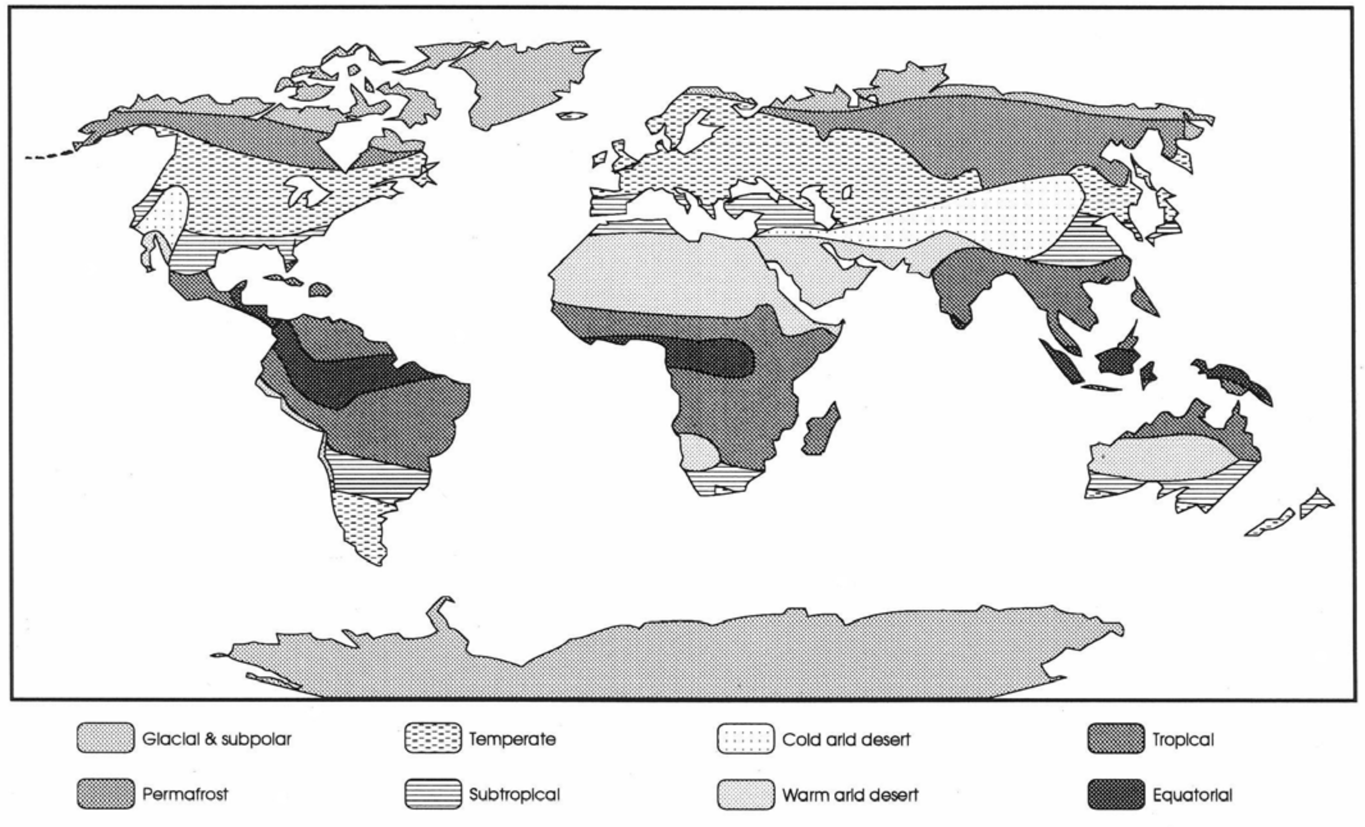


Figure 5-2 *Morphoclimatic zones.*
based on Budel, 1982

The surface environment of the earth can be divided into a series of zones developed under different climatic regimes with different climatic histories (Fig. 5-2). One of the most useful classifications for geochemists is that of Büdel (1982), which has been used as a basis for understanding the geochemistry of tropical and subtropical terrains in a definitive text by Butt and Zeegers (1992). The classification takes account of the extensive tropical weathering which extended into high latitudes during the Cretaceous, Tertiary and earlier times, and the modification of large areas as a result of Pleistocene glaciation. It does not, however, take account of mountain belts, although changes with increasing altitude generally correspond to those associated with increasing latitude.

The variations in soils, types of duricrust, thickness of weathering zone and their relationship to mean annual temperature and mean annual rainfall are shown in Fig. 5-3 modified after Pedro (1984). Variations in Eh, pH, electrical conductivity and the activity of some major cationic and anionic species have been added. It is apparent that there is little chemical modification of bedrock chemistry in polar and cold temperate regions, in contrast to arid, tropical and equatorial terrains which are typically affected by prolonged and deep weathering.

The values of different sample media are discussed in relation to four mainterrain types:

1) glacial, subpolar, permafrost;
2) temperate and subtropical;
3) cold and hot deserts; and
4) tropical and equatorial.

5.2 Sample media for regional surveys

Sample media selected for multi-purpose geochemical mapping at the regional scale should indicate the composition of the surface environment and of bedrock.

Other important criteria include:
(1) region-wide availability of the media selected, with overlap at least in some parts of the region with media selected for the geochemical reference network;
(2) simplicity of sampling - sampling methods should be practical and robust, so that they can be used in all environments after simple training and without the need for accompanying specialists such as botanists or geomorphologists;

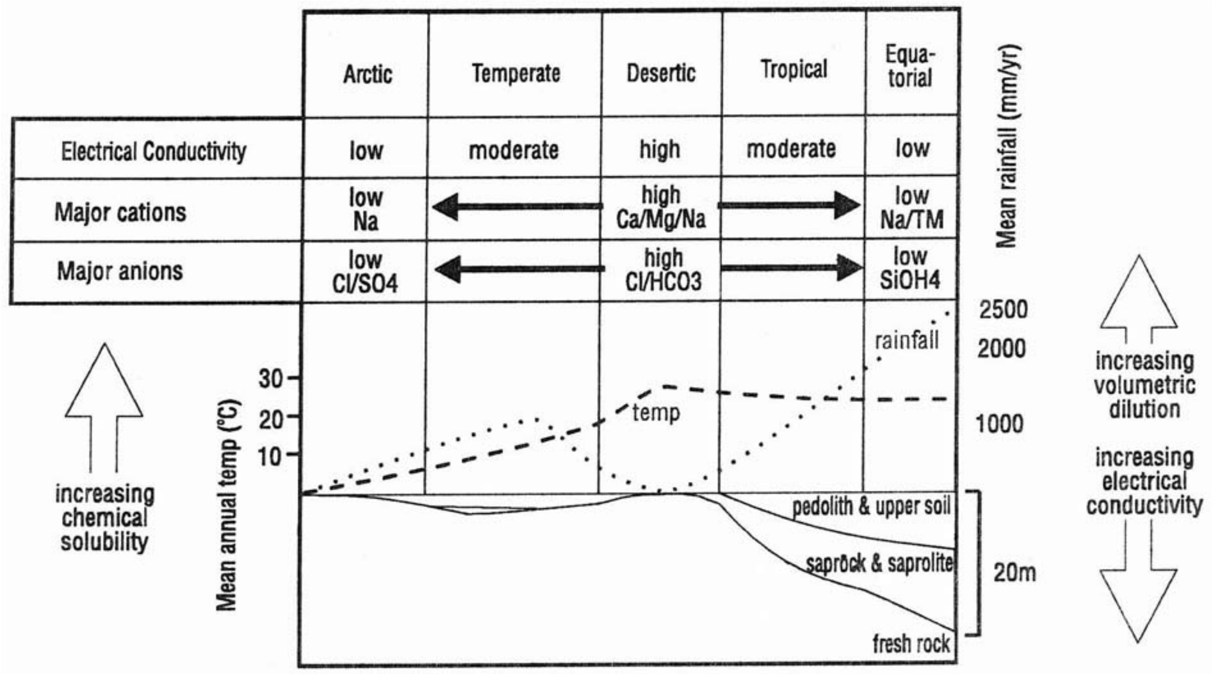


Figure 5-3 *Generalized relationships between surface/groundwater chemistry and climate.*
based on Pedro, 1984

(3) the sample media selected should also be of value for mapping using a range of sample densities from wide-spaced sampling in unmapped regions to densities of one sample or more per km^2 where higher resolution mapping is required; and (4) state of development - ideally the methods should be "plateau" techniques, with well established procedures requiring no further research and development.

The most widely occurring and widely used media are active stream sediment, regolith (soil, *sensu lato*) and to a lesser extent water. More recently "overbank sediment" has also been suggested as a widely occurring sample medium. (see discussion in Section 3.2). Other media used for national or regional geochemical mapping in particular terrain types include lake sediment (e.g., Friske and Hornbrook, 1991; Davenport, 1990), till (e.g., Koljonen, 1992) and organic matters (e.g., SameckaCymerman and Kempers, 1992).

Stream sediments have been the most extensively used media for multi-purpose geochemical mapping (Table 2 in Plant et al., 1988) and the behaviour of a large range of elements in the stream environment in many different parts of the world is well known (Plant and Hale, 1994). Geochemical maps based on stream sediment have been shown to provide a basis for geological mapping, mineral exploration, and metallogenic studies, as well as for agriculture, forestry, land use planning and environmental science generally (Darnley and Garrett, 1990). Thus stream sediment is recommended for use wherever possible. Where conditions are unfavourable for the use of stream sediment a substitute medium must be chosen (see Table 5-1) and the analytical values obtained should be calibrated against those obtained using stream sediment, based on samples from a zone of overlap.

Although regolith is an almost universal medium, in many countries its use has been limited to obtaining local rather than regional data (Butt and Zeegers, 1992; Kauranne et al., 1992). However, the exceptions are significant and important. Regolith has served as the medium for extremely low density sampling of the entire USA by conventional geochemistry (Shacklette et al., 1971, Shacklette and Boerngen, 1984) and also by airborne gamma ray spectrometry (Duval 1991). All of China has been mapped using regolith samples (Xie and Yin, 1993). Garrett (1994) has recently undertaken a reconnaissance survey covering 850 000 km^2 of the Canadian and adjoining US prairies. In some environments, for example in lateritized terrains, considerable expertise is needed to interpret soil data (Butt and Zeegers, 1992). Recent comparative studies suggest that active stream sediment samples reliably indicate the geochemical patterns shown by high-density soil sampling (Appleton and Greally, 1992). It is recommended that wherever possible soil samples be collected in conjunction with stream sediment samples.

Surface water, which is a readily available sampling medium in temperate and equatorial regions, is increasingly used for geochemical mapping at different scales and has particular significance for environmental studies. Sampling and treatment is described in Chapter 6. Ideally, water samples should be collected at all stream sediment sampling sites.

These three types of media and the particular modifications needed in different physiographic terrains are considered further below together with media suitable for particular physiographic regimes.

Overbank (floodplain) sediments (Ottesen et al., 1989) have been proposed as a sampling medium for wide-spaced geochemical mapping of Europe, and methods for sampling are described in Chapter 4 above. The medium has the potential for distinguishing both natural geochemical variation and patterns related to anthropogenic interference (Demetriades et al., 1990), but may require expert geomorphological assistance at the sampling stage to allow reliable interpretation (Macklin et al., in press). Moreover, overbank sediment may not occur in the low-order tributary drainage systems normally used for geochemical mapping at a regional scale. Hence, the method is not considered further in this chapter.

Till forms the basis of national geochemical mapping in Finland (Koljonen, 1992) and Sweden, and has also been used in glaciated terrains elsewhere, in North America and Russia. Regional till data from Finland and Sweden have been utilized in mineral exploration and environmental studies.

Lake sediments, which are mostly employed in Canada in wet shield areas with poorly developed drainage (Friske and Hornbrook, 1991), have the advantage that, with suitable sampling, long-term changes can be detected, but clearly this method along with till sampling has limited geographical range.

Glaciated areas in North America	- lake sediment or till
Glaciated areas in Europe and Asia	- till or lake sediment
Desert areas with topographical relief	- dry (ancient) stream beds
Desert areas without relief	- regolith
All other areas	- regolith, preferably residual soil

Table 5-1 *Sample media which can be used in regions where conditions are unfavourable for the collection of stream sediment samples.*

5.3 Sample media in different physiographic terrains

This section provides a brief review of the characteristics of different physiographic terrain types as a basis for modifications to standard stream sediment, water and soil sampling methods, as well as indicating special sample types which may be of particular value for preparing regional multi-purpose maps. Specific sampling instructions for each method and terrain type, together with the references on which they are based, are given in the appendix (Section 12.5).

5.3.1 Glacial, subpolar, permafrost regions

These regions are presently glaciated or were glaciated during the Pleistocene. The glaciation removes chemical weathering residua in most areas, leaving bare rock pavements or exotic morainic and other types of clastic deposit. Lowlands or plateaux are often covered by thick moraine or glaciofluvial deposits. The geochemical response from bedrock may be blanketed or diluted. Surface tributary stream drainage may be disturbed or entirely disrupted in such environments and may be replaced by a system of lakes interconnected by short stream sections. Organic matter is not readily oxidized in the low ambient temperatures of such environments and thick accumulations of peat or muskeg may give rise to surface conditions characterized by low Eh/pH. Surface waters will generally have low conductivity and Fe and Mn may be mobilized in the mainly podzolic soil profiles and redeposited in lower horizons or in stream channels, giving rise to anomalously high values for the first row transition elements, and also Ba and Ag.

Stream sediment sampling as a basis of regional geochemical mapping has been carried out in Greenland (Steenfelt, 1987; 1993b), Alaska (Weaver et al., 1983), Yukon (Coker and Ellwood, 1981) and northern Scandinavia (Bølviken et al., 1986) for example. A special modification not considered further here has been the use of organic stream matter (aquatic moss, aquatic plant roots) (Samecka-Cymerman and Kempers, 1992). No regional geochemical maps based on systematic soil sampling have been published for such terrains, probably reflecting the exotic nature of soil parent material and its variability in organic content and profiles (Kauranne, 1992).

In Canada considerable research and development has been carried out into lake sediment sampling for regional geochemical mapping and large areas of the Canadian shield have been mapped using these methods (e.g., Friske and Hornbrook, 1991). Comparisons between lake and stream sediment samples (Davenport, 1990; Garrett et al, 1990) suggest that such data can be combined, although statistical manipulation is required. In the Geochemical Atlas of Alaska (Weaver et al., 1983), the two datasets are simply presented together and false geochemical boundaries are shown.

In Finland much work has gone into studying till profiles and regional geochemical maps prepared using basal till samples have been published for Finland and Sweden (Bølviken et al., 1986). Samples of undisturbed humus/forest litter may be of particular value for indicating surface contamination in such environments (Ek, 1987).

5.3.2 Temperate regions

The northern margin of the temperate zone extends across the glaciated landscape of North America from British Columbia to Nova Scotia, and across Eurasia from S Scandinavia to SE Siberia. In the southern hemisphere the southern margin of the temperate zone crosses South America, the tip of Africa, SW and SE Australia and New Zealand. Methods such as stream sediment sampling described above are appropriate. In general, however, temperate regions are characterized by increased rain fall and temperature, the characteristic soils are brunisols and chernozems, and pH/Eh, and the conductivity of surface waters generally increases relative to polar regions. Active stream sediment, surface water and soil sampling methods are particularly useful in such environments. Large parts of these regions have been occupied by man since prehistoric times, however, and until recently they have been the areas most affected by industrial development and contamination. Special precautions based on the recommendations of Cooper and Thornton (1994) should be adopted to avoid local contamination while allowing more regional pollution patterns to be mapped. No special sample types are recommended for such terrains and the general methods for stream sediment and soil sampling are described in the appendix (Section 12.5). Regional geochemical maps based on stream sediment and on soil sampling are available for many parts of Europe (Demetriades et al., 1990), Canada (e.g., Rogers et al., 1987; Garrett, 1994), China (Xie and Ren, 1993), Japan (Kamioka et al., 1991; Shiikawa, 1991), and USA (Hoffman et al., 1991).

5.3.3 Desert regions

Deserts are characterized by exceptionally low rainfall with high evaporation rates as a result of high temperatures and/or strong winds, and they are affected by extremes of temperatures. The most extensive and well documented deserts are hot deserts characterized by extremely high temperatures, such as those of North Africa, Saudi Arabia and Western Australia. Evidence exists that some deserts were formerly subjected to extreme leaching under tropical conditions during the Cretaceous and Tertiary; in Western Australia it has been suggested that the landscape was formed initially during the Proterozoic (Butt and Zeegers, 1992). Deserts soils are typically calcretes. Important constituents are resistate detrital quartz and zircon, and secondary clay minerals. Calcareous soils enriched in U and other elements mobile in conditions of high pH are a feature of inland drainage basins. Organic material in desert soils is minimal. Surface waters are highly oxidizing, with very variable pH (frequently with high pH values). They generally have higher salinity than those in other environments, with chloride rather than bicarbonate as the main anionic species. Drainage systems were generally developed during wetter periods and present day flow is ephemeral. Published geochemical maps are available for China (Zheng, 1992) and the Arizona desert (Hoffman et al., 1991) for example.

Geochemical maps, mainly for mineral exploration purposes, have also been prepared by the private sector or government organizations over Saudi Arabia (Rains and Allen, 1985), parts of the Sahara (Bugrov, 1974) and Western Australia (Smith, 1989). The fine material of surface residue in such environments is generally of aeolian origin, and a coarse fraction has been used in such surveys to provide information on local bedrock. It is recommended that for the preparation of regional geochemical maps in such environments sampling be based on the collection of both coarse and fine fractions in order to provide information on the distribution of environmentally important trace elements as well as those giving information on bedrock. Ground water sampling may be of particular value in such environments (Giblin, 1994).

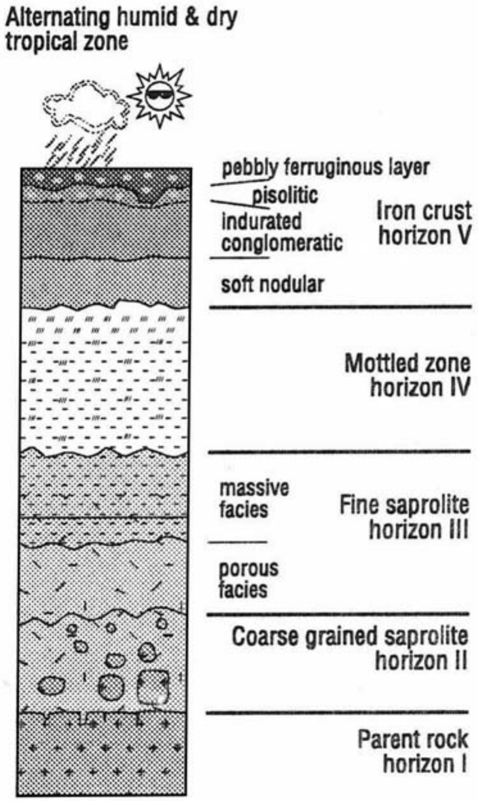


Figure 5-4 *Typical lateritic iron crust profile.*
based on Nahon and Tardy, 1992

5.3.4 Equatorial regions

Surface soils in these environments may have been deeply leached under a range of climatic conditions, including long periods of high rainfall and high temperature, to which they have been subjected from Tertiary times or earlier, in some areas as far back as the late Proterozoic (Butt and Zeegers, 1992). Surface conditions vary widely but there is generally intense oxidation, a lack of organic debris (which is generally stored in the biota rather than in soils) and the formation of stable insoluble secondary minerals such as clays (especially kaolinite) which increase the Al/Si ratio of the surface material. In some environments laterites are common, and may extend tens or hundreds of metres downwards before fresh rock is encountered. A typical lateritic iron crust profile is shown in Fig. 5-4, together with a diagram summarizing the stable secondary assemblages of such profiles. The surface may be highly complex, however, and the profile may be truncated and/or buried by later detritus (Butt and Zeegers, 1992). Despite the complications, regional geochemical maps showing variations in important trace elements of significance for economic and environmental purposes have been prepared using soils over Jamaica (Simpson et al., 1991), and using stream sediment over Zambia, Zimbabwe, Bolivia, Indonesia, etc. Since the principal aim of the project is documentation of the surface environment the instructions given in the appendix (Section 12.5) are based on these surveys although a more sophisticated approach for follow-up of exploration or environmental purposes should be based on the methods of regolith sampling described by Butt and Zeegers (1992).

5.4 Planning and execution of regional sample collection

It cannot be over emphasized that quality control is vital throughout the activity. It is crucial that the data produced for national and international geochemical mapping are reliable and reproducible. Measures should be taken at all stages to control the quality of the sample collection, treatment and analysis (see Chapter 8 for more detailed suggestions). The following details are written primarily from the perspective of stream sediment sampling; minor modifications may be required where other media are employed.

5.4.1 Sample size

The long-term aspects of international and national geochemical mapping programmes necessitate that sufficient quantities of sample material are obtained to allow several different types of analytical treatment to be performed. The amount of sample collected should ensure that a minimum of 100g of the fine fraction material (see below) is available for analysis and reference.

5.4.2 Sample spacing

Samples should be collected from each cell of a predetermined pattern. In practice the cell size and sample spacing will be influenced by the availability of suitable sample sites, reflecting factors such as the drainage pattern, type of land-use and accessibility. Distances between drainage sample points will controlled by the size and shape of drainage basins, the required resolution of the maps to be produced and the length of the dispersion trains from the targets being sought. Regolith sample points should be distributed as evenly as possible over the survey area.

Initially, a network of global reference samples should be collected for standardization and monitoring purposes (see Chapter 4). Subsequently, samples should be collected at higher density to serve national interests (e.g. for mineral exploration, geological and environmental investigations). Sample density can be further increased using the same methods to prepare high resolution geochemical maps for specific purposes. Some examples of currently used sample densities are listed in Table 5-2 (note that these use a variety of media). Others may be found in Plant et al. (1988) and Demetriades et al. (1990).

In order to distinguish geochemical patterns related to geochemical or metallogenic provinces such as tin belts, porphyry copper belts in the Cordilleras, and chalcophile corridors in greenstone terrain a sample density of at least 1 per 100 km^2 is recommended. As a guideline, the sample spacing should not be greater than half the width of the feature to be distinguished on the geochemical map.

Irrespective of the size of the survey area the number of sample localities should exceed at least 300 and preferably 1000, in order to obtain statistically reliable geochemical patterns.

Country	Sampling density / km^2
U.K., China, Germany, Japan, U.S.A.	1
Germany	3
Finland	4
Canada, Sweden	10 - 15
Greenland, Nordkalott	20 - 30
Russia	0.25, 4, 100
Finland	300
Norway	500

Table 5-2 *Examples of sampling densities used by national geochemical mapping programmes.*

5.4.3 Sample-site selection

Sample sites should be selected to provide even coverage using low-order streams. Catchment basins should be no larger than 100 km^2. If the survey is specifically for geological or mineral exploration purposes sites should not be close to potential sources of contamination, e.g. present and ancient mining sites, roads, habitation, industry, dumping sites etc. However, if the objective of the survey is to map geochemical baselines in the environment as they now exist such contaminated sites may be included. Sites should be selected in such a way as to sample the survey area as efficiently as possible with as low order streams as possible.

The selected sites should be marked out on appropriate field maps or air photos prior to the sampling. Duplicate samples should be collected at a minimum of 3% of the sample sites. Randomization prior to analysis is recommended. See Section 8.3.2 for further discussion on this and related topics.

5.4.4 Collection of samples

Samples should be representative and this is often best accomplished by collecting composite samples. In the case of stream sediments this means collecting at least 5 subsamples from the active or most recently active stream bed along approximately 50 m of the stream channel. For soil and till this entails compositing samples from 5 pits or 5 sites in bigger excavations.

Tools should be made of wood (unpainted), aluminium or polyethylene (plastic), and containers of paper (specially manufactured “Kraft” sample bags) or polyethylene.

If the preselected site appears to be unfavourable another site, in the same cell, preferably in the same catchment basin or soil type area, must be sought.

5.4.5 Field observations and measurements at the sampling site

Once a sample locality is visited it is advantageous to obtain as much information as possible about the site. The nature of the information required depends on the physiographic conditions as well as on the purpose and logistics of the survey. It is suggested that pH and conductivity of the stream water be routinely measured. It is recommended that the gamma-radiation at each sampling site should be measured with a calibrated gamma-ray spectrometer (see Chapter 7).

5.4.6 Sample documentation and sample site documentation

The site documentation should include administrative information containing sample number, sample type, geographic location, altitude and date of sampling, as well as a descriptive part characterizing the sample site and surroundings (see Chapter 8). The use of field description forms which are either directly computer readable or designed so that the data may easily be transferred to a database is recommended (see Sections 12.4 and 12.5). The forms will vary from survey to survey and depend on the purpose of the survey, the sample media and the terrain. The minimum information needed is the site documentaion noted above and a characterization of the sample medium, the surroundings (geology and land use), and possible contamination risks. Each sample (including duplicate samples) should have a unique number. To avoid misnumbering in the field, it is recommended that sample containers be prenumbered.

5.4.7 Sample preparation and storage

In most areas it is recommended that the upper limit of the size fraction used for analysis be in the range 0.10 mm to 0.18 mm, but specific instructions for the four terrain types are included in Section 12.5. The recommended fraction (< 0.10 - 0.18 mm) is most commonly used for analysis and is relatively easy to obtain in most terrains. If it is scarce a coarser fraction should be used. If the purpose of a regional survey demands the use of an alternate grain size fraction the recommended grain size fraction should be obtained from a representative number of samples and the difference in element composition between the recommended and actual alternate grain size fractions should be documented. The stream sediment sample must be sieved either at the sample site using wet- or dry-sieving (see instructions by BGS) or by dry-sieving in the laboratory (using polyethylene sieving cloth on polyethylene or wooden frames). In the latter case the samples must first be dried at a maximum of 40°C, to minimize the loss of volatile elements such as Hg.

Grinding is recommended and should be carried out using high-alumina ceramic or agate equipment. The preparation room must be clean and free of dust and the equipment cleaned between each sample.

As samples will be analysed by several methods (see Chapter 6) it will be necessary to divide each into several portions. Samples must be thoroughly homogenized before dividing, which should be done with a sample splitter.

Sample material remaining after analysis should be stored properly in good quality containers (e.g. polystyrene) in a non-contaminating environment. The archived samples must be identifiable and retrievable for future use.

5.5 Summary of recommendations

Sample collection:

(1) national mapping should be performed according to internationally compatible standards;

(2) at least one sampling procedure should be applicable and used consistently in any given geographic area, from global to regional scales;

(3) stream sediment samples from tributary drainages are the preferred sample medium, complemented by regolith samples;

(4) water should be sampled in conjunction with stream sediments wherever possible;

(5) if stream sediments cannot be collected, acceptable substitutes are regolith, till or lake sediment;

(6) where a change in landscape requires a change in sample media, sample media collected in neighbouring blocks must overlap to allow comparison of data;

(7) stream sediment catchment basins should be not more than 100 km^2;

(8) analyses should be undertaken on composites of 5 or more subsamples;

(9) duplicate samples should be obtained from at least 3 per cent of sites; and

(10) systematic labelling and documentation is essential.

Sample preparation:

(11) contamination must be avoided in sample collection, preparation and storage by appropriate choice of tools, equipment and containers;

(12) wet or dry sieving may be employed;

(13) upper limit of drainage sediment grain size fraction analysed should be in the range of 0.10 - 0.18 mm;

(14) a minimum of 100 g of the sieved fraction is required;

(15) non-stream sediment samples should be reduced to < 0.1 mm prior to analysis;

(16) sample material not required for immediate analysis should be archived for future use, in contaminant-free permanent containers; and

(17) systematic labelling and documentation is essential.

6 Geoanalytical Requirements

6.1 Introduction

Progress in geochemical mapping since it began in the 1950s has been due principally to the development of new and improved analytical techniques, providing better sensitivities for more elements, more rapidly. The analytical requirements for the establishment of a global geochemical database, designed to facilitate international geochemical mapping, need the best of the existing techniques. However, because the data are required for long-term reference purposes and comparisons over long distances there are some special considerations which need attention.

Most geochemical mapping has been undertaken to assist in discovering mineral deposits. Geochemical surveys in the 1950s were regarded as a new method of prospecting to enable the mining industry to locate unexposed mineralization, e.g. Cu, Pb-Zn or Ni, usually within a geographically restricted area. Hence the work was narrowly focused and, at best, semi-quantitative. The national mapping programs, which began 15 to 20 years later, expanded the approach which had been started by the mining industry so as to provide information about a wider range of elements of possible economic interest (see Table 2-2). It is only in the last decade that national programs have begun to add elements primarily because of their environmental significance. Only in isolated instances (e.g. in Sweden) have there been national geochemical mapping programs (other than water surveys) directed specifically to environmental studies. In general the elements determined and methods selected have been chosen according to the presumed principal mineral potential of the region under investigation.

Emphasis on mineral exploration considerations has influenced the types of sample collected, sample preparation, the analytical methods employed and the way they have been used. Cost-effectiveness, judged from a mineral exploration viewpoint, has been a prime consideration. This has not prevented large and unique data sets being acquired which have important environmental implications, but the establishment of environmental baselines was not the original purpose of most of the available mapping.

For both industry and government surveys, cost has been a limiting factor in the design of projects, with the necessity to counterbalance sampling density, the comprehensiveness and quality of the data to be obtained, against the size of area to be explored. Thus, elements considered as unlikely to be concentrated in economic amounts within a map area have not been determined; higher-cost, sensitive (and thus more precise) methods have generally been avoided if less sensitive, inexpensive, methods could provide adequate data. These generalizations can be verified by close inspection of various national survey publications (see references).

The **list of elements determined**, comparing one region with another, has varied widely. This is illustrated by Table 2-2 which indicates one of the many inconsistencies which exist in a selection of the available large-area datasets from different parts of the world. This table shows how few elements are included in and are common to the majority of published regional map sets. Of 29 regions considered on 5 different continents, only 3 elements (Cu, Zn and Pb) are included in all the map sets. The common omission of rock-forming elements such as Na, Mg, K, Ca and of minor and trace elements such as P and B, which can provide information about mineralizing processes and are also agriculturally important, illustrates the limitations of many existing databases.

Limits of detection have improved progressively with time as new methods have been introduced, but in many regions which have been mapped, important elements such as Ag, Au, Cd, Hg, W, Sb, have not been detected over large parts of the region although there is no reason to suppose that they are not present. The limits of detection have been too high. A number of elements of economic and environmental significance have not been included in mapping programs because the necessary analytical methods have not been available or were too expensive to apply. Xie (1990) has illustrated the clear economic benefits of lowering detection limits.

Accuracy of determination and comparability of data have been of secondary concern. With an emphasis upon exploration and in the absence of preexisting information, anomalous concentrations have been the prime target. Mineral occurrences can be discovered by mapping the contrast between mineralized and unmineralized areas. It is common practice in exploration to analyse a selective particle size fraction of the material collected in order to focus on a particular mineralogical component. Individual elements are not uniformly distributed in all size ranges. Similarly, partial chemical extractions have been widely used in analytical work because they are convenient to use and often effective for the specific purpose of finding sulphide mineralization. In this context, although careful and consistent work is required, absolute accuracy is not meaningful.

The **precision** of measurements is essentially a function of concentration. Precision of measurements has received increasing attention and shown steady improvement through the years, because whatever has been sampled, and however it has been analysed, it has been expected that the numbers produced should be repeatable. In general, the relative standard deviation (RSD) for the major elements should be less than 3%, the RSD for minor and trace elements should be less than 10%, the RSD for certain trace and ultratrace element should be less than 30%. It is important to state the confidence level of the quoted precision. However, in practical terms it is the combined uncertainties of the sample media selected, sample collection, sample preparation, and sample analysis processes that affect the reliability and significance of maps produced.

In order to establish global geochemical baselines and meet the need for geochemical maps which are quantitatively consistent irrespective of national boundaries the above factors need to be reassessed, taking into account the capabilities of present day geoanalytical methods.

6.2 Review of geoanalytical methods

This section and related supplementary information contained in Section 12.6 is taken from a report prepared by G.E.M. Hall, Canada, (Hall, 1991).

6.2.1 Introduction

The techniques most used in modern laboratories for the analysis of rocks, sediments and soils, and the individual merits of these methods, are briefly reviewed in this section and at greater length in Section 12.6. The growth of geochemical exploration since the 1950s has gone hand in hand with advances in analytical techniques.

Colorimetry and DC arc emission spectrometry are now considered to be obsolete techniques and consequently these topics are not discussed. However, it may be noted that colorimetry possessed one advantage lost with later developments. The method could produce limited data in the field (for heavy metals), facilitating rapid on-site investigations. This is of no significance in terms of the high-quality multielement determinations required to establish baseline data, but for many practical applications of geochemistry, long waiting times inherent in present multi-stage laboratory procedures are a handicap.

There are still some specialized usages for flame atomic absorption spectrometry (F-AAS); graphite furnace (GF-AAS) has recently enjoyed a revival. The extremely high sensitivity of GF-AAS is counterbalanced by its low productivity (1 or 2 elements simultaneously and long cycle time). Probably the most widely used technique in 1993 in terms of volume of data produced is inductively coupled plasma atomic emission spectrometry (ICP-AES). ICP mass spectrometry (ICP-MS) is a more recent development, with applications development commencing about 1983 and still in progress. ICP-MS has the advantage of sensitivity combined with essentially simultaneous multi-element capability. Its capital cost, however, is about twice that of ICP-AES and it is more problem-prone than the latter.

Of great importance when considering an analytical method is whether a sample decomposition procedure is required and, if so, what qualifications or limitations this imposes on the results obtained. In the case of solution based techniques such as AAS, ICP-AES and ICP-MS it is essential to specify how the analyte was put into solution. Which acid or fusion mixture was used? Was it appropriate for the minerals present? An ICP is simply a source of energy used to volatilize, atomize and ionize an analyte. Decomposition procedures are time consuming and they are the weak link in geoanalytical methods. For this reason X-ray fluorescence (XRF) and neutron activation analysis (NAA) have a special position in geoanalysis because these methods measure the total amount of an element in a sample, irrespective of the form in which it occurs; minimal sample preparation is required. Gamma ray analysis techniques, which can be applied *in situ* or in a laboratory to both natural and anthropogenic gamma emitting elements are discussed in Chapter 7.

6.2.2 Decomposition techniques

In choosing decomposition techniques, the following criteria must be addressed: the chemical and mineralogical properties of the sample; the elements of interest; the constraints imposed by the analytical technique(s) to be employed (e.g., interferences, especially from major constituents); and the precision and accuracy limits acceptable to meet the objectives of the program.

The material must first be reduced to a particle size not greater than 150 μm, preferably 75 μm (200 mesh sieving). Decompositions are based largely on two methods of breaking up the crystal lattice: the use of acids, or fusions. The terms “partial” or “total” are often used, somewhat inconsistently, to describe the effectiveness of digestion. For the purpose of establishing a global geochemical reference network, and as a starting point for international geochemical mapping, it is recommended that the first priority be to determine the “total” amount of each element in a sample. Methods should be used which permit all elements to be determined. This indicates the need, for certain elements, to use methods with very low detection limits.

6.2.2.1 Acid digestion

Acid digestions in common use include aqua regia and various mixtures of HF-$HClO_4$-HNO_3-HCl; different combinations can be employed for different objectives. The advantages enjoyed by acid as opposed to fusion decomposition include: extraneous salts are not added to the analyte solution; acids can be obtained at a high degree of purity; Si can be volatilized with HF, thus reducing salt content; and, procedures are adaptable to large scale production. Note that so-called *total* acid attacks, do not dissolve the refractory minerals cassiterite, wolframite, chromite, spinel, beryl, zircon, tourmaline, magnetite and high concentrations of barite, amongst others. Ignoring this fact can lead to misinterpretation of data and subsequently to incorrect hypotheses.

6.2.2.2 Fusions

The great efficiency of fusion compared to acid attack is due to the effect of the high temperature (500-1100°C). Heterogeneous reactions taking place in the melt are of two types: acid-base and oxidation-reduction. Alkaline flux reagents include Na and K carbonate (and bi-), Na and K hydroxide, lithium meta or tetraborate and sodium tetraborate; acid fluxes include Na and K hydrosulphate, Na and K pyrosulphate, boron trioxide and hydrofluoride. Oxidative reagents comprise largely Na_2O_2, KNO_3 and $KClO_3$ while carbonaceous substances such as flour and starch are added to flux mixtures for a reducing action. The drawbacks of a fusion are: (1) the potential addition of contaminants due to the high flux:sample ratio (3:1 to 10:1); (2) the high salt concentration introduced and subsequent need for a higher dilution factor; and, (3) the difficulty in streamlining the operation for high throughput.

6.2.3 Analytical techniques

6.2.3.1 Atomic Absorption Spectrometry (AAS)

AAS was applied to geoanalysis in the early 1960s following the availability of commercial instrumentation and it remained the leading technique in the analysis of solutions until the advent of ICP-AES in the late 70s. The reason for its decline in favour of ICP-AES is due mainly to the fact that only one element at a time can be determined by AAS and hence it cannot compete in speed with multi-element techniques. Also, the short linear dynamic range of AAS necessitates dilution for the more highly concentrated analytes which leads to reduced productivity and greater error. The principle advantages of AAS comprise its specificity, simplicity, low capital outlay, ruggedness and relative freedom from interferences. The most important geological applications of AAS now lie in the specialized areas where flame atomization is replaced by graphite furnace or vapour generation/quartz tube modifications. Elements which can be determined by AAS are given in the Section 12.6.

6.2.3.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

The first ICP emission spectrometer was introduced commercially in 1975. Its advantage over the established technique of AAS is the ability to determine 20-60 elements simultaneously in a cycle time of 2-3 min. Furthermore, the long linear dynamic range of 3-5 orders of magnitude meant that both major and trace elements could be determined on the same solution (i.e. no dilution). In 1992 it was the leading technique in production-orientated geoanalytical laboratories. Elements which can be determined by this method are given in the Section 12.6.

6.2.3.3 Instrumental Neutron Activation Analysis (NAA)

Since the advent of high resolution germanium detectors in the 1960s, NAA has played a major role in the determination of trace elements in geological samples. The technique is particularly sensitive for the REEs (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), As, Sb, Sc, Co, Cr, Cs, Hf, Ta, Th, U and Au. Renewed interest in exploration for Au and the PGEs in the 1980s led to the widespread application of this technique in the analysis of rocks, sediments, soils and vegetation. Features such as the unrivalled simplicity of NAA, its flexibility to handle a range of sample weights (e.g., 1-30 g) and its ability for *direct analysis* without sample decomposition have encouraged the use of laboratories attached to nuclear facilities.

The simplicity, productivity, relative freedom from matrix effects and particularly the absence of need for decomposition procedures, which can lead to both loss of analyte and contamination, ensure NAA a continuing important role in geochemical analysis. Its capability in determining the REEs, Au, As, Sb, Hf and Ta and other elements clearly demonstrates that it is a technique complementary to others such as ICP-AES and XRF whose strength lies in analysis for the majors and base metals. Elements which can be determined by this method are given in the Section 12.6.

6.2.3.4 X-Ray Fluorescence Spectrometry (XRF)

XRF was introduced in the 1960s for the routine analysis of rocks for major elements and a select suite of trace elements, namely Sr, Rb, Y, Nb and Zr. Samples are prepared as fused discs or pressed powders. The availability of extremely stable high power X-ray tubes and the development of mathematical procedures to correct for absorption-enhancement effects have resulted in such excellent precision in silicate analysis that figures of merit are essentially limited by the degree of sample inhomogeneity.

In summary, XRF is applicable to the determination of elements from F to U at concentrations in the parts per million (ppm or mg/kg) to per cent range but is limited in the variety of matrices studied, silicates being by far the most common.

Matrix corrections require special attention in unusual samples and the lack of well characterized similar standard reference materials (SRMs) is a hindrance. The technique is easily adaptable to automation and sample preparation is simple, without problems associated with dissolution. Discs or pellets can be stored for repeat analysis. XRF is an exemplary technique in analysis for the major elements and the traces Rb, Sr, Y, Zr, Nb, Pb and Th and performs well for Co, Ni, Cu and Zn. There has been a trend in some laboratories to replace this method by ICP-AES but the precision of XRF in the above determinations is outstanding in silicate and carbonate matrices and its capabilities are considerable for routine automated analysis.

6.2.3.5 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The first commercial ICP-MS instrument was introduced in 1983. By 1992 over 400 units were in use world-wide, but few commercial geoanalytical laboratories were using the technique routinely. The attractive features of ICP-MS are simple spectra, wide linear dynamic range (10^4-10^5), flexibility, the ability to measure isotope ratios as well as elemental concentrations, and excellent detection limits in solution in the range 0.01-0.1 ng/ml for most elements. Its high sensitivity makes it an attractive technique for ultra-trace analysis; it is not suitable for major element determinations. Spectral interferences are far fewer than in ICP-AES and are relatively easy to predict. Elements below mass 80 tend to suffer the most interferences and care is needed in this region.

There have been three application areas where ICP-MS has had a major impact in geoanalysis. These are in the determination of REEs; Au and PGEs; and a group of refractory elements not well served by more established techniques, namely Hf, Ta, Mo, W, Zr and Nb. In many cases the critical factor in computing the detection limit in a method based on ICP-MS is not the sensitivity of the analytical technique but the random contamination of the blank incurred in the sample preparation procedure.

The extreme sensitivity of ICP-MS benefits in two ways the determination of those elements of low natural abundance: detection limits below "natural background" can be achieved so that background *itself* can be estimated reliably; and efficiency and, therefore, cost can be improved so that multiple analytical techniques need not always be employed. For example, in the past XRF would have been chosen to determine Zr and Nb and NAA to determine Hf and Ta. These now form part of a larger package (including Mo and W) based on $LiBO_2$ fusion and ICP-MS where detection levels as low as 20 ppb (ng/g) in the sample can be reached. Undoubtedly, the use of ICP-MS will grow as the need for lower detection levels in geochemical mapping is accepted.

6.2.4 Waters and vegetation

The precision, accuracy and detection limits required for geochemical surveys based on water analysis are more rigorous and challenging than those required for current environmental monitoring programs. This is borne out, for example, by the Canadian Water Quality Guidelines list of 16 cations applicable to the quality of drinking water and freshwater aquatic life (Environment Canada, 1979). It is clear from this manual that the "average" level reported for some elements in Canadian and US surface waters is too high and is an artifact of an inadequate detection limit, e.g., Sb is said to average 1 *ppm* (μg/ml) in US streams while the range in Newfoundland lakes and streams has been measured as 1-160 *ppt* (ng/l) (Finch et al., 1992).

Until the advent of ICP-MS, inexpensive water analysis was only possible for major constituents and a few trace elements such as U and B which might be of interest to mineral explorers. U can be determined easily to < 0.1 μg/l by laser induced fluorescence. The analysis of natural water by ICP-AES requires a preconcentration process for most trace elements. Whilst almost any element can be determined at its natural level if sufficient effort is put into preparation procedures prior to analysis by ICP-MS, -ES, GFAAS etc, methods incorporating a twenty-fold or greater preconcentration by solvent extraction, coprecipitation, ion exchange or evaporation are inconvenient, expensive and often troublesome. Henshaw et al. (1989) analysed 250 lakes from the Eastern U.S. by direct ICP-MS for 49 elements and found that sensitivity was sufficient to allow determination of more than half these elements. ICP-MS is being increasingly used for water analysis.

Analysis of vegetation is in general well served by NAA, either as a pressed pellet, or preconcentrated as an ash for the determination of involatile elements.

6.2.4.1 Sample preservation and avoidance of contamination

Ideally, a water sample should be analysed as soon as possible after collection and be kept at 4°C in the interim. This is not feasible with large numbers of samples and in remote locations so the practise of adding acid upon filtration at 0.45 μm (this size is simply convention) has evolved. It has been found that the recommended ratio of 1 ml of nitric acid per litre of water encourages flocculation in some samples, e.g. those containing significant amounts of humic acids. HCl is the preferred preservative for some elements, e.g. Au, PGEs and those that form hydrides. The merits of HCl versus HNO_3 and their optimum concentrations are currently under evaluation. Mercury requires the presence of a strong oxidizing agent such as dichromate and thus must be treated separately. Addition of acid will change the equilibrium between species (e.g., As (III), As (V), and methylated forms) and further work needs to be carried out to ascertain the most suitable storage conditions for these species.

Uncontaminated sample collection and preservation are the biggest problems in obtaining reliable data on trace elements in waters. The present ability to measure at ppt (ng/l) levels has created a new industry of making “ultrapure” reagents, whose cost is obviously higher than “reagent-grade” labels. The sample containers themselves are a concern - polypropylene is recommended, Teflon is prohibitively expensive and its reputation for cleanliness is debatable. Investigations into alternatives are taking place. Contamination is experienced in laboratories with respect to various elements such as Zn, Al, Fe, Te, Pb, Bi and Pt. Dedicated facilities including glass/plastic ware, instrument and methods involving few manipulations can assist in minimizing contamination. A dedicated Clean Room is desirable.

6.2.5 General comment - need for independent quality control

Communication between laboratory and field staff is of paramount importance. Users of analytical data must monitor the validity of the results reported and those generating the data should be aware of the purposes for which the data are being utilized. Blind confidence should not be placed upon any laboratory’s quality assurance and control program.

Such programs may not always suit the types of sample matrices submitted or be rigorous enough to satisfy requirements close to limits of detection. Normally, laboratories evaluate a new method by its application to well characterized SRMs, available commercially from a number of organizations such as the CANMET Canada; Institute of Geophysical and Geochemical Exploration, China; NIST (formerly the U.S. National Bureau of Standards) and the United States Geological Survey. They then standardize their own internal controls against these for frequent insertion in sample batches. For the purpose of regional mapping, the organizations responsible should develop and standardize their own bulk control samples, the matrices of which are typical of those found in the region under study. Replicate data for these controls will allow computation of precision and accuracy of the methods used. In order to assess the relative magnitude of analytical variability (precision) versus the spatial geochemical variability and bias introduced during sampling, replicate analyses of the survey samples should be undertaken and Analyses of Variance determined. This matter is further discussed in Section 8.3.2.

For extensive references relating to analytical methods see the recent special issue of the Journal of Geochemical Exploration entitled Geoanalysis (Hall, 1992). This is a reference book for geochemists on the current state-of-the-art and describes not only the capabilities and limitations of major methodologies but the accuracy and precision expected, practicalities of usage, the suite of international reference samples available and discussions on data quality. Attention is also drawn to Geostandards Newsletter (editor K. Govindaraju), published in France twice a year by the International Working Group on Standards.

6.3 Analytical requirements for International Geochemical Mapping

6.3.1 General

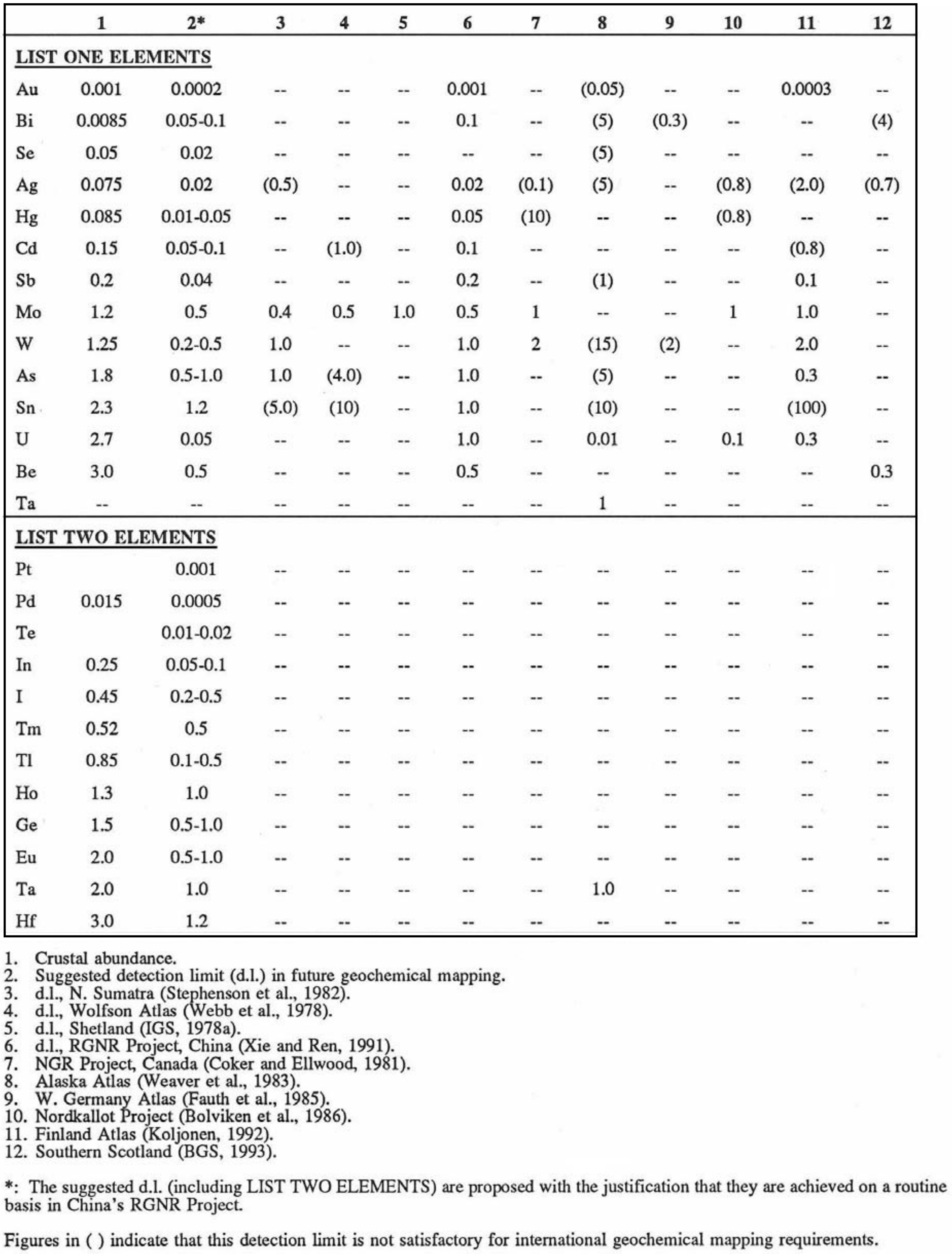
It is assumed that in general, even with stringent and comprehensive analytical requirements, the costs of sample collection, shipping, preparation and storage will exceed analytical laboratory costs.

The analytical requirements to arrive at a comprehensive and satisfactory global geochemical database need to be considered under two headings:

(1) requirements for the geochemical reference network, described in Chapter 4; and
(2) complementary requirements for national and international organizations engaged in the production of regional survey data.

National and regional surveys must be tied into the global geochemical reference network so that geochemical map data at any scale can be followed continuously across borders, from one jurisdiction to another. To achieve this, the global geochemical reference network and detailed regional surveys must be tightly linked, methodologically and spatially, through shared standards, common sampling points and sample media, and matching analytical requirements.

There is a potential difficulty in that a small number of countries have already conducted a substantial amount of geochemical mapping to their own unique national or regional specifications. In some respects these may differ from recommendations contained in this report, which have been prepared in order to supply a common global perspective. Where the differences apply principally to analytical requirements, and original sample material has been retained, then it should be possible to reconcile differences by reanalysis. If original sample material has not been retained, or there are major differences in the types of sample material collected, a percentage of the original sample sites should be resampled according to these international recommendations. There are serious difficulties in trying to reconcile data based on significantly different sample media (see Chapter 3). Actions must be determined on a case-by-case basis and cannot be further considered here.



	1	2*	3	4	5	6	7	8	9	10	11	12
LIST ONE ELEMENTS												
Au	0.001	0.0002	--	--	--	0.001	--	(0.05)	--	--	0.0003	--
Bi	0.0085	0.05-0.1	--	--	--	0.1	--	(5)	(0.3)	--	--	(4)
Se	0.05	0.02	--	--	--	--	--	(5)	--	--	--	--
Ag	0.075	0.02	(0.5)	--	--	0.02	(0.1)	(5)	--	(0.8)	(2.0)	(0.7)
Hg	0.085	0.01-0.05	--	--	--	0.05	(10)	--	--	(0.8)	--	--
Cd	0.15	0.05-0.1	--	(1.0)	--	0.1	--	--	--	--	(0.8)	--
Sb	0.2	0.04	--	--	--	0.2	--	(1)	--	--	0.1	--
Mo	1.2	0.5	0.4	0.5	1.0	0.5	1	--	--	1	1.0	--
W	1.25	0.2-0.5	1.0	--	--	1.0	2	(15)	(2)	--	2.0	--
As	1.8	0.5-1.0	1.0	(4.0)	--	1.0	--	(5)	--	--	0.3	--
Sn	2.3	1.2	(5.0)	(10)	--	1.0	--	(10)	--	--	(100)	--
U	2.7	0.05	--	--	--	1.0	--	0.01	--	0.1	0.3	--
Be	3.0	0.5	--	--	--	0.5	--	--	--	--	--	0.3
Ta	--	--	--	--	--	--	--	1	--	--	--	--
LIST TWO ELEMENTS												
Pt		0.001	--	--	--	--	--	--	--	--	--	--
Pd	0.015	0.0005	--	--	--	--	--	--	--	--	--	--
Te		0.01-0.02	--	--	--	--	--	--	--	--	--	--
In	0.25	0.05-0.1	--	--	--	--	--	--	--	--	--	--
I	0.45	0.2-0.5	--	--	--	--	--	--	--	--	--	--
Tm	0.52	0.5	--	--	--	--	--	--	--	--	--	--
Tl	0.85	0.1-0.5	--	--	--	--	--	--	--	--	--	--
Ho	1.3	1.0	--	--	--	--	--	--	--	--	--	--
Ge	1.5	0.5-1.0	--	--	--	--	--	--	--	--	--	--
Eu	2.0	0.5-1.0	--	--	--	--	--	--	--	--	--	--
Ta	2.0	1.0	--	--	--	--	--	1.0	--	--	--	--
Hf	3.0	1.2	--	--	--	--	--	--	--	--	--	--

1. Crustal abundance.
2. Suggested detection limit (d.l.) in future geochemical mapping.
3. d.l., N. Sumatra (Stephenson et al., 1982).
4. d.l., Wolfson Atlas (Webb et al., 1978).
5. d.l., Shetland (IGS, 1978a).
6. d.l., RGNR Project, China (Xie and Ren, 1991).
7. NGR Project, Canada (Coker and Ellwood, 1981).
8. Alaska Atlas (Weaver et al., 1983).
9. W. Germany Atlas (Fauth et al., 1985).
10. Nordkallot Project (Bolviken et al., 1986).
11. Finland Atlas (Koljonen, 1992).
12. Southern Scotland (BGS, 1993).

*: The suggested d.l. (including LIST TWO ELEMENTS) are proposed with the justification that they are achieved on a routine basis in China's RGNR Project.

Figures in ( ) indicate that this detection limit is not satisfactory for international geochemical mapping requirements.

Table 6-1 *Detection limits for elements with crustal abundance of less than 3 ppm.*

6.3.2 Geochemical reference network - analytical requirements

Samples which are to form part of a global reference network justify the greatest care and attention in all respects at all times. Data must be comparable. The analytical requirements for reference network samples are governed by the following desiderata, bearing in mind that some are not attainable in the short term for all elements, depending upon the media:

> (1) All elements in the periodic table should be determined (except H, O, Tc, Po, At, Fr, Ac, Pa and inert gases other than Rn), plus total loss-on-ignition (see Fig.6-1);
>
> (2) The total amount of each element present is the most fundamental (and reproducible) quantity in any sample, therefore direct measurement techniques, e.g. XRF or NAA, or total extraction procedures should be employed as a first priority. In this context accuracy is very important; the use of standard reference materials is discussed below;
>
> (3) Analytical methods should be employed which have a limit of detection significantly below the anticipated abundance of each element in the various specified sample media. Methods with insufficient sensitivity to produce reportable values for any given element in at least 80% of the samples cannot be considered satisfactory. It should be noted that average abundances of a number of elements (e.g. Ag, Au, Bi, Hg) in various media are not well established.
>
> (4) High analytical precision is essential. The use of methods providing low limits of detection provides the best assurance of good precision for trace elements. However, for all elements, it is the combined errors and uncertainties of site, sampling, preparation, and analysis that affect the significance of the data;
>
> (5) Non-destructive methods of analysis should be used where the above requirements can be met, to allow the use of large sample weights and in order to reduce sample wastage; and
>
> (6) The amounts of the principal natural and anthropogenic gamma emitting isotopes in the regolith should be determined, as a component of geochemical baseline data.

Table 6-1 shows crustal abundance data for elements with crustal abundances below 3 ppm (column 1), detection limits achieved in some past and current geochemical mapping projects (columns 3 - 12), and a list of suggested detection limits (column 2), based on analytical methods now in use in China.

It should be noted that samples from the Global Reference Network sites could have the supplementary function of being used to study and monitor the dispersion of degradation products of organic pollutants in the environment, e.g., from pesticides and herbicides, solvents and plastic containers.

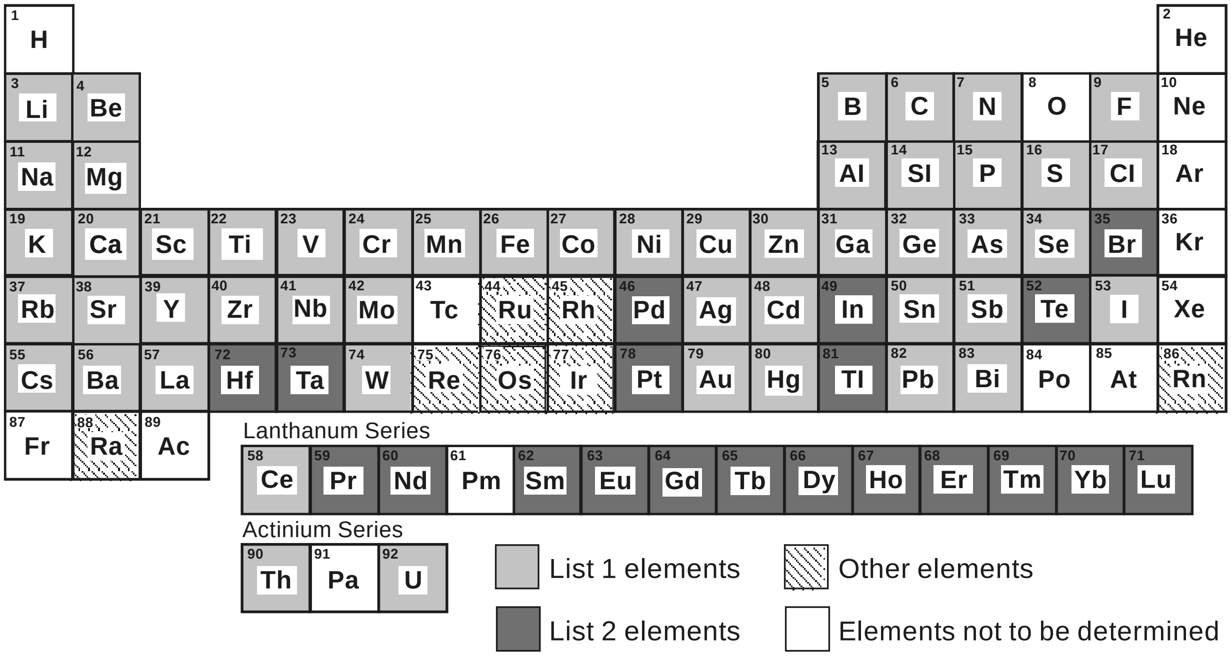


Figure 6-1 *Recommended list of elements.*

It is recommended that an evaluation of the best methods for the specific analytical requirements relating to the geochemical reference network, should be determined by the Geoanalytical Committee of the Association of Exploration Geochemists. From this evaluation, specific laboratories can be invited to participate in the analysis of samples collected for the geochemical reference network. Two examples of analytical schemes in current use in China and Finland are described in Section 12.6.1. The organizational and financial implications of implementing the analytical and other aspects of the recommendations are further discussed in Chapter 10.

Recognizing that the desiderata with respect to limits of detection for some elements in some media are beyond the capabilities of existing analytical procedures, every encouragement should be given to the appropriate authorities to sponsor the requisite research and development which will enable the requirements to be met in the not-too-distant future.

Concentration Range	∧ log C
< 3 dl	< ± 0.3
> 3 dl	< ± 0.2
1 - 5%	< ± 0.2
> 5%	< ± 0.1

A: Allowance of bias in the determination of elements in **primary** SRMs.

Concentration Range	∧ log C
< 3 dl	< ± 0.2
> 3 dl	< ± 0.1
1 - 5%	< ± 0.1
> 5%	< ± 0.05

B: Allowance of bias in the determination of elements in **secondary** SRMs.

dl = detection limit

Table 6-2 *Allowance of bias in the determination of elements in China's primary and secondary SRMs.*

6.3.3 Use of standard reference materials

Analytical bias, both interlaboratory or batch-to-batch within a laboratory, must be reduced to a minimum in order to generate globally comparable data. This can be achieved by selecting the best methods and using standard procedures in conjunction with routine monitoring of data quality. Primary and secondary standard reference materials (SRMs) must be prepared and used in these procedures. The Chinese "GSD" and the Canadian "STSD" series of SRMs are internationally recognized stream sediment samples, well documented with recommended values of many elements, and are proposed for use as primary SRMs for geochemical mapping. Primary SRMs can be used for the selection of optimum analytical methods prior to the initiation of a geochemical mapping project. The preferred method will be that which yields analytical data closest to the recommended values.

A set of primary SRMs should be inserted in each batch of 500 samples during routine multi-element analysis (approximately 4% of the total). The analytical bias between different national surveys can be determined in this way and if necessary the results from SRMS in each batch can be utilized for levelling data. Global geochemical network samples from within each country or region will constitute secondary SRMs. Four secondary SRMs should be inserted in each batch of 50 or 100 samples. These samples can be used for the monitoring of between-batch and between-map bias.

The logarithmic deviation, log△ C, of the determined values with the recommended values of primary or secondary SRMs can be used to monitor the between-batch, between-method, between-map or between-laboratory bias. Criteria established in China's national geochemical mapping project can be used for reference (Tables 6-2, A and B). If the SRM data obtained during any part of the work are outside tolerance limits, then determinations should be repeated.

6.3.4 Proposed arrangements for reference sample analysis

It is recommended that in order to minimize the problems which can arise in establishing inter-laboratory comparability of data, because of the importance of establishing consistent worldwide reference data, only a small number of laboratories should be engaged on the task, each selected for its demonstrated and recognized expertise in a particular method of analysis.

If possible, a single laboratory should be responsible for one type of analysis performed on one type of sample media, collected worldwide. It is also desirable that where possible some elements should be determined by more than one method in order to cross-check results.

It is discussed and recommended elsewhere in this report that samples will be collected from approximately 5000 cells worldwide and each cell should be sampled at 5 to 10 sites, following the principles outlined in Chapter 4. The media sampled will be as follows:

	Humus
Regolith	Upper A_{25} (residual and/or overbank and/or floodplain)
	Lower (C horizon)*
Drainage	Sediment (stream and/or lake sediment),
	Water

*Collection of a lower overbank and/or floodplain sample is **optional**.

Thus each cell will provide a minimum of one sample type (regolith), probably 3 or 4 other sample types, depending upon the landscape. As a maximum, there could be 8 types of solid sample, **plus** humus and water samples, from 10 separate sites. A composite will be prepared from each cell for each type of sample. Thus, at the completion of reference network sampling there will be approximately 5000 of each type of *composite* sample. Because humus and water samples will not be obtained in arid areas, there will be smaller numbers of these. Lake sediments will be collected from less than 8% of the world's surface. In order to apply ANOVA statistical procedures it has been recommended (in Chap. 4) that samples from each site should be analysed separately, because the cost of sample collection, particularly from remote areas, is substantial and the value of the additional information provided is considerable. However, the analysis of individual samples will increase the analytical cost for each sample media up to ten-fold, and it will take time to obtain all the data.

It is important that all samples of a given type should be visually examined by a small group of scientists experienced with surficial materials in order to note variations or discrepancies. Therefore it is recommended that each type of sample should be sent to a designated receiving laboratory which would co-ordinate all work on that particular sample type. Logically this laboratory could be responsible for applying one analytical technique, for example XRF, NAA, ICP-AES or ICP-MS, on this sample type or possibly on all sample types. This laboratory would be responsible for distributing splits of the samples to other participating laboratories responsible for other techniques. In this way laboratories accepting responsibility for certain methods could be responsible, ultimately, for handling up to 50 000 samples of a given sample media. Allowing for replication of analyses, the total number of analyses could be of the order of 10 per cent greater than the number of sample sites for that particular media. This volume of work is not considered excessive in terms of the number of samples commonly processed by production-orientated laboratories, given that samples will be received over a number of years. Even under ideal circumstances, with high priority and adequate funding, it is estimated that sample collection would take at least five years.

6.3.5 National and international geoanalytical requirements

The production of geochemical maps at scales commonly ranging from 1:1 million to 1:50 000, is normally the responsibility of national organizations. In addition to providing a global overview, the prime reason for the establishment of the geochemical reference network is to make it possible for researchers to compare and relate geochemical phenomena anywhere in the world.

It is proposed that a split of analysed reference samples from each cell in the geochemical reference network should be retained in the country or region of origin, for ongoing reference purposes and quality control of subsequent geochemical work in that country. These sample splits will serve as secondary standard reference materials (SRMs). As analytical data for these reference samples become available, a copy will be forwarded to the responsible national earth science institutes in the countries of origin. The existence of reference data and materials relevant to every region will make it possible for neighbouring countries to compare and connect their detailed work and contribute to part of a single international database.

Recommended field sampling methods to encourage greater commonality for regional geochemical surveys are given in Chapter 5. With respect to analytical requirements for these surveys, it is assumed that many countries will wish to use and develop their own analytical capabilities. Those not in a position to do so should, as an alternative, provide specifications for the work to be carried out by others, but these specifications should be compatible with recommended international procedures and employ the locally available reference materials.

The existence of international recommendations regarding the selection of sample media and analytical methods is not intended to suggest that organizations should not choose what they consider to be the optimum sample type, sample spacing or analytical method for their own particular purposes. However, it is strongly recommended that whenever other media or methods are chosen, these should be linked to the global network, by sampling at the same sites as are used for global reference network and using the secondary standard reference materials (SRMs) from these sites to establish a known relationship between their own analytical procedures and those recommended for international use.

It is recommended above that for the global geochemical reference network it is desirable, ultimately, to obtain data for almost the entire periodic table. It is unlikely that many countries will see a need to make detailed maps for so complete a list. Nevertheless, given the heterogeneous collection of data in existing datasets it is highly desirable that a common range of elements of known economic and environmental importance should be determined in every country, by standard methods. If some of the necessary facilities are lacking, rather than accept inferior data, consideration should be given to having some of the work undertaken in an internationally recognized laboratory. The recommended elements to be determined are be grouped into packages (Fig.6-2)

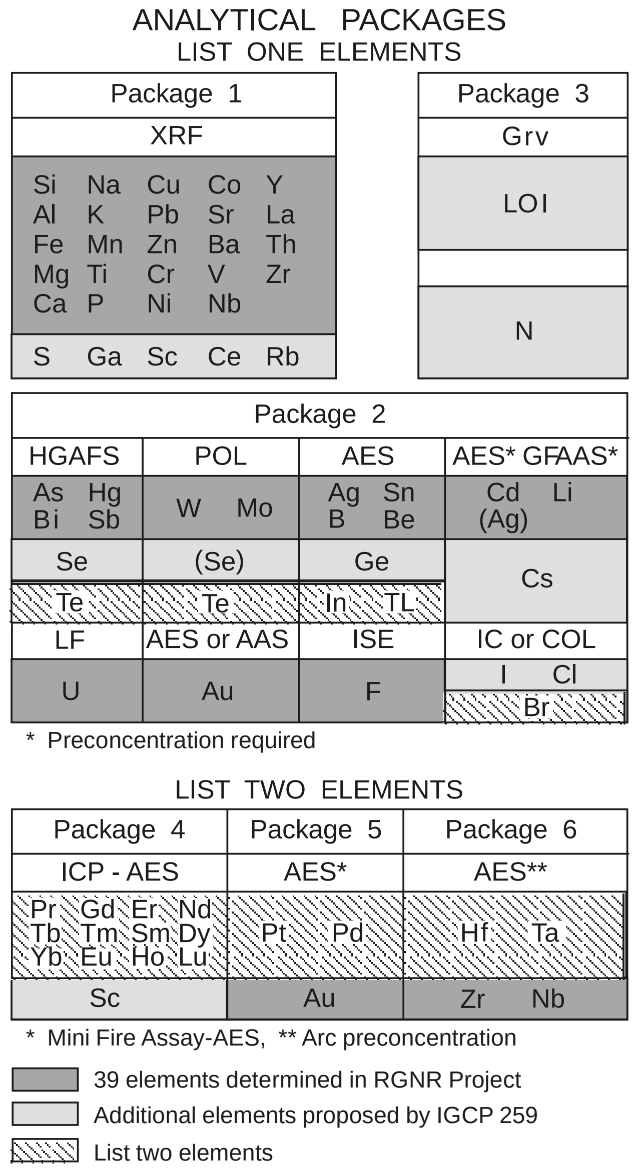


Figure 6-2 *Analytical packages for List 1 and List 2 elements.*

-List (1) elements, for economic and environmental purposes, include a group of rock-forming major elements and a group of minor, trace and ultra-trace elements (to total 51) that should be determined in any new geochemical mapping project;
-List (2) elements that could usefully be added depending upon the funding of the project and the availability of laboratory facilities.

Analytical precision will depend upon the method used and the element determined. Generally speaking, the RSD for the major elements should be less than 3%, the RSD for minor and trace elements should be less than 10%, the RSD for certain trace and ultratrace element should be less than 30%.

6.4 Summary of recommendations

The analytical requirements for the purpose of producing internationally comparable geochemical baseline data are as follows.

(1) Given the many applications of baseline data, a comprehensive multi-element approach is essential. Analytical requirements are considered in two categories,
(a) for the global geochemical reference sample network (GRN); and
(b) national or regional surveys conducted by national or international organizations.

(2) Samples collected as part of the global geochemical reference network (GRN) should ultimately provide abundance data for 78 elements, using methods with limits of detection significantly below presently estimated crustal abundances. The following elements are not to be determined: H, O; inert gases (except Rn); Tc, Pm, Po, At, Fr, Ac and Pa.

(3) Analytical requirements for national or regional surveys must be fully compatible with those for the GRN. Where possible identical methods should be used but alternative multi-element schemes based on the techniques of XRF, ICP-AES, NAA etc. can be employed as long as the criteria of precision and accuracy are met. In order to portray the spatial distribution of elements as completely as possible, detection limits must be as low as possible.

(4) A proposal is made for a standard list of elements to be determined; elements are classed into List 1 (51 elements) and List 2 (20 elements) (see Fig. 6-1); Ru, Rh, Re, Os and Ir require the establishment of satisfactory methods and detection limits; Ra and Rn require radiometric methods.

(5) For national surveys, if analytical facilities are insufficient to cover all List 1 elements initially, missing data should

be added at a later date. List 2 is of lower priority, but potentially important.

(6) For the purpose of establishing reproducible baseline data of permanent value, analytical methods should be employed which provide the total concentration of each element present. Sample decomposition, where required, must therefore be total.

(7) Partial decomposition (partial extraction) methods have many variants in different laboratories and are difficult to standardize, so they are NOT recommended for any data that may be used for international compilation or correlation.

(8) With respect to national and regional surveys, it is recommended that if more than 20% of the reportable values for any element determined fall below the limit of detection, the results for that element should be considered as unsatisfactory and alternative methods considered.

(9) Strict quality control, through the use of appropriate primary and secondary standards is essential, and the manner in which standard reference materials have been used and the resulting quality control statistics must be reported with each dataset.

(10) The Chinese series GSD, GSS and the Canadian STSD standard samples are recommended to be used as primary SRMs in international geochemical mapping. For national surveys, primary and secondary standard reference materials (SRMs) should be used to monitor the analytical accuracy: primary SRMs to monitor the international or interlaboratory bias, and secondary SRMs to monitoring the routine between-batch bias within a laboratory.

(11) Radioelements are to be determined by gamma ray spectrometry, according to the procedures recommended in Chapter 7.

7 Radioelement Mapping

7.1 Introduction

7.1.1 General

Radioactive elements (radioelements or radionuclides) form part of the global environment. Their distribution and mode of occurrence are subject to the same natural laws as non-radioactive elements. Despite the fact that potassium is an essential constituent of cells in plants and higher animals, many members of the public are nervous about any manifestation of radioactivity (^{40}K is a gamma and beta emitter). In many countries the outdoor natural radiation intensity varies by a factor of 10 between different areas, arising from geological and environmental factors. Larger natural variations occur in some regions. In order to provide a factual basis for public reference and education, as well as scientific investigation, the distribution, abundance and gamma flux generated by naturally occurring radioactive elements needs to be on record as part of a common database containing information about all the elements.

As a consequence of the use of nuclear power in various forms over the past 40 years (for electrical generating stations, ships and satellites), accidents have occurred and anthropogenic radioelements have escaped into the environment. It is prudent to assume that, from time to time in the future, further accidental releases will take place. Whether an individual accident constitutes a hazard, and if so of what magnitude, needs to be assessed in the context of knowledge concerning the natural radiation background and local geochemistry of the area affected by each accident. Baseline data should be available before accidents happen and therefore the measurement of natural gamma radiation, and knowledge of the distribution of naturally occurring radioelements, are important components of international and regional geochemical mapping.

The radionuclides can be considered in two groups, those which are naturally occurring, i.e., K, U and Th, plus their daughter products, and those produced, deliberately or accidentally, by nuclear reactions as a consequence of human activities. The latter group, including nuclides such as ^{137}Cs, ^{95}Zr, ^{131}I, which are potentially hazardous to health, are chemically indistinguishable from the non-radioactive isotopes of the same elements normally present in the environment. Each radionuclide can be identified by its specific gamma energy emission, so gamma ray surveys provide the most effective method of recognizing the presence of these nuclides and mapping their abundance.

Gamma radiation methods have a second important role in systematic geochemical mapping because the detection and quantitative estimation of radioactive elements can be carried out *in situ*. Gamma radiation can be measured at a distance of tens, up to a few hundred metres, from its source, providing a form of remote-sensing. This facilitates the acquisition of continuous profiles across any land surface from a moving vehicle, or preferably a low-flying aircraft. In many terrains, especially those which are thickly forested and/or with high relief, logistical problems commonly prevent the optimum selection of sample sites on the ground and present a problem for surveys based on conventional surface sampling methods. In these circumstances airborne sensing has a unique advantage.

Although the naturally occurring radioelements are few in number, they are of considerable geochemical significance, because of their almost ubiquitous distribution and sensitivity as indicators of geological processes. The use of gamma ray spectrometry for quantitative mapping of surface radioelement distribution was established during the late 1960s. By measuring the gamma flux from ^{40}K, ^{214}Bi and ^{208}Tl, the surface abundance of K, U, and Th can be determined, expressed as per cent K, ppm equivalent uranium (eU) and ppm equivalent thorium (eTh) respectively. Potassium, U and Th, which directly or indirectly (via daughter products) are responsible for the natural radiation background, are found in measurable amounts in almost all rocks and soils, K as a major element, U and Th as trace elements. Spatial radioelement patterns can be used to differentiate lithologies and indicate zones of alteration. Interpreted in conjunction with other data these patterns can delineate areas of potential mineralization, which are not restricted to U and Th minerals. In addition to minerals commonly associated with U and Th, such as Sn, W, Nb, P, Be and rare earths, some types of Au, Cu, Co, Ni and Fe deposit are associated with characteristic radioelement signatures.

The development of atomic bombs for military purposes, followed by the introduction of nuclear reactors as an energy source, encouraged U exploration during the period from 1950 to 1980, and stimulated the development of gamma radiation methods for U exploration. It also stimulated geochemical exploration methods in general. The development of airborne survey methods took place during this period, culminating in high sensitivity gamma ray spectrometry, which began to be used for regional mapping during the 1970s.

In the context of recommendations for International Geochemical Mapping this section is principally concerned with ground (field portable) and airborne gamma ray measurements, with emphasis on the latter. It has been prepared by A.G.Darnley and M.Tauchid, drawing extensively for recent technical information upon IAEA Technical Report 323 (IAEA, 1991), the authors of which were R.L.Grasty, H.Mellander, M.Parker and A.Y.Smith. For more detailed information than can be included here, reference should be made to various Technical Reports of the International Atomic Energy Agency, Vienna (IAEA, 1991) and appropriate titles in Section 11.2.

7.1.2 Relationship between airborne and ground surveys

The area which can be sampled by a single ground traverse with a portable gamma ray spectrometer is many times less than the area which can be sampled by a single airborne traverse. A shoulder high detector is dominated by the radiation received from a 10 m swath; a detector on vehicle-mounted mast can be effective over a 25 m width, whereas an airborne survey flown at 125 m will respond to a 250 m band. Therefore, airborne equipment can survey an area many times faster. A more important consideration is that a person or vehicle on the ground is greatly handicapped by thick vegetation, fallen trees, swamp, water courses, steep slopes or large outcrops and may not see particular features because access is very difficult. An airborne system is much less affected by such problems and even in difficult terrain can search almost 100% of the surface.

Carborne ground surveys can be effective in open prairie or open savannah woodland, but in rugged terrain roads or tracks take the easiest routes across country and so may provide very uneven coverage and miss significant features.

7.1.3 Ground gamma ray spectrometry

Modern portable gamma ray spectrometers are relatively compact and lightweight (10kg), reliable and simple to use. Properly calibrated according to the method recommended by the IAEA (1979), they can provide *in situ* measurements of ground surface concentrations of K, eU and eTh. Detection limits/sensitivities of 0.25% K, 0.5 ppm eU, 1 ppm eTh are readily attainable, with repeatability within statistical limits which are set by concentration levels and counting time. To ensure meaningful measurements the geometric relationship between detector and ground must duplicate the calibration geometry, i.e., a fixed distance above an effectively infinite area flat source, or on the surface of a smaller (minimum 1.5 m diameter) source. For more information concerning the use of field portable gamma ray spectrometers, see IAEA, 1979.

In the context of the International Geochemical Mapping project the main function of ground measurements with a portable gamma ray spectrometer is to provide a link between data gathered by conventional geochemical sampling of the A soil horizon or upper regolith and related (coincident as far as possible) airborne gamma ray spectrometer profiles. Each type of measurement can provide K, eU or U, and eTh or Th data. A standard method of calibrating an airborne system is to fly over a test strip with a known surface concentration of radioelements. This is the basis for radioelement maps produced by airborne gamma ray spectrometry.

7.2 Airborne gamma ray spectrometry (AGRS)

7.2.1 General

Airborne gamma-ray spectrometry (AGRS) is an important component of the International Geochemical Mapping project because it permits geochemical mapping of radioactive elements (both naturally occurring and man-made) by remote sensing. Data can be reported in terms of radioelement abundance and nuclide dose-rate. The technique is, in practice, unique amongst geochemical methods in that it may be applied across any land surface. Quantitative correlation of ground and airborne data can be assured within known limits because airborne equipment is calibrated by relating airborne to ground measurements, under controlled conditions, over test ranges several km in length. The existing literature indicates that the reverse of the calibration process has an important application. In compiling geochemical maps for large regions, based on conventional surficial geochemical sampling methods, significant differences are commonly observed in element base levels for individual survey blocks, especially where methods have not been standardized. Uncertainty then exists as to the extent to which apparent changes in base level are due to real geochemical differences, or to the methods employed. Continuous profiles of surface Th and K abundance, derived from airborne data, can provide an independent continent-wide reference level against which estimates of Th and K, derived from various direct sampling techniques, may be compared (Darnley, 1993). This comparison enables inconsistencies in Th and K data to be recognized, which may in turn raise questions concerning the consistency of other data. This is important in the context of establishing reliable global geochemical baselines.

The most recent overview of airborne gamma ray spectrometry (AGRS) surveying is contained in IAEA Technical Report No. 323 (1991). The contents of this report, which illustrate the various considerations which enter into the execution of the method are summarized in Section 12.7.1.

7.2.2 Quality considerations in AGRS

Users of airborne gamma ray spectrometry data need to be aware of important considerations relating to survey parameters, equipment, calibration and data processing which affect the quality, and therefore the usefulness, of the products. Appropriate decisions concerning items listed in (a) and (b) must be taken before a survey is commenced; the methods to be adopted for item (c) should also be determined in advance:

(a) survey parameters: these include required sensitivity and spatial resolution, which influences detector volume and aircraft groundspeed, accumulation time and sampling rate, flying height, and flight line spacing and direction;
(b) equipment: selection of aircraft type; detector volume; sensitivity and reliability of ancillary equipment for measuring height and position; and
(c) calibration and gamma flux corrections.

These items collectively affect the validity of the results obtained and the extent to which detailed inferences may be drawn. The subject of flight-line spacing is analogous to questions concerning sample spacing in conventional geochemical surveying and is discussed in the following paragraph. The other technical items are specific to gamma ray spectrometry and are outlined in Section 12.7.2.

7.2.3 Flight line spacing

The selection of an appropriate flight line spacing for an airborne survey poses many of the same questions as apply to the selection of sample interval for a conventional ground geochemical survey. The key questions are, what size and shape of features need to be recognized? What contrast is expected between "background" and the features of interest?

AGRS is a regolith mapping technique, responding to whatever radioelements are present in (or on) the surface materials (including vegetation). This follows from the physical limitations of the method, whereby 90 per cent of the emerging radiation originates from within 25 cm of the surface, due to absorption within material surrounding the disseminated sources, radioactive mineral grains. Radiation originating from significantly greater depths is totally absorbed before it reaches the surface.

After processing, gamma ray spectrometry data collected on or above the ground surface are directly comparable with data from the analysis of regolith samples collected from 0 to 25 cm depth. However, whereas the along-line sample interval for a conventional soil survey is a matter of choice, gamma ray spectrometry conducted from a moving vehicle produces a continuous profile.

A single AGRS flight line at a ground clearance of 125m collects useful data over a width of approximately 250m. Thus to obtain nominal 100 per cent ground coverage of a larger area the flight line spacing should be not more than 250m. Because of the high cost, such intensive coverage is only undertaken in special circumstances over relatively small areas. For large regions where there are few reliable data it is generally prudent and much more cost-effective to conduct mapping in stages, first delineating the large features and subsequently investigating them in more detail.

As discussed elsewhere in this report, there are geochemical features of all sizes on the earth's surface. Of those that are well known, the continents represent one extreme example; of more economic significance, the SE Asia tin belt, the Sudbury nickel basin (Ontario), the Athabasca uranium basin constitute others, with dimensions ranging from 10^2 to 10^3 km.

If general information is required for reproduction at an "atlas" map scale of, say, 1:10 million, 10 km line spacing will provide adequate definition. A preliminary global overview at 1:40 million, could be provided with 40 km line spacing. The US NURE Program, which resulted in the production of radioelement maps of the entire USA was flown with an average line spacing of approximately 10 km (see Plate 3-7). In Canada some preliminary surveys have been flown with a line spacing of 50 and 25 km with 5 km adopted for more general reconnaissance purposes. Subsequently limited areas, deemed to have the greatest mineral potential, have been reflown with much closer line spacings (e.g., 500 or 250 m) for exploration purposes.

A similar philosophy has been followed in radioactive fallout mapping, for example in Sweden following the Chernobyl accident. Wide line spacing was used for a quick-look to establish the broad pattern. This was then followed up over contaminated areas by closer line spacing as necessary.

7.2.4 Products from AGRS mapping

Products from natural radioelement mapping may consist of profiles along each flight line or profile maps. Maps on which the data are plotted as profiles along horizontal axes formed by each flight line provide a quick and useful means of viewing the results of a survey. They can be produced on a field computer. Sometimes features can be seen on these maps which do not survive the subsampling and smoothing implicit in gridding and contouring operations.

Most map products require the data to be interpolated onto a regular grid. There are many ways for this to be done. Many of the standard geophysical gridding algorithms are unsuited to radiometric data, because of the inherent statistical variations. A suitable gridding algorithm is one which takes the average of all data points lying within a circular area, weighted for distance from the grid point.

Contour maps in one form or another are still the most widely used product of most airborne spectrometer surveys. The choice of algorithm, contour interval and style will normally be made after some experimentation, in consultation with the end-user of the data, but will generally involve a minimum of smoothing to respect the raw data as closely as possible.

Use of computer produced colour contour maps is now widespread. Again, the gridding algorithm, colour palette and other variables are usually determined after some tests and experiments. These maps are a very effective means of displaying the data and should be regarded as the principal map product for regional surveys.

Another effective map presentation is the colour ternary map, on which each radioelement is represented by one of the three primary colours, with intensity varying according to the radioelement concentration. There are several different ways to produce these maps, which give informative and semi-quantitative results. Section 12.7.2.3 contains additional information.

7.2.5 Other permanent records

In addition to field tapes carrying the raw data, there must be a digital archive containing processed records of both flight line data and gridded data. There should also be a complete report describing all technical details of the work so that the manner in which the work was conducted can be reconstructed and assessed. For further information see Section 12.7.2.3.

7.3 Fall-out monitoring using AGRS

Airborne gamma ray spectrometer systems designed for mapping geologically distributed radioelements can also be used for mapping fall-out products.

7.3.1 Principles of fall-out monitoring

Environmental contamination may take many forms. If man made nuclides enter the atmosphere from a known location, depending upon a variety of factors relating to the mode of injection, half-life of the contaminants, ambient weather conditions, both large and small scale meteorological phenomena control the fall-out distribution. Superimposed upon the movement and interaction of the large air masses which flow continuously across the continents, localized features such as shorelines, topography and elevation, etc., control precipitation and hence the rate and quantity of fall-out in a given area. There can be large variations in fall-out accumulation over a distance of a few km. Hence the approximate distribution pattern may be predicted from meteorological observations, but the prediction is likely to cover a large area and needs to be confirmed by actual measurements.

If the contamination is of a different kind, for example arising from a number of point sources lost along a surface transportation route, or scattered from a crashing aircraft or satellite, the problem is rather different and must be approached in a different way.

Use of airborne gamma ray spectrometry for fallout mapping is possible because most man made nuclides can be distinguished from those occurring naturally. The detection limit is dependent on the system used, the survey parameters and the ground concentration of natural gamma ray emitters. Based on Swedish experience after the Chernobyl accident, a 5% increase in mean gamma ray exposure rate can be detected at an altitude of 60 metres using detectors of 16.8 litres of NaI.

Nuclide	**Most important gamma energies keV**	**Half-life days**
Man-made:		
^{95}Zr	724,756	65
^{95}Nb	765	35
^{99}Mo	740	3
^{103}Ru	497	40
^{106}Ru	512	368
^{131}I	364	8
^{132}Te	230	3
^{134}Cs	605,795	730
^{137}Cs	662	11000
^{140}Ba/La	1596	13
Natural:		
^{40}K	1460	
Uranium series:		
^{214}Pb	350	
^{214}Bi	609,1120,1764	
Thorium series:		
^{228}Ac	910,960	
^{208}Tl	583,2620	
Natural emitters are presented without notes on half-life due to the very long half-life of their respective parent nuclide.		

Table 7-1 *Examples of man made and natural gamma emitters present in the environment.*

If the exposure rate is too high, there will be problems using the standard airborne geological system because of dead-time effects due to the high count rates. Depending on the count rates, this can be overcome by switching off individual detectors or detector packages. If the fall out is too high for a large volume NaI system, solid state detectors could be used instead with the added benefit of a much better energy resolution.

7.3.2 Fall-out nuclides

Most of the man made radioactive nuclides in the environment originate either from nuclear bomb tests, nuclear reactors or from nuclear power stations. The most important gamma ray emitting nuclides, man made and natural, that can be expected are presented in Table 7.1. Most of the gamma energies of the man made nuclides are well below the energy interval normally used for measuring the natural radioelements potassium, uranium and thorium. However, the ^{140}La gamma ray peak at 1596 keV interferes with both the potassium and the uranium windows.

7.4 Recommendations for global mapping

7.4.1 General statement

(1) Radioactive elements are of special public concern. Data to show their spatial distribution should be an essential part of any comprehensive global (and also regional) geochemical databases.

(2) The technique of gamma ray spectrometry enables the abundance of radioactive elements to be determined quantitatively. Its principal advantage is that in addition to being a laboratory technique, determinations can be undertaken rapidly, *in situ*, from a moving vehicle or from a low-flying aircraft. Gamma ray spectrometry is a standardized technique which can provide a continuous quantitative profile of radioelement abundance over any type of land surface. If profiles are closely spaced, an entire surface can be mapped. In addition to profiling or mapping natural radioelement distribution, radioactive fall-out can be identified, measured and delineated. The relevant data should be acquired as part of the collection of baseline information.

(3) Airborne gamma ray spectrometry can be used to provide an inter- and trans-continental Th reference datum to assist in levelling geochemical maps from geographically diverse regions.

(4) In order to obtain standardized data, methodologies recommended by and promulgated through the publications of the International Atomic Energy Agency should be followed (see references).

7.4.2 Use of existing data

It is recognized that in many countries there has been a significant past investment in radiometric (gamma radiation) surveys of various types, especially during the 1960s and 70s, primarily related to uranium exploration. Much of this work was sponsored by national governments or international agencies; in general, where surveys were sponsored by the mineral industry, attention was focused on small areas selected according to suspected mineral potential. This often resulted in overlapping patchwork coverage of priority areas. The early work, and most industry-sponsored surveys, were of a qualitative nature. Standardized methodology began to be introduced into some of the national/international agency large-area surveys during the 1970s. In the interests of economy, before new work is commissioned, there should be a review of existing data:

(1) Countries should make an inventory of all regional airborne and carborne gamma ray spectrometric surveys, and note all the relevant information (date of survey, system used, calibration, type of data processing and storage used, type of map produced, availability of the data). Data quality and completeness of documentation is more important than age, although obviously older data is likely to have been obtained with low-sensitivity equipment. Note that it is important to make a repository of all records and assure adequate storage of the data to prevent damage. The shelf life of most magnetic tapes is 10 years and where possible data should be transferred to an optical disk type of storage medium.

(2) If radiometric calibration facilities exist, but they have not been compared (intercalibrated) with internationally recognized facilities, this should be arranged through the IAEA.

(3) Where several separate areas have been surveyed, numerical data should be normalized/levelled, using the nearest available recognized calibration facility. If results of these surveys were not presented in terms of radioelement abundances (concentration of the three radioelements), a back-calibration exercise should be carried out so as to allow the preparation of quantitative geochemical maps (see Grasty et al., 1995).

(4) For environmental health radiation monitoring purposes, a map of air dose rate (Gy s^{-1}) or effective dose equivalent (mSv a^{-1}), should be produced.

(5) Where sufficient data are available, they should be sub-sampled onto an appropriate grid suitable for the production

of a regional or national atlas and ultimately the radioelement map of the world.

7.4.3 Collection of new data

Although it is desirable from the point of view of minimizing costs to make the maximum possible use of existing data, it should be recognized that many past surveys were undertaken with inadequate equipment and insufficient quality control. At best, they were qualitative rather than quantitative. There is often incomplete information concerning equipment, survey and data reduction parameters. If the data were not digitally recorded in a readily recoverable format the difficulty and cost of retrieving information can greatly exceed its value. In these circumstances, and for the many parts of the world where no gamma ray surveys have been carried out, it is necessary to collect new data, following recommended procedures.

(1) Many of the comments made above are applicable to newly collected data. Particular attention must be paid to calibration and standardized data reduction procedures, according to IAEA guidelines.

(2) ***In situ* ground measurements.** In order to link airborne with ground measurements, including conventional sampling for the non-radioactive elements, *in situ* measurements with a field portable gamma ray spectrometer (GRS) should be made at each subsite where a geochemical regolith reference sample is collected. Thus, several measurements should be made at each site in the 160 × 160 km primary sampling grid.

(3) With a modest increase in the equipment required, useful additional information can be obtained by using the same portable GRS to obtain a continuous profile whilst in transit in a road vehicle between sample sites (i.e., a carborne survey). If the 160 km cell sample sites are located close to surface transportation routes, then a continuous profile could be recorded along these routes where conditions are suitable, as a modification of the method used for reconnaissance purposes by Shacklette and Boerngen (1984).

(4) **Airborne gamma ray spectrometry.** The preferred method of obtaining comprehensive radioelement baseline data over a large region is by means of airborne gamma ray spectrometry. Widely spaced profiles are of comparable significance to widely spaced surface samples, but with the important advantage of being continuous along-line and not restricted or diverted by difficulties of surface travel or access. Continuous profiles enable the boundaries encountered en route to be identified as gradational or sharp, and in the latter case their exact position can be located. For an example of long profiles crossing a succession of major geological units within the Canadian Precambrian Shield see Fig. 3-4, taken from Darnley et al. (1971).

In order to complement the 160 × 160 km primary sampling reference grid it is recommended that flight-line spacing should be 80 km, and preferably 40 km or 20 km in populated areas, so that most points in the ground sampling network (which may be irregularly spaced for reasons of access) can be overflown. Where the ground sampling follows a straight (or nearly straight) corridor, it is obviously much simpler to arrange to overfly the sample sites. For the purpose of checking for possible level problems between isolated blocks of ground geochemical data it may be desirable and advantageous to insert additional flight lines whilst a suitably equipped aircraft is in the region.

“Option 3” in Section 4.3 envisages the simultaneous combination of ground geochemical sample collection and AGRS, by using a medium to large-sized helicopter for transportation between ground sites and the collection of airborne gamma ray spectrometry profile data en route. For negligible additional complication and cost, aeromagnetic data could also be collected, providing a link with existing geophysical datasets. Straight-line profiles could be flown at a maximum spacing of 80 km apart. Such an operation could be undertaken rapidly and efficiently, irrespective of ground conditions. In difficult terrain, costs for this combined operation could be less than for separately conducted ground sampling and airborne measurements. Such a combined operation would provide the fastest way of obtaining comprehensive global geochemical coverage.

(5) Irrespective of the flight line-spacing, data are normally collected along each line at constant 1s intervals. In order to produce a map which is not directionally biassed, along-line data must be smoothed over a distance proportional to line spacing. This reduces the amplitude of features. For this reason contoured maps are progressively less satisfactory as line spacing increases, so that when this exceeds 10 km profile maps are usually the preferred product.

7.5 Concluding comment

Subject to proper calibration and use, gamma-ray spectrometry is a unique tool for mapping the distribution of all radioactive elements, whatever their origin, in the surface of the regolith (termed the A_{25} horizon); the data which are acquired are an essential part of the description of the geochemical environment. In addition to providing baseline data for radioelements, the use of gamma ray spectrometry, because it can readily provide continuous profiles, facilitates the establishment of a continuous Th reference network to which all elements in the regolith, sampled at discrete sites and measured by other methods, can be related. It provides an independent method of monitoring geochemical level changes across all types of land surface.

8 Data Management

8.1 Introduction

Recommendations on the management and presentation of geochemical data for international geochemical mapping have been developed by the technical committee on data management. The initial responsibilities of the committee were to make recommendations on:

- the organization and contents of a world index of geochemical surveys,
- methods for levelling and normalizing diverse data sets,
- standard formats for cross-border studies,
- map preparation for principal user groups, and
- evaluation of data interpretation methods for principal user-groups.

During the work of the committee *methods of quality assurance* were added to the recommendations. Information on data quality is crucial for successful levelling of international data and any usage of merged data sets. Recommendations on usage of geographic information systems and image processing were also added as they offer tools to integrate geochemistry with other data.

An evaluation of data interpretation methods was not undertaken as they were considered less important than the basic issues. It is proposed that recommendations on interpretation methods be a task for a possible new international geochemical mapping project.

At an early stage it was decided that a database containing all raw previous survey data suitable for international mapping compilation would be difficult and too expensive to build and maintain. However, it was considered that local averages for relatively large blocks (geographic areas) would form a reasonable volume of data that would be manageable on personal computers or work stations, and would assist investigations on a global scale. To support this block database it was recognized that a bibliographic database containing information on the data sources used in the block database would be essential. These databases would be of manageable size and could be distributed to national and international agencies for their use. Therefore, the committee focussed its attention on the problems that these databases presented.

For new sampling in support of the Global Reference Network, the committee would make recommendations for the preparation and maintenance of an appropriate single database once the sample media and analytical data requirements had been defined. Some recommendations are detailed, while others are very general. The committee avoided making rigorous recommendations on subjects that must vary with time or national conditions. The recommendations on storage of geochemical data, for example, are made in order to facilitate easy transmission for international purposes, not to standardize the internal structure of national geochemical databases. Most recommendations must be considered as minimum requirements. The more quality control data that are available, for example, the better and more reliable will be the assessment of the quality of a whole data set.

The preparation of the technical committee's report, and communications between its members, was greatly facilitated by use of electronic mail using the Internet. The Internet is an appropriate technology for distributing project data files, databases and documents to, at least some, potential users in the future.

8.2 Databases

The storage and management of large data sets from national and international geochemical surveys is difficult and expensive on the global level, even with the most recent technology such as high capacity optical storage systems. However, general information about surveys and average local concentration levels can be collected practically and managed in a simplified and compressed form using microcomputers. Such information can be used for overviews and statistical summaries of geochemical surveys in connection with international geochemical mapping.

The recommended databases are (1) an *index database* or catalogue containing general information about available geochemical survey maps and data, (2) a *block database* containing average elemental contents within ½° x ½° latitude-longitude blocks, and (3) a *bibliographic database* containing references relevant to surveys in the index database. Some fields of the index database are equal to those used by the WEGS working group (Demetriades et al., 1990). Therefore selected WEGS data for surveys in Western Europe can be added easily to the index database. Figure 8-1 shows the logical relationships between the databases. The databases are described in detail in the appendix (Section 12.8).

It is recommended that a permanent organization take the responsibility for managing, updating and distributing the databases. However, survey data should be collected and entries for the international databases should be prepared by the organizations responsible for the geochemical surveys.

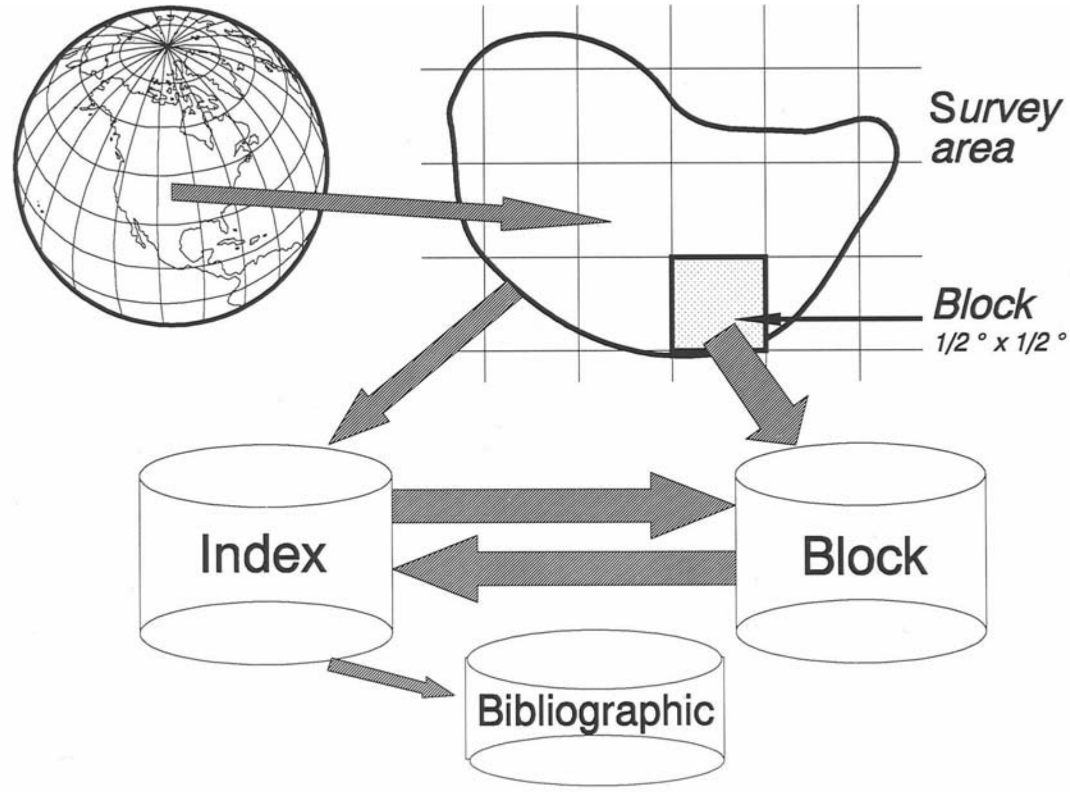


Figure 8-1 *Logical relationship between databases.*

The structure of the Index and Bibliographic databases is simple (flat) where each record is identified by a unique survey or bibliographic ID number and contains the relevant information. These records can be appropriately indexed in order to rapidly make the most common retrievals. The Block database is more complex and will likely consist of at least two tables to accommodate the different geochemical data, i.e., for measured parameters (1) and details on sample media, methods of analysis, etc. (2), together with a large index that the database management software builds itself. In selecting database software to manage such data many factors come into play, including functionality, ease of data exchange, cost and availability. For International Geochemical Mapping a major criterion must be ease of data exchange. Any database package must be capable of importing and exporting standard ASCII files where data items and records are clearly delimited by consistent ASCII characters. In addition, in recent years many de facto personal computer data exchange formats have developed. Database software or translation programs permit the exchange of data between many different database formats and are available for all the common operating systems in use today (DOS, Windows NT, UNIX, OS/2, System 7, VMS, etc.).

The established exchange formats for databases do not readily extend to the complex structures of geographic information where data types consist of points, lines and polygons, each with their own particular attributes. Some spatial data exchange formats exist, e.g., DIGEST which is used for the Digital Chart of the World project to assist international aviation and other activities. Use of the first generation of geographic data exchange formats has brought to light a number of limitations for more general use. Current research is aimed at developing more general new standards. A leading contender in this field is SAIF (Spatial Archive and Interchange Format) a draft Canadian Geomatics Interchange Standard of the Canadian General Standards Board (1992). Currently the ISO (International Standards Organization) is investigating the establishment of a geomatics study group whose task would be to make recommendations on spatial data exchange formats. It is important to recognize the need for international standards for spatial data exchange between Geographic Information Systems (see Section 8.7).

8.3 National and survey databases

The block data are derived from survey data sets maintained by national Geological Surveys and other national and international organizations responsible for their acquisition. The following sections describe procedures that are used by many major survey organizations to maximize the return on their investment in undertaking regional geochemical surveys.

These procedures help ensure that the data are of the highest quality.

In the following sections the term sample is used in its geological sense, i.e., to identify an individual piece of the natural environment collected for geochemical analysis, rather than in the statistical sense, where it connotes a set of individuals collected to represent some statistical target population. The term data set is used to indicate sample in the statistical sense.

8.3.1 Quality assurance

The interpretation of regional geochemical data is based on the information derived from chemical analyses of samples processed in several stages. The excellence of the interpretation depends on the quality of the data produced in these stages and the skill of the interpreter. Random variation is an unavoidable inherent component of the information relayed by geochemical samples. Sampling variability is due to lack of regional representativeness of the samples, and lack of local representativeness of single sampling units. These experimental errors are a function of the sampling grid and the type and size of single samples. Any stage of sample treatment following the sampling, such as storage, preparation, dissolution and analysis, will add variability to the final data. The natural patterns and distributions of elements are always more or less distorted.

In general, sampling and analytical variability cannot be totally removed, but they can be minimized according to the circumstances. The recommendations are concerned with basic arrangements for measuring and storing information about unavoidable error components at the various stages of a mapping programme.

8.3.2 Sampling, preparation and analysis

The effect of local heterogeneity, or sampling error, can be reduced by clustered sampling where several samples are taken near or at the same site and composited to a single sample. Composite samples reflect the local average level of element contents better than single samples and are consequently locally more representative. This procedure is recommended particularly for regional investigations, where large scale anomaly patterns defined on a sparse grid are of interest. Compared to single sample analysis, compositing reduces the need for analyses without an increase in sampling costs or significant losses in information (Garrett and Sinding-Larsen 1984).

The use of sampling and analytical replicates is recommended. Data from replicates can be used to estimate the corresponding components of variation. The cheapest and still statistically acceptable replication design in two stages is the unbalanced two-level design (Fig.8-2). This design results in two additional analyses at control sites. The unbalanced two-level analysis of variance model can then be applied offering a tool for comparison and estimation of the variance components (Garrett and Goss, 1979 and 1980).

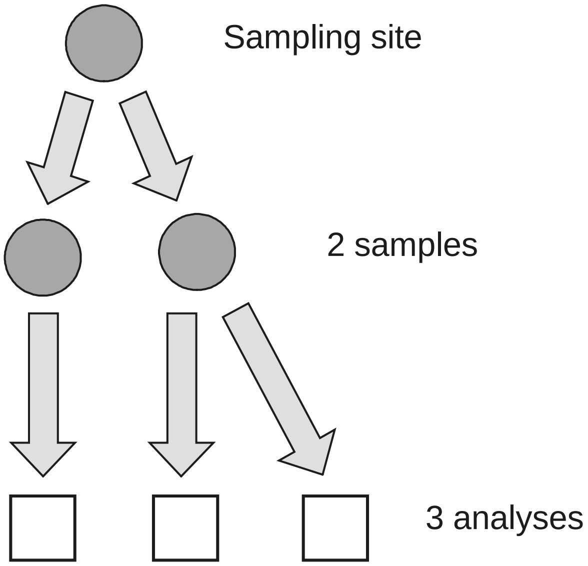


Figure 8-2 *Unbalanced two-level design.*

The recommendations below are relevant for new mapping programmes only and are often difficult to accomplish afterwards. If old data sets are considered then any available information on quality, quantitative or qualitative, should be utilized.

The recommendations are summarized:

Composite samples (5-8 subsamples) are recommended to reduce sampling error and the cost of analysis. If the resources for preparation and analysis are sufficient then the subsamples should be separately analysed. The mean of the separate samples will closely approximate the single composite value, but the individual analyses will provide valuable information on the scale of local variability. Variation of sampling density in regional investigations should be avoided.

Duplicate samples should be collected at least on every 30th site (randomly distributed over the whole area) and *duplicate analyses* obtained of one of these to yield an unbalanced analysis of variance design.

Control reference samples (secondary SRMs) should be inserted at a similar frequency to monitor for analytical drift. Monitoring is also important for standardizing batches of analyses particularly if the batches are distributed for analysis to several laboratories.

Randomization of samples prior to analysis in order to remove any systematic relationship between order of analysis and geographic location is recommended where this is logistically possible. Through randomization any systematic between-batch variations in analytical level are transformed to increased analytical variability. This converts data that would be reflected as areas of shifted background levels, and are artifacts of the lack of accuracy in the geochemical analyses, into increased local noise. Where randomization is impractical, care should be taken to include sufficient control reference samples, and to monitor their analyses, in order to detect between-batch variations. If such variations are found the batches should be submitted for re-analysis and the new data employed if they are satisfactory.

Parameters of preparation and analysis that are crucial for interpretation (preparation method, mesh size of screens, the analysed sub-sample weight or volume, method of dissolution for partial analyses, detection limit, calibration range, dilution coefficient, etc.) should be recorded.

Data should be reported to a maximum of 4 or 5 significant figures. Premature round-off should be avoided as it complicates subsequent data analysis (see below).

Quality control results can be reported by means of ***unbalanced analysis of variance (UANOVA)*** or other statistical methods and by *graphs*.

A ***handbook*** (electronic or manual) is recommended for the documentation of ***methods and changes of methods*** (which will inevitably occur in long-term projects!) and any observations relevant to the interpretation and use of the data.

8.3.3 Databases

The quality of geochemical data is also affected by factors inherent to digital processing, such as, precision and presentation of data output from instruments, round-off errors, precision and presentation at storage and, finally, the data presentation within the application program employed to assist interpretation. These factors are relevant to both manual and automatic data recording and tend to cause problems especially in those extraordinary situations when data are of poor quality. Presenting data precise only to within ± 5 ppm is not necessarily catastrophic for the data quality, but the interpreter has to be aware of the round-off, because such data are not continuous but discrete, and this may result in spurious statistics. This discretization error may become more severe if the later results of computations are further rounded-off. It is therefore recommended to avoid round-off procedures and to store the data in as unchanged form as possible (Gustavsson, 1992). The resolution of readings should be better than 1%, and at most 10% near the detection limit.

Today, data storage devices cost so little that the data can be stored exactly as output from the instrument without the need to reduce the information for cost reasons. The data should be checked for errors and corrected before storage in a database or file. It is worthwhile expending considerable effort, especially computer resources, on diagnostics at the input stage because errors once introduced into a database are difficult to identify and usually are revealed later only by chance, if at all. In the worst case erroneous results in the database will be widely used, just like the correct ones. Errors are not necessarily detected in statistical summaries and may well distort them.

Good laboratory practice and a good geochemical database system provide the user with information about data quality and conditions affecting the quality of the data set. Single measurement values can be annotated with flags indicating poor quality if they lie below the detection limit or outside the calibration range. General method-dependent quality information such as accuracy and precision should be included in the above-mentioned documentation (see Chapter 6). The date of analysis should be stored for each sample, or batch of samples, and each event of the analysis. This is particularly important when measurements contain drift or bias varying with time and require correction. The date of analysis is also an important attribute of the measurements that permits the identification of results obtained before or after substantial changes in the analytical procedure during the life-time of the database. Such changes are unavoidable because analytical facilities must change to take advantage of methodological advances.

The recommendations are:

Check and correct all data at the ***earliest possible stage.*** Extensive use of computer time is recommended, because some error types are difficult to detect or correct once data are finally accepted in a database;

Store ***dates of sampling and analysis*** to track sources of various problems that will occur (and for environmental monitoring purposes);

Use a ***unique sample label adding codes describing the path of methods*** from the field via preparation to analysis yielding a unique label for the analysis—then each value can be easily identified and associated with a sample even when the same sample is analysed in many ways;

Add a code to the label indicating ***duplicate sample and duplicate analysis;***

Store analyses with ***measured precision:*** avoid truncation or rounding-off values. This is particularly important if dilution coefficients are used;

Store values of contents as ***floating-point values,*** with a decimal point unless all values for that variable are integers, using sufficient significance (to a maximum of 4 figures);

Use element specific ***units of measurement consistently*** in the whole database;

Store the coordinates of sampling sites in ***both national and geographic systems*** (latitude and longitude with a precision of 0.01 degrees or better); and

Use a common database system, making sure that the data can be ***exported/imported*** in ASCII format from the database.

8.4 Levelling and normalization of existing data sets

8.4.1 Introduction

Due to the large amount of data already accumulated for systematic regional or national geochemical surveys in the world, and the high cost of repeating these surveys to new specifications, it will be necessary to compile existing discrete data sets in order to prepare international maps. In many instances this compilation will require a levelling or normalizing procedure. Even if at first inspection it would seem that data sets could be immediately merged, it is prudent to undertake some checks to ensure against wasted effort and subsequent embarrassment.

Before continuing, some comment must be made on the selection of data sets for compilation. The methods described below are geochemically blind, they simply manipulate numbers. Therefore, it is essential that a geochemist select only those data sets for compilation that are measuring the same “kinds of metal” in comparable media. Clearly, there should be no major problems in merging data from total determinations in like sample media. However, it would likely be inappropriate to attempt to level sets of cold partial extraction and total data; and similarly stream sediment with heavy mineral concentrate data.

Two situations arise, depending on the amount of information and/or sample material at hand. Firstly, at the planning stage of a new survey that will abut an old survey that sampled similar media, it should be ascertained whether a number (> 30 and < 120) of sample sites in the old survey can be re-occupied and sampled in an overlap study using the procedures of the new survey. If this cannot be done the availability of sample material from the old survey should be investigated. If possible cuts of these samples (> 30 and < 120) should be obtained and be submitted for analysis with the samples of the new survey. A third, and poorer, option can be exercised when the same International Reference Materials or local control reference materials (secondary SRMs) have been analysed in both surveys. These situations will then permit levelling using what are described as parametric procedures below. Secondly, resampling may not be possible, and in this case the non-parametric normalization procedures described below may be employed.

In the following sections the term normalization is used in its mathematical sense, i.e., to adjust the representation of a quantity so that this representation lies within a prescribed range (Parker, 1974), or, any process of rescaling a quantity so that a given integral or other functional of the quantity takes on a pre-determined value (Morris, 1991), rather than in the statistical sense, where it connotes a transformation of a data set so that it has a mean of zero and a variance of one.

8.4.2 Parametric levelling

Where data for the same sites or samples, or control samples, are available they should be displayed as simple x-y plots with similar x- and y-axis scaling. To ease subsequent data manipulation the data for the survey which it is wished to level to should be plotted on the y-axis. The user has to determine if plots should be plotted with or without a logarithmic transformation. A good initial guide is, if when plotted without a logarithmic transformation the data “fan out” at higher levels, the data should be logarithmically transformed for reasons related to homogeneity of variance and the subsequent numerical steps. If the data plot close to the 45 degree diagonal, no further work is required and the data for that variable can be merged (Fig.8-3a). If it is wished, the regression of x on y may be computed and a formal statistical test undertaken to determine if the slope constant differs significantly from unity.

If the data fall along a generally straight line but off the 45 degree diagonal it has to be determined if the levelling involves a simple positive or negative shift, is dependant on absolute level, or is a combination of both. To do this the regression of x on y is computed and the intercept (a_0 term) and slope (a_1 term) of the regression ($y = a_0 + a_1x$) tested for being significantly different from zero and one respectively. If only the intercept is significant a simple positive or negative shift equal to the value of the intercept may be applied (Figure 8-3b). If only the slope is significant a multiplier equal to the slope is applied (Figure 8-3c); and if both are significant both shift and multiplier terms must be applied (Figure 8-3d). If a logarithmic plot was required to obtain homogeneity of variance, then all calculations need to be completed in logarithms, with a final conversion back to the original scale.

If an inspection of the initial x-y plots exhibits non-linearity, transformations may be investigated that linearize the plot. In selecting appropriate transformations the user is well advised to consider the underlying physical processes involved in the chemical or physical measurement procedures. If a logarithmic rule or a Poisson counting process is involved a logarithmic or square-root transformation may be adequate.

In the most serious cases of non-linearity some form of polynomial or non-linear curve fitting might be considered. However, if it is necessary to go to these lengths to merge data sets it might be wise to reconsider the desirability of the act and the credibility of the results. Situations may arise where no correlation - linear nor non-linear - is shown between the data sets to be levelled (Figure 8-3e). Then levelling with this procedure or any direct method must be considered impossible.

Duplicate samples and analyses provide important data to be used in estimating the goodness of fit and the significance of the regression model.

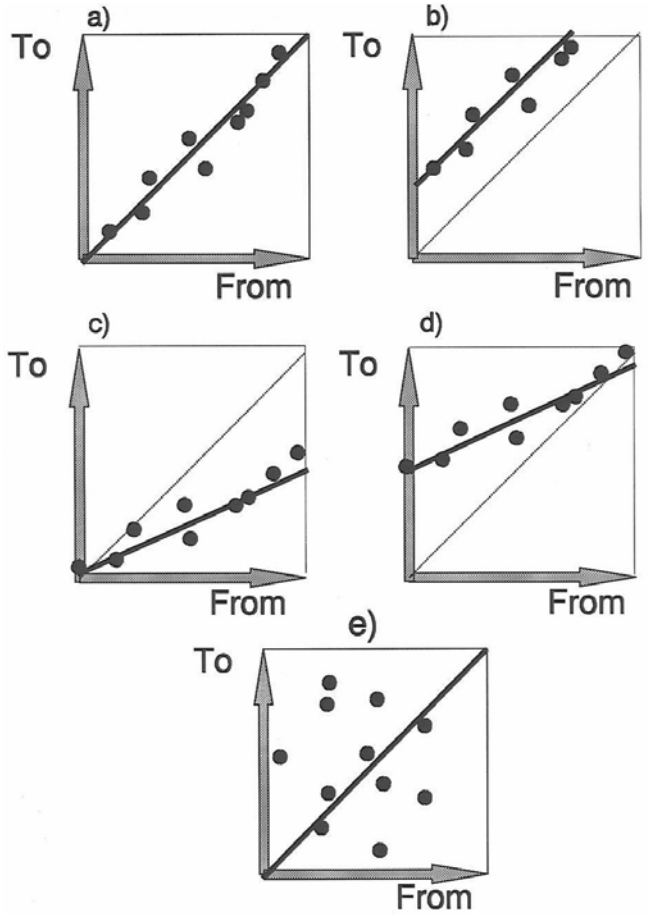


Figure 8-3 *Various situations that may occur in parametric levelling: (a) no levelling; (b) shift; (c) multiplier; (d) both shift and multiplier required; and (e) parametric levelling impossible.*

8.4.3 Non-parametric normalization

Normalization, as distinct from levelling, is based on the concept of the Clarke. For any sufficiently large survey area its average composition, preferably estimated by the median, converges on the Clarke for the chemical component as determined by the selected procedure in the selected material. In this sense the Clarke has a broader meaning than the expected crustal abundance according to some stated author. As a fall back position such a crustal abundance Clarke may be used. Three procedures will be described below, Fractile Normalization, Clarke Normalization, and Quantile Regression. These procedures have not been used extensively for International Geochemical Mapping, however, initial experiments indicate that they can be useful.

In the following sections on non-parametric normalization the terms fractile and quantile are used. These two quantiles are related, fractiles are representations in the range zero-to-one of the rank or ordered data items, and quantiles are measurements in the original scale. Every defined quantile has a corresponding fractile, and every defined fractile has a corresponding quantile. For example, what value (quantile) corresponds to a point three-quarters the way up the ranked data (fractile)? This also happens to be the value of the third quartile or 75th percentile. Conversely, what is the normalized rank (fractile) corresponding to a particular measurement (quantile) in the ordered data set? Where necessary linear interpolation rules are used to estimate the required quantity between known actual values, and rules are available for handling “ties”, i.e., when there are multiple occurrences of the same measurement value (quantile).

8.4.3.1 Fractile normalization

Experience with this procedure is limited (Garrett et al., 1991). It is recommended that only very large data sets, comprising tens of thousands of samples from large areas of the earth’s crust be normalized using this procedure. The key underlying assumption is that the medians of the data sets to be normalized all approach the Clarke value, which need not be known *a priori.*

The data or each of M sets are transformed to their fractiles. To obtain the fractiles the data for a variable in the set of size N are ranked from lowest to highest. The fractile is then the position of the value, i, in the range 1, ..., i, ... N, expressed as (i - 0.5) / N. Note that this scaling ensures that the values zero and one are never quite reached.

Following the fractile transformation for each variable in terms of its own data set, the data sets, now all in the range zero-to-one are merged. The single unified data set expressed as fractiles may now be plotted in map form. In doing this it is necessary to mark on the map the boundaries between the M surveyed areas, and to prepare M geochemical legends indicating the relationship of the contours, colours or patterns on the map to the original measurements in each of the M regions surveyed.

8.4.3.2 Clarke normalization

When an acceptable Clarke is known *a priori*, and the user is willing to accept that the data sets to be compiled do not contain any significant shifts that should be reduced by the levelling procedures described in Section 8.4.2, Clarke

Normalization may be employed. The procedure involves the reduction of each geochemical value to a Clarke ratio. Two ratios (CR) are in common use, they are:

CR = c / C (1), and
CR = c / (c + C) (2)

where c is the geochemical value or concentration and C is the Clarke. Equation (1) is simple and familiar, a value of 1 indicates equality with the Clarke, and values in the range zero-to-one indicate concentrations less than the Clarke, and values in the range one-to-a-large-number indicate concentrations greater than the Clarke. The problem with this scale is that it is asymmetric and human perception of the difference from one is non-linear. The second equation (2) is less familiar but has the advantage that it is symmetric, in the range zero-to-one, and the Clarke is indicated by a value of 0.5.

Once the data, for say M data sets, have been transformed they may be merged and displayed. A single geochemical legend is prepared that shows the relationship between the contours, colours or patterns for specific Clarke ratios and the Clarke's measurement units.

An alternative procedure when the M data sets are each very large would be to use the medians for each variable in each data set. This procedure makes the same assumptions as used in fractile normalization, i.e., the areas are large enough that their Clarkes approach a common global value. It may be prudent to mark on the map the boundaries between the M surveyed areas.

8.4.3.3 Quantile regression

This method is based on a proposal by Conradsen et al. (1991) and is a hybrid of aspects of Fractile Normalization and Parametric levelling. In a sense it is a step forward from Clarke Normalization as it uses more than one "control point", the Clarke in that case, to undertake the levelling. For this procedure to be valid data must be available from a common geochemical landscape in two or more surveys. By this is meant that there must be data from areas with similar bedrock that have undergone similar erosional and secondary environmental histories. Such a situation may arise, for example, along a common border between two countries (Fig.8-4).

One "control" survey is selected as that to be levelled to (see Section 8.4.2), and 9 quantiles corresponding to the 9 fractiles, 0.1, 0.2, 0.3, ..., 0.9, are estimated for the common landscape area. The same quantiles are computed for the common landscape area in the adjoining survey area. The quantiles for the "control" survey should be plotted on the y-axis against the quantiles for the adjoining area on the x-axis for visual inspection. The Parametric levelling regression procedure may be used to estimate the transformation coefficients from these 9 pairs of quantiles. These may then be used to level the "new" survey to the existing "control" survey. Conradsen et al. (1991) propose that additional surveys can then be levelled to the "control" or other already levelled surveys.

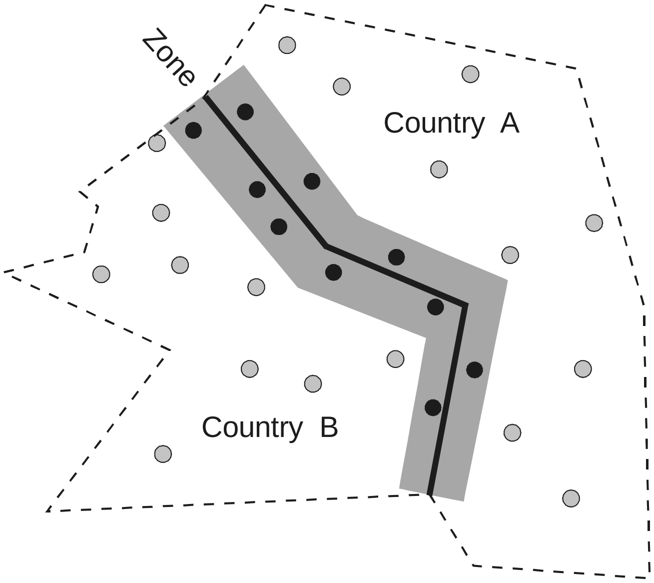


Figure 8-4 *In Quantile Regression the deciles of the distribution of two national datasets can be estimated using data within a zone along a common border.*

Besides the report of Conradsen et al. (1991) no other applications of this procedure to geochemical data are reported to the knowledge of the technical committee. However, a number of comments may be made on this procedure. Firstly, the necessity for care in selecting areas with similar geochemical landscapes must be stressed. Clearly the validity of the whole mathematical procedure rests on that geochemical consideration. Secondly, the selection of the proposed 9 quantiles is arbitrary on the part of this committee. In connection with this it should be remembered that the precision of such non-parametric estimators as quantiles is a function of the data set size and the statistic being estimated. The central quantile, median, is estimated with greatest precision, and the precision then falls off to the outer quantiles (Wilks, 1962). Therefore, it may be prudent to use a weighted regression so that the outer quantiles, which will be in greater error, have less influence in estimating the regression coefficients. To improve the precision of the quantile estimates large data sets for the common landscape areas should be used. However, this usually means broadening the geographic area, thus possibly introducing samples representative of other landscapes which may not be lead to an improved levelling.

8.4.3.4 Comparison of non-parametric methods

Clarke Normalization against an *a priori* Clarke is a simple procedure, and has the advantage that it facilitates international comparisons when widely accepted Clarke values are available as reference values.

When internal Clarkes are used, derived from the individual surveys themselves, the procedure is very similar to Fractile Normalization. In comparing these two procedures it should be noted that Fractile Normalization is keyed to the actual data distributions. Thus the geochemical scale of the presentation is set by the data themselves, i.e. a narrow data range is expanded to appear larger than it is, and the converse. In contrast, the use of Clarke ratios may unduly compress the geochemical presentation and hide perfectly valid spatial differences in the data.

The Quantile Regression procedure is a hybrid, relying on the quantiles to replace common points in geographic space, International Reference Materials, or local control reference samples (secondary SRMs), but still using a regression procedure so that a set of directly comparable data in original measurement units can be estimated. The major problem is in selecting adequate control areas with large enough sample sizes to provide an acceptable levelling. Clearly this leads to an impossible situation, the larger the populations the better the quantile estimates, but of a control area that is more likely to be inhomogeneous. If data from an atypical geochemical landscape are included in order to increase the data set size and the precision of the quantiles, the levelling will in fact not be improved. Therefore, while presenting this procedure as an enhancement of local Clarke Normalization we recommend that despite its appearance as an improvement on the other methods of non-parametric normalization it should be employed with great care.

As with all such techniques the objective of the data presentation must be borne in mind, and the most appropriate methodology be selected.

8.4.4 Use of airborne gamma ray spectrometry for levelling

Airborne gamma-ray spectrometry (AGRS), as described in Section 7.2, can provide a continuous quantitative measurement of the K, eU and eTh contents of the regolith under the line of flight. Approximately 90 per cent of the response is obtained from the upper 25 cm of the surface. Concordance between AGRS and ground-measured radio-element data has been demonstrated over small (km) and continental (10^3 km) distances, and, under controlled conditions, is the basis for calibration (Darnley, 1993).

Abundance profiles of eTh and K produced by AGRS overflights can be used as reference levels across regions, countries, or continents. They offer a way of cross-checking (and levelling where appropriate) the abundances recorded for these elements in conventionally sampled regolith data along or adjacent to each flight line. Thorium provides the most reliable reference level, with K as second choice. The eTh content of the regolith determined by gamma ray spectrometry is normally in close agreement with Th determined by other "total" methods (e.g., INAA or XRF). Thorium is contained in resistate minerals which are little affected by chemical weathering. In contrast, U is more readily mobilized in the surface environment, leading to a possible separation from the decay products causing a discrepancy between U and eU determinations, since the latter depends on the gamma emission from a decay product, ^{214}Bi. For this and other reasons, eU is potentially unreliable for reference purposes. Potassium is not subject to disequilibrium problems, but estimation by gamma ray spectrometry involves more corrections for extraneous variables than is the case for eTh, hence a reference level based on K is a second choice. Gamma ray measurements acquired under atypical soil moisture conditions should be avoided unless appropriate calibration adjustments have been made.

Thus, a calibrated AGRS system can be used to provide:

(1) an independent measurement of the radioelement distribution in blocks of **regolith data**, where the data obtained by conventional regolith or soil sampling include "total" Th and/or K determinations; and

(2**)** standardized radioelement regolith data across geochemical survey blocks where other sample media have been used; if "total" Th and K abundances are available for these media, the AGRS data can draw attention to level differences resulting from the changes in sample media.

Numerical adjustments are only valid given an adequate number of samples in the sets being compared. It is important to note that if systematic, statistically significant, discrepancies between datasets are found with respect to Th and/or K abundances, then data for other elements should be checked independently.

The use of parametric levelling methods (see Section 8.4.2) relies upon the successful pairing of data values in the two surveys, original regolith geochemistry and AGRS data. This may, or may not, be possible. The area that the ground geochemistry conceptually represents, e.g., a polygon surrounding the sampling site, would have to be defined. Similarly, the data for the flight path corridor that intersected the ground sampling polygon would have to be defined and the airborne data for that the coincident area averaged. This task is most easily completed using Geographic Information System (GIS) software (see Section 8.7). Levelling could then be accomplished by the parametric methods described.

If data values for the two survey techniques cannot be successfully paired the use of the quantile regression procedure (see Section 8.4.3.3) could be considered. If this procedure was to be used it would be advisable that in the planning of the overflights a sufficiently large area was selected so that an adequate statistical sample of ground geochemical data was available in order to reliably estimated the desired quantiles.

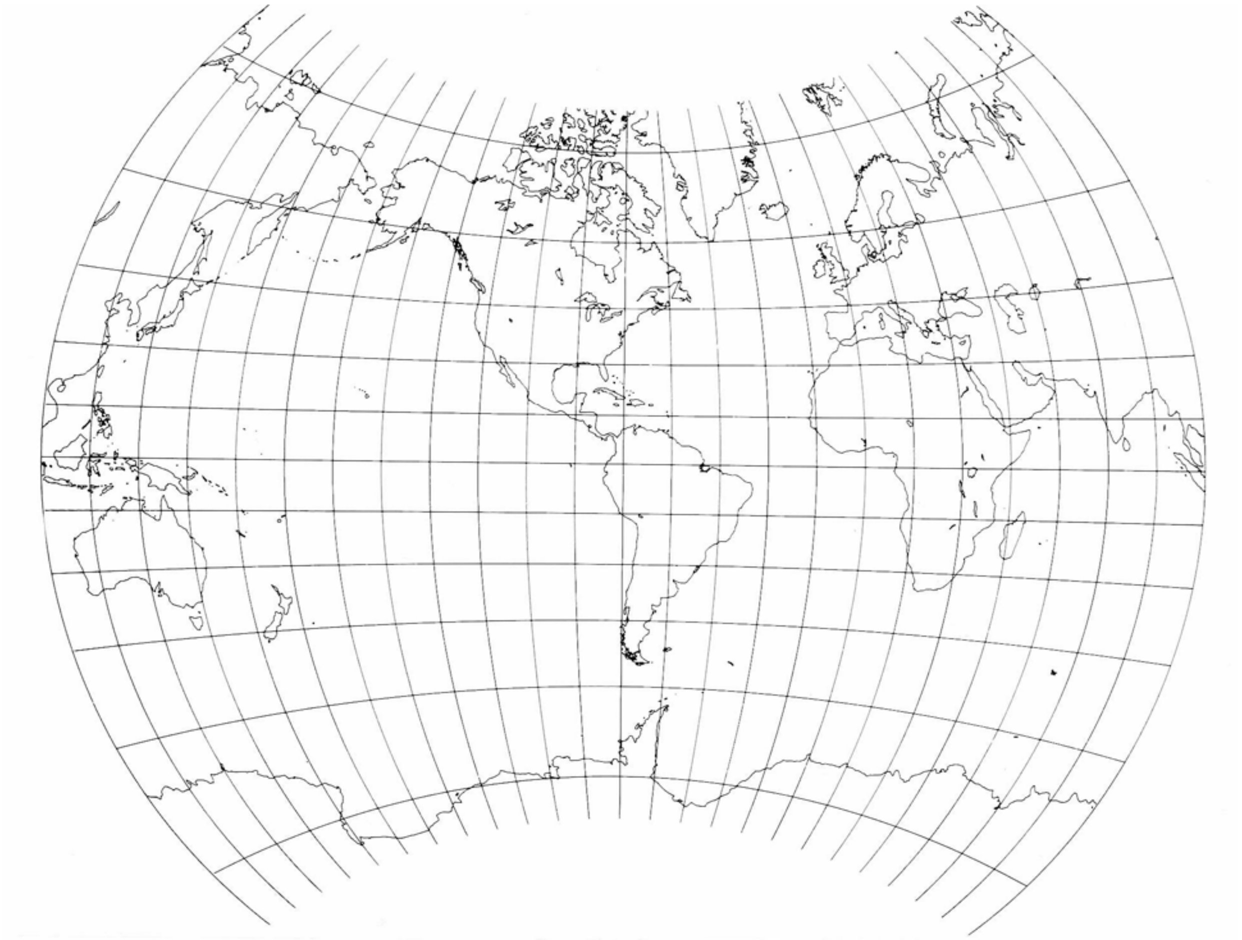


Figure 8-5 *van der Grinten projection.*

from Snyder, 1987

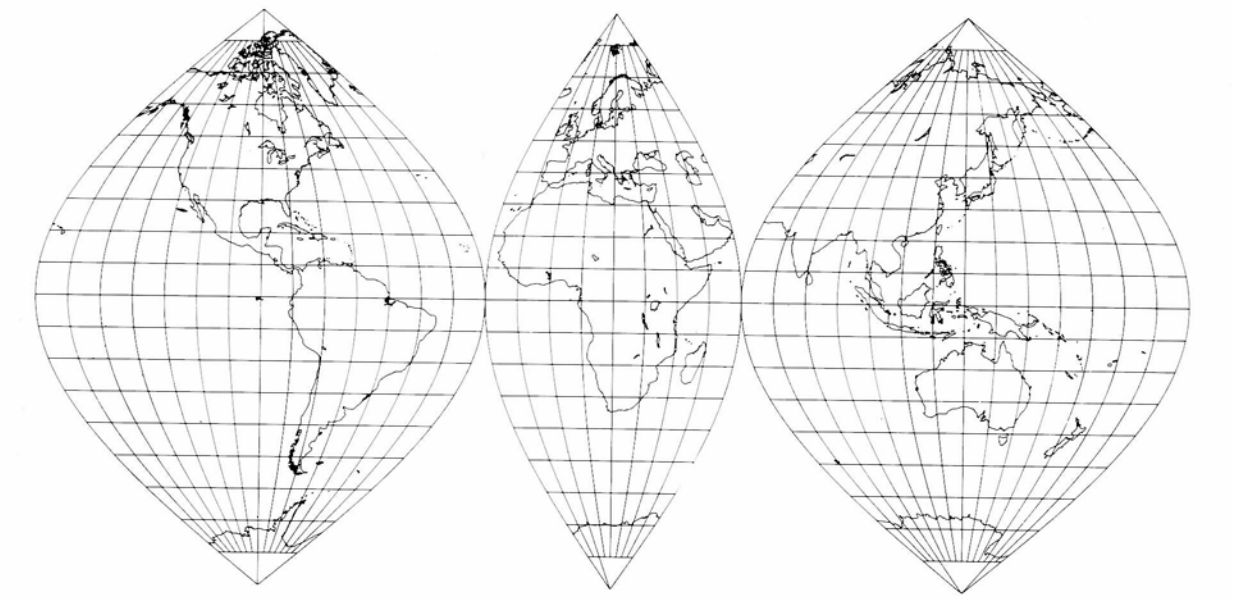


Figure 8-6 *Goode's Interrupted Homolographic projection.*

from Snyder, 1987

8.5 Map projections

The recommendations for map projections are based on the assumption that data from one or more nations is to be presented in map form. Clearly, the map projections for international purpose should be well-known and widely used, so that software for the necessary transformations is readily available. The recommended choices are:

- *Equal-area projections*; for wide areas Albers' or Lambert's are preferred because the size of patterns is often relevant.

If a global map is desired then one of the frequently used projections for physiographic maps, for example, should be selected to make visual comparison easy. Such projections used by the National Geographic Society are:

- Van der Grinten projection (Fig.8-5)
- the modified Goode's Interrupted Homolographic Projection (Fig.8-6)
- Robinson projection (compromise distortion, not equal-area)

National sample coordinates should be transformed to geographic coordinates (*latitude and longitude in decimal degrees*) by the local data holder when the data are submitted for international mapping purposes. That will facilitate transformations between projections at a later date.

8.6 Map preparation

The recommendations on map preparation consider principles for making geochemical maps visually readable and consistent for international purposes. If several data sets are compiled, the method of interpolation, smoothing and display should be the same over the whole area.

Smoothed gridded data and coloured/shaded surface presentations are recommended, because the aim of the international maps is mainly to show large regional patterns and zones. The interpolation and smoothing methods are difficult to standardize. Window size and the smoothing function, which determine the degree of detail in the maps, should be related to the point density of survey data. The selected method of interpolation and smoothing should be one which is widely known and accepted, such as:

- moving weighted average
- moving weighted median
- Kriging

The ***colour scale*** should logically increase from cold to warm colours and the class limits should be based on one of the following schemes:

- distribution percentiles
- a scale based on the Clarke:
  e.g., c/(c + Clarke), where c is the concentration
- a logarithmic scale

The scheme based on the Clarke is recommended (Beus and Grigorian, 1977; Fortescue, 1992) in situations when values independent of measurement scale are desired. If data are presented as symbols the *symbol size*, not shape, combined with *colour* if appropriate, should indicate concentration. Preference should be given to circular symbol, and it should be remembered that the human eye perceives symbol size by area not diameter.

Latitude and longitude lines/marks should be presented on the maps to mark the global position of the area.

The ***legend*** should, besides ordinary map explanation (area, scale, northing direction, date, etc.), contain relevant information about sampling, preparation and analytical methods and data quality. An inset index map showing the location of the study area and a cumulative frequency plot of the measurements should also be displayed in the legend.

8.7 Geographical Information Systems (GIS) and image processing

In Section 8.2 the committee has recommended that data be georeferenced in either UTM or latitude and longitude (geographic) coordinates (see also Section 12.8). Georeferencing of the data establishes a link for the spatial presentation of the data. The committee has recommended that three databases be created to catalogue and manage the geochemical data (Index, Block, and Bibliographic). Georeferencing of the Block Database establishes the ability to spatially manage, analyse, and present the data using a Geographic Information System (GIS). The development and uses of GIS's are highly varied and an introduction to the design and use of GIS can be found in Aronoff (1989), Maguire et al. (1991), and Maguire and Raper (1992). Visualization of spatially based data can be carried out using a variety of presentation formats. For data that are distributed over a regular array of points such as remotely sensed satellite data, image analysis methods are commonly employed. The subject of image analysis goes far beyond the scope of that required for geochemical data and a thorough treatment of the subject can be found in Serra (1982). For sparsely spaced data, a number of mathematical methods are available to grid the data into regular arrays to which image analysis methods can be applied. Alternatively, sparsely spaced data can be presented in a number of other formats as outlined by Howarth (1983).

8.7.1 Representation of geochemical data

Geochemical samples are commonly collected at specific sites that are considered to be points. In the averaging process described in Section 8.2 (see also Section 12.8) the Block Database contains levelled and averaged data in ½ degree grid cells. Thus, for the purposes of this project, the data have been defined as spherical rectangles that for practical purposes can be considered unit grid cells, or pixels. This basic unit cell defines the smallest possible measurement of area. Attributes associated with the unit grid cell are contained in separate tables. In the databases defined in Section 8.2 the Block Data table is an associated table that contains the averaged chemical abundances. Each record in this table corresponds to a grid cell location. Thus, a ½ degree grid cell may present arsenic abundances derived from the Block Database. Additionally, statistical or other mathematical methods may be applied to individual elements or groups of elements to assist in the interpretation of the data. Each record of this "transformed" data may be presented in the same grid cell format.

8.7.2 Geographical Information Systems (GIS)

GIS's require a spatial definition of the data plus attribute tables that contain information at that coordinate. Geographic information systems can be used to manage and present geochemical data. Examples of this have been presented by Bonham-Carter (1989a,b), Hausberger (1989), Gaál (1988), Kuosmanen (1988), Mellinger (1989), George and Bonham-Carter (1989), Burrough (1991), and Townshend (1991). In particular, a GIS facilitates the organized storage and management of spatially based data that are linked to a number of other features, which for the purposes of International Geochemical Mapping are data from the Block Database, or other georeferenced data sets.

The regular array of ½ degree cells provides the framework for the basic information about an area in terms their geochemical, or other measured, attributes. These data may include, topographic spot elevations, elevation contours, streams, lakes, catchment area boundaries, geology, soil types, slope maps, vegetation maps, climatic variation, rainfall, transportation infrastructure, radiometric data, aeromagnetic data, gravity data. These data may be in point, polygon, or regular grid cell (raster image) form. A GIS facilitates the integration and analysis of these various types of data to create derivative or thematic maps that display the relationships of this information with the geochemistry. Not all GIS's can accommodate or analyse different types of data. Thus, one or more systems may be required for analysis. This potentially powerful tool permits computer-based integration procedures and can provide new insights into geochemical data.

Depending on the nature of the geochemical data (stream sediment, soil, lake sediment, or lithogeochemical) various types of analysis can be performed that are dependent on the type of associated data present. Point, polygon (vector), and raster (regular array cells) can be overlain, merged and analysed through the associated map merging and database querying. Raster image grid cells can be considered as points providing there is an associated attribute record of data with each grid cell.

8.7.3 Examples of GIS with geochemical data

An example of analysis and querying is as follows. Given the regular block averaged geochemical data, one can overlay soil classification or geology polygons. Even more specifically, only those polygons that meet specific criteria defined in the attribute tables that define the polygons can be displayed. These criteria may be in turn, based upon specific selection criteria in the Block Database. Thus, selective retrieval and enhancement can assist in visualizing and interpreting the geochemical data, based on associated attributes.

As an additional example, the interpretation of stream and lake sediment data is enhanced by integrating digital elevation models to create catchment basins that clearly show the position of a sample within a drainage basin. Note, however, this can only be carried out using original survey data, not block averaged values.

8.7.4 Image Analysis Systems (IAS)

Section 8.6 discusses the desirability of producing maps that represent smoothed gridded data and coloured/shaded surfaces. The Block Database described in Section 12.8 is a regular array of smoothed gridded data and can be considered to be a raster image. Image analysis is primarily used for presentation purposes to enhance the results of an analysis or to show variation within data. Image analysis manipulates integer scaled raster data using a number of matrix based methods and after the use of additional integer scaling procedures represents the resulting transformed data on various graphical output devices using colour, intensity, and hue.

Image analysis procedures must be used with caution. It must be remembered that the data are integer scaled, commonly to the range 0-255, prior to commencing analysis. Various image processing algorithms use multivariate transformations, such as principal components analysis. The results of such analyses can always be imaged, but they may not be meaningful. Prior to analysis of an image, an evaluation of the data analysis method should be undertaken to determine its appropriateness to the task. A successful application of an IAS is presented in

Plate 8-1, where three component mapping clearly reflects the correlation of geochemistry to geological units (BGS, 1992).

8.7.5 Discussion of the benefits of GIS and IAS use

Both GISs and IASs have useful roles to play in the management, analysis and display of geochemical data. GISs facilitate the management of complex spatial data sets, and can handle point, vector and polygon data. In addition, modern GISs also contain a variety of data analytical and presentation tools. The latter includes the preparation of “traditional contour style maps”. The strength of IASs is in their ability to rapidly present data in “map” form. However, the user must be continuously aware of the scaling and transformation procedures being used by the IASs. These may either mask true relations or features, or create visual artifacts due to the procedures themselves.

In conclusion, both GISs and IASs have application in International Geochemical Mapping. The very nature and volume of the data calls for the use of GISs to manage them. The need to graphically present and review large volumes of data makes the use of IASs very attractive. As in all such endeavours care must be taken in selecting the most appropriate tool, and using it judiciously.

8.8 Summary of recommendations

The committee’s essential recommendations are summarized and briefly described below:

(1) The following databases are required, which can be managed on personal computers or work stations:

a *Global Reference Database* which will contain new data consistent with the proposed GRN specifications. This multi-table relational database will contain all information concerning the sampling, analysis and derived data for the 5000 GRN sampling units.

an *Index Database* for administrative and general information on other geochemical surveys;

a *Block Database* for averages of element contents in moderately large blocks (½ x ½ degrees spherical rectangles) to be used for global presentation of data;

a *Bibliographic Database* for reports and publications relating to the geochemical surveys described in the index file.

In practice the three latter databases will be integrated into a single relational database.

(2) The following quality control procedures are required to estimate variability due to sampling and analysis:

composited sampling, as an economical method to reduce sampling error;

replicate sampling and analyses (using an unbalanced two-level design) for estimating the significance of the geochemical relief in relation to the sampling and analytical variability;

control reference samples to be included in the batches in order to monitor for analytical drift; and

randomization of samples to remove spatial artifacts that could arise in the data as a result of between-batch shifts in analytical level.

Data values should be stored with a maximum of *4 significant figures*, care should be taken at low levels close to the detection limit to retain as many significant figures as possible in order to avoid unnecessary round-off that can deleteriously impact graphical and statistical representations and summaries of the data.

(3) Databases must meet the following conditions:

consistent content, this includes common agreed content and representation (format and units of measurement) for geographic, field and geochemical data;

data import/export facilities must have the ability to work with ASCII tables and also some of the *de facto* database standards that have developed in the personal computer field.

(4) With respect to levelling and normalization of existing data sets:

parametric, linear or non-linear, levelling of two data sets is recommended when resampling data, or samples or reference materials analysed in both data sets, are available;

non-parametric normalization is recommended for simultaneous presentation of multiple data sets using:

the fractile method,
Clarke normalization, or
quantile regression;

airborne gamma ray spectrometry may provide a useful tool in some instances to overfly adjoining or isolated survey areas so as to use the resulting eTh or K data to assist in levelling the ground geochemical survey data sets.

(5) For presentation of data on maps:

equal-area map projections are recommended for international and global maps. For global maps the Van Der Grinten, Robinson or the Goode’s Interrupted Homolographic projections are appropriate;

coloured surface maps are recommended, based on interpolated and smoothed data, using well-known methods, such as moving weighted average, moving weighted median, and Kriging. Some recommendations are also made on colour scale and class limits.

(6) *GISs and IASs* can be used as tools to manage, display, manipulate and process geochemical data within an integrated environment. Such an environment promotes synergistic interpretation of the data.

9 Data Applications

9.1 Introduction

Data concerning the spatial distribution of chemical elements in the earth's surface materials have many diverse applications, being relevant to many areas of science and technology and many problems of human concern. Mineral, agricultural and forestry resources, animal and human health, are all linked to, or affected by, the geochemistry of the earth's surface. Applications have developed and evolved over the past 40 years as the extent of available data has become known, and as its comprehensiveness and quality have improved. Each decade has seen a growing number of increasingly specialized conferences, with a corresponding increase in published papers, reports and text books describing both methods and applications. There is now no shortage of literature illustrating the applications of geochemical mapping at the local or regional level, but it should be noted that only a relatively small number of university departments in the industrialized countries have specialized in disseminating this knowledge and conducting related research. It is perhaps for this reason that the applications of spatial geochemical data are not as widely known as they should be outside the geochemical community. It is not possible for this report to do more than underline the existence of the extensive and detailed applications literature by listing some recent review papers in the bibliography. There is no single source-book concerning methods of using and interpreting geochemical data. It should be noted that there is extensive Russian literature concerned with theoretical and applied geochemistry. Fortescue (1992) provides a recent bibliography of Russian literature relating to environmental geochemistry. In Russia and countries formerly associated with the USSR, spatial geochemical data have often been presented (in reports and maps) in a manner not easily reconciled with that used elsewhere. Rather than convey information in the form of a collection of single element abundance maps, it has been common practice to present multi-element data in the form of complex ratio maps. By using particular element combinations and ratios as indicative of particular features or processes, this can facilitate interpretation for a specific purpose. However, in the absence of single element data other investigations cannot be pursued and multiple-use regional compilations cannot be made.

Geochemical map data hardly exist on a continental or global scale, for reasons that have already been given. Maps portraying the spatial distribution of a single element are the most useful initial product for general information purposes. Some examples are illustrated in Figure 2-5 and Plates 3-2, 3-3, 3-6 and 3-7. As a consequence the significance of data at this scale is still being recognized and applications are still being discovered. In terms of the specific applications of data to be produced by the International Geochemical Mapping project, its prime purpose is to connect the detailed data sets which are the basis for the many types of application study refered to above (and below). Global data are necessary to provide a quantitative framework for global process studies. They provide:

(1) a global overview of the geochemistry of the planet's surface, demonstrating quantitatively the regional variations that are present;
(2) a global reference network based on various sample media at known locations which can be used to monitor subsequent changes in the environment; and
(3) a means of comparing, and possibly normalizing, some existing large data sets.

Data applications follow from the assembly of a reliable global geochemical database, stored in digital form, as described in Chapter 8. This database must be accessible, its existence must be well known, and there is a need for a continuously updated library of software applications. The growing specialization and compartmentalization of the sciences has tended to result in a lack of awareness of the useful information that exists in neighbouring fields, so it is particularly important to facilitate comparative studies.

The most convenient way of summarizing and presenting spatial earth science information is by means of maps at different scales. The steady accumulation of geochemical data

Cell size km	**Area km^2**	**Map scale 2 mm pixel**
1 x 1	1	1 : 500 000
2 x 2	4	1 : 1 000 000
4 x 4	16	1 : 2 000 000
10 x 10	100	1 : 5 000 000
20 x 20	400	1 : 10 000 000
40 x 40	1600	1 : 20 000 000
80 x 80	6400	1 : 40 000 000
160 x 160	25600	1 : 80 000 000

Note: Scales used in typical school atlases are in the range from 1 : 1 000 000 (national maps) to 1 : 90 000 000 (global maps).

Table 9-1 *Sampling density and atlas map scales.*

in compatible digital files will allow far more flexibility in presentation than has been the case until recently, and will simplify periodic revision as new data are acquired. Given the possibility of preparing maps which are tailor-made for each specific enquiry, it seems probable that in the future the only maps which will be printed and distributed in large numbers will be for general education and index purposes. They will serve to advertise what is available in the digital database.

Table 9-1 provides a guide to the linkage in geochemical mapping between sample density and map scale for general information purposes (e.g.in an atlas), where it is not required to show the position of individual sample sites. If the precise position of sample sites is required, then 1:100 000 or 1:50 000 scale maps or aerial photographs are required.

9.2 Examples of specific applications

Beginning in the 1950s, there has been a steady growth in the number of publications describing applications of geochemical maps and related data, demonstrating the types of interpretation that can be made. Initially studies were restricted to mineral exploration applications over small-areas. In the 1960s research began to show the relevance of the data to agriculture, animal and human health (Thornton, 1993). The interpretation of geochemical data largely depended upon a laborious compilation into map form, followed by visual comparison with other map data, also the result of manual compilation. Differing scales and projections limited what could be done. Until recently it has been difficult to make comparisons over large areas, because not only has the geochemical data been incompatible, but so have other data sets. Manipulation of diverse information has been very time consuming and so has been attempted only rarely.

The availability of more types of earth science, environmental and land-use data in compatible digital "layers" will facilitate the number and variety of correlation studies. Chapter 8 contains a review of the relationship between geochemical data and geographic information systems (GISs). GISs are becoming a basic tool for many types of multi-component spatial investigations and geochemical data will become part of the basic geographic information base (see Bonham-Carter, 1994; Gustavsson and Kontio, 1990). As indicated, most of the past studies have been applied over small areas, examining a few hundreds or thousands of km^2, although a few have covered much larger areas. At an elementary level it is useful to be able to superimpose geological contacts upon a geochemical base as demonstrated in Plates 3-4 and 3-5 in this report. Plate 8-1 is a 3-component geochemical map (Ni-Cr-Mg) of the English Lake District, showing how this mode of presenting geochemical information facilitates the delineation and separation of different geological units. It is regrettable that many of the geochemical atlases which have been published to date in different countries (see bibliography) have contained only generalized or sparse interpretative comments. Users have been expected to make their own interpretations. The series published by the British Geological Survey (BGS 1987, *et seq*), which contain more extensive interpretative material, demonstrate the amount of new geological information that can be derived from detailed geochemical mapping if sufficient professional time is devoted to the task of interpretation. There is no reason to doubt that similar advances in knowledge could be made in other, non-geological, fields using geochemical data sets of this type, if there was comparable intellectual effort.

Some recent publications showing the variety of correlative studies that have been made between geochemical map data and other phenomena include:

- human diseases (Tan et al., 1988, Atlas of Endemic Diseases of China)
- animal health in developing countries (Appleton and Ridgway, 1993)
- environmental survey; Warsaw, (Lis, 1992); Germany, (Birke and Rauch, 1993)
- regional environmental anomalies (Painter et al., 1994)
- soil derivation (Garrett, 1994)
- lithology (Regional Geochemical Atlases of UK, e.g., BGS, 1987 *et seq.*)
- metallogenic provinces (Xie and Yin, 1993)
- mineral occurrence and gravity data (Plant et al., 1991)
- tectono-stratigraphic units, (Steenfelt, 1990; Stone et al., 1993)
- regional gravity anomalies (Darnley, 1981)

For additional background information relating to the application and interpretation of geochemical data, see the general references in Section 11.2, and past volumes of the Journal of Geochemical Exploration and also Applied Geochemistry.

Until recently there appear to have been few efforts to correlate changing land-use patterns with comprehensive geochemical data. In 1988, at the first meeting of the scientific advisory council for the IGBP, the Data and Information Systems Committee endorsed the IGM project as a contribution to IGBP (IGBP, 1989). Since that time a number of IGBP meetings relating to global data and land use problems have taken place and reports have been published, but matters relating to the geochemical database have been confined largely to the major plant nutrients, e.g. C, N, P. However, detailed studies relating to trace elements in plants and ecosystems are now beginning in a number of countries, for example under the auspices of the International Union of Biological Sciences and the International Association for Ecology (Markert, 1994). There is considerable scope for cooperation between earth scientists, chemists and biologists.

9.3 Summary

The advent of digital geographic information systems, in conjunction with satellite imagery, is in the process of revolutionizing the correlation and study of all types of earth science and environmental datasets. A variety of computer software suitable for data interpretation have been developed over the past decade, for example to assemble and weight criteria relevant to ground selection for mineral exploration, and to assist mineral resource assessment of large areas (see General Bibliography). Comparable software is being developed for land-use planning taking into account a variety of agricultural and health parameters. It is certain that new interpretive uses for geochemical data will be discovered and new connections with other phenomena will be recognized as detection limits are lowered, data quality improves and coincident data for all elements become available.

10 Implementation

10.1 Introduction

In order to establish global geochemical baselines and produce an international series of geochemical maps, the scientific considerations outlined in the preceding chapters indicate that it is necessary to implement two parallel and related activities:

(1) the creation of a global geochemical reference network; and
(2) the adoption, by national and international mapping organizations, of the recommended standard methodologies for the purpose of relating their own datasets to the global network.

Each of these activities complements the other; both are needed in order to meet the objectives. This chapter discusses some of the factors involved in implementing the recommendations made in previous chapters and makes some suggestions.

The authors of this report believe that the task is urgent because the results impinge on many human activities. As populations grow, so does the importance of the data; if environmental conditions are changing it is essential to have reliable data concerning all the variables which affect the biosphere. The time required to accomplish the task is primarily dependent upon to the priority attached to it by funding agencies. The knowledge, experience and technology required to accomplish the work already exist. The necessary human expertise is available if it can be mobilized. If the task is given high priority, for example as part of a major program to establish "global environmental baselines by the year 2005", the geochemical reference network as proposed could be in place within 10 years. The estimated costs for such a reference network are of the same order of magnitude as a single NASA Shuttle launch, currently US$378 million (see below). This is a small sum in terms of annual space exploration expenditures, but very large in relation to total earth science budgets, which are declining in most countries. The necessary scientific work could be done by existing earth science institutions, but changes would have to be made to the established priorities.

With or without "top-priority", a substantial measure of international support will still be necessary to obtain and compile geochemical reference network data for the world within a finite period of time. National organizations must be consulted and their participation encouraged. As indicated above, with strong international backing, it is estimated that under favourable circumstances, the task could be accomplished within 10 years. "Favourable circumstances" implies:

(1) formal acceptance of the project's objectives and methods, by ICSU or other body of comparable standing;
(2) acceptance by a substantial number of national organizations;
(3) commitments with respect to adequate funding;
(4) rapid agreement on the identification of the analytical facilities to be used for the reference network samples; and
(5) the full cooperation of all parties concerned at the regional and local level with respect to logistical support and, where relevant, local security.

Given progress on the above items, the following process could begin, in sequence, within the regions which first express interest:

(1) preliminary planning, discussions with regional agencies and/or national authorities;
(2) detailed operational planning;
(3) regional sampling and analysis;
(4) verification of data;
(5) compilation;
(6) dissemination of data; and
(7) preliminary interpretation jointly with national institutions - it is envisaged that national institutions would want to be responsible for follow-up investigations.

Several of the above stages could and should overlap. Stages 3 and 4 might require at least 3 years for completion, to allow time to arrange entry to difficult areas and also to conduct any resampling which might be required. At the present time there are some parts of the world where civil disorder prevents entry for scientific purposes and sampling in these areas would have to be deferred.

From the above paragraphs it is apparent that there are a mix of organizational, financial, scientific and technical issues to be dealt with on a long term basis before a global geochemical database can be completed. To find ways of accelerating the process, the committee has considered a number of options. It is possible to reduce the number of sample types to be collected and hence the number of sites to be visited and analyses to be undertaken. If, for example, only A_{25} regolith samples were to be collected, or more restrictively, only floodplain regolith samples, a rapid global overview could be obtained. However, the resulting data would have limited value with respect to more detailed regional or national databases based on other sample media. The importance of commonality with respect to sample characteristics at the global, regional and local scales has been stressed earlier in this report, and it is essential to the concept of a comprehensive global reference network.

However, if a rapid and relatively low cost global overview is required within, for example, 5 years, a preliminary reconnaissance confined to floodplain sampling in each 160 × 160 cell could be initiated. The result of this decision would be to increase the cost of the overall project, and extend its duration, due to the necessity to revisit every cell at a later data in order to collect the other recommended sample media. These other media are important in order to provide reference materials for surveys at the national level, and more clearly indicate the range of abundance variations in the geochemical background.

10.2 Organizational requirements

10.2.1 Project coordination, long-term continuity and sponsorship

The world's atmosphere can be monitored by satellite or aircraft by any agency that has the necessary resources, similarly the world's oceans can be sampled by any ship. Direct sampling of the land surface is more difficult to arrange because of the number of jurisdictions, interested agencies, property rights, etc. potentially involved. Because of the number of organizational and technical steps involved it seems highly unlikely that any group of scientists convened under a non-government organization, however enthusiastic, could sustain or manage an international sampling activity (other than as a small test project in a sympathetic jurisdiction) over the period of time required for completion. The systematic approach which is required militates against an *ad hoc* temporary organization.

Assuming that the importance of the information to be obtained is recognized by the international scientific community, there is a clear need for a single permanent agency to accept formal responsibility for securing funds, managing and coordinating these activities according to scientific guidelines determined by an external advisory committee.

The execution of the overall task requires continuity, to be provided by a dedicated management group with expertise in each of the specialities involved. The work should be performed under the authority of an international organization (which could be an existing one). Uncertainties in the world political and economic situation could make it difficult to adhere to a strict program schedule. This reinforces the argument for a clearly defined management structure and an identifiable responsible agency. An obvious model is provided by the International Atomic Energy Agency, which has provided scientific and technical coordination in matters connected with uranium resources and uranium exploration for more than 35 years.

International coordination of a geochemical database is partly an administrative task, partly a scientific task. Unless this issue can be continuously monitored and kept on course, local needs will always tend to dominate the agenda and it may prove impossible to accomplish the objective of a reliable and comprehensive global database. For this reason it seems particularly important that there should be an international office dedicated to encouraging national programs to adhere to international mapping standards.

10.2.2 World Geochemical Data Centre

As data begin to be assembled, there is a need for an agency to take responsibility for global geochemical data, and to provide liaison with organizations dealing with other global data sets. In the same manner as national geological surveys, provide a permanent central repository for all types of earth science data and samples, and serve as a convenient starting point for new enquiries or investigations in a particular country, it is highly desirable that data relating to a **global** geochemical database should be available from a single address. A World Geochemical Data Centre is required as a focal point, responsible for long term data management. This centre must be closely linked to regional centres, which could co-ordinate the periodic monitoring of reference sample sites in the context of global change and other environmental issues.

At the present time no international agency has a mandate which would enable it to support the ongoing managerial, custodial and scientific activities associated with the acquisition and maintenance of a comprehensive global geochemical database. The International Atomic Energy Agency has some responsibilities with respect to radioactive substances in the environment but these responsibilities do not apply to associated non-radioactive substances. From a geochemical point of view it is undesirable to manage separately databases for radioactive and non-radioactive elements. As an interim measure it is suggested that an approach could be made to the leading national geological organizations of the world to invite one or more of them to accept a specified short-term responsibility for geochemical data management. Again, as an interim measure, regional reference sample repositories could be established, possibly with the assistance of UNESCO Regional Offices for Latin America, SE Asia, etc.

A World Data Centre system has existed under ICSU auspices since 1958 and at the present time consists of about 40 centres operated in various countries at national expense (ICSU, 1989). These are mostly focused on geophysical data. Specialized data centres relevant to IGBP activities have been set up recently for Soil Geography and Classification, Global Runoff (in Koblenz, Germany), and Greenhouse Gases Data (in Tokyo, Japan) (IGBP, 1992).

10.2.3 Regional Coordination Centres

In addition to a single international focal point for the activity, discussed above, it is highly desirable that in different parts of the world there should be regional centres of excellence and expertise concerned with all aspects of surficial geochemistry, perhaps co-located with institutions concerned with other earth science or environmental specializations or global change studies. These regional centres could, where necessary take responsibility for encouraging and monitoring geochemical data collection according to global database requirements in the countries of their region. They could undertake training, assist in the interpretation of geochemical data, conduct investigations and research and generally ensure that maximum value is obtained from the database in the context of the problems of their region. Regional Centres have been designated in connection with a variety of international scientific studies, e.g., seismic and volcanic hazards, and geochemistry could logically be added.

10.2.4 Technical assistance for developing countries

The IGM project involves modern technology and very strict quality control, both of which are important to developing countries. The IGM project is particularly relevant to economic and environmental issues. Mineral industry development is often the first stage in industrialization, but haphazard exploitation of mineral resources can create serious environmental problems. Many public authorities are attempting to define safe limits for the chemical composition of the environment, but these limits are commonly established with inadequate knowledge of natural geochemical variations, sometimes causing unnecessary alarm and requiring unrealistic precautions. The availability of a systematic geochemical database serves many purposes; it assists mineral exploration and provides baseline information relevant to agriculture, forestry, animal and human health, and the establishment of prudent environmental controls. The acquisition and application of a detailed local database should involve the nationals of a country, and it is possible and useful to provide the training and equipment for this through technical assistance.

Once a preliminary reference sample network has been established, with international assistance, within a developing country, the opportunity would exist to establish a well equipped chemical analytical laboratory for the continuation of locally directed geochemical and environmental chemistry projects. Local personnel can be trained and involved in proper sampling procedures as part of the initial reference-sample collection exercise. A national analytical laboratory, with a well trained staff, can become, or provide, the nucleus for other specialized analytical laboratories which are required to service other scientific and industrial activities within the country.

10.3 Scientific and technical considerations

10.3.1 Provision of Standard Reference Materials

One of the key on-going responsibilities of the co-ordinators of International Geochemical Mapping must be to arrange the assembly, supervision and distribution of primary analytical reference materials, both for the geochemical reference network samples and for the purpose of maintaining analytical standardization in subsequent investigations. The experience of the few organizations that have undertaken this type of responsibility is that it is much more time consuming and onerous than might be supposed. The preparation of standard reference materials requires long-term anticipation of requirements and meticulous quality control. The most reputable international analytical laboratories have to be involved in the many duplicate analyses required for the certification process. The nominal charges paid by recipients of standard reference materials have generally not reflected the true cost of preparation and certification.

10.3.2 Access to data and samples

The international geochemical mapping project will not fulfil its purpose unless the data are well known and readily available in a variety of standardized formats. The bulk of the data should be released in digital form (CD-ROM, together with direct downloading over Internet, is the preferred mode in 1994), but a selection of printed products, including attractive coloured maps and explanatory posters, must be available for general distribution to schools, libraries, etc, in order to draw attention to the information and its significance. Funds may be required to ensure that selling prices are not so expensive as to inhibit purchase. Distribution could take place through UN and national earth science and environmental outlets.

It is assumed that each country participating in an international geochemical survey will wish to retain data and sample material pertaining to its own territory. In general, developed countries have established routine procedures for the release of scientific data collected wholly or partially at public expense, and with less consistency, access to public sample collections is usually possible subject to various conditions and restrictions. It is recommended that all countries participating in the IGM-Global Geochemical Baselines project should undertake to allow access and use of primary (wide-spaced) reference data and radiometric profiles, and access to samples for scientific research purposes, subject to agreed conditions.

10.3.3 Introduction of new techniques

Procedures in geochemistry, as in other areas of technology, are not static. It is desirable to introduce new methods which provide significant improvements in sensitivity, selectivity, cost, etc., as soon as they are firmly established. However, the assembly of a coherent, systematic, global database requires that changes in methodology should be undertaken in such a way as to avoid or minimize discontinuities in data sets. Changes must be fully documented. Some organization, such as the suggested World Geochemical Data Centre guided by an external advisory committee, should carry responsibility for this. The longer the period of time over which a global database is assembled the greater the probability that there will be changes. One of several reasons for collecting large samples and archiving excess material, is to be able to take advantage of new analytical methods as they develop.

10.4 Cost factors in geochemical surveys

The principal cost considerations involved in obtaining wide-spaced geochemical baseline data are summarized in the Appendix (12.10.2). It should be noted that many of the cost considerations also apply in general terms to the conduct of more detailed national and regional surveys. Because in many countries these latter activities progress relatively slowly, it is recommended that wide-spaced sampling should be given priority and be planned as a separate exercise. Costs for any given professional activity or service vary with time from country to country, and also according to the volume of work undertaken by an organization, so only the variables involved can be listed. *To obtain high quality data at minimum cost good advance planning and trained teams are required. The greatest costs are incurred if work is found to be unsatisfactory and has to be repeated.* It is not possible to anticipate all the cost components which might be encountered in some parts of the world, but the principal factors can be identified, based on experience in many areas. For further discussion, see 12.10.2.

10.5 Total project cost

The direct cost of implementing the project can be broken down into four components:

(1) cost of sample collection, which primarily relates to the mode of transportation (surface or air) and time required to reach sampling sites;
(2) cost of sample preparation and analysis;
(3) cost of complementary airborne gamma ray spectrometry; and
(4) cost of planning, training workshops, sample and quality control, compilation and management.

It is assumed that national geological survey organizations would provide local logistical support at cost. Long term costs relating to archival sample storage, data management and distribution are not considered.

It is impossible to provide anything other than an order-of-magnitude cost estimate for the total project until plans, participation, national involvement, timing, rate of progress can be decided. Based on Canadian experience, which has both easily accessible areas and large inaccessible regions, (therefore approximating to the world’s surface as a whole), sample collection is, on average, twice as expensive as analysis, but the requirement for the provision of specialized analytical services (for exotic elements and lowest possible detection limits) will probably reduce the historical 2:1 ratio. If a decision were taken to combine sample collection with AGRS profiles (Option 3 in Chapter 4) this approach would probably be cheaper than the cost of (1) plus (3) above. Several cost estimates have been made in the course of preparing this report, starting with different assumptions; the present “best estimates” for items (1) to (4) above, have totals in the range US$ 300 - 400 million.

In order to provide perspective regarding this cost in relation to other data collection expenditures, figures have recently (May 1994) been obtained from the NASA Johnson Space Center Information Branch, Houston, Texas, concerning the current NASA space flight budget. Eight space shuttle flights are planned for 1994 with a budget of US $4 billion. Some of these are stated to be for the purpose of building an environmental database. The figure of US $378 million, quoted in the first section of this chapter as the basic cost of a shuttle mission, is the “cancellation cost saving”, i.e., the expenditures related directly to launch preparation (for fuel, other expendable items, and refurbishing of reusable equipment, including the shuttle itself) if a single mission is cancelled. No development, amortization, or specific mission charges are included. US $378 million is approximately the cost of establishing the global geochemical reference network.

The numerous observations of Earth from space collected over the past 30 years have amply demonstrated the importance of obtaining a global overview of every measurable parameter. Unfortunately the subtle geochemical variations of the Earth’s surface cannot be mapped from space. The authors of this report are of the opinion that establishing a geochemical reference network, with its many environmental and economic ramifications, has a utility value at least as great as, for example, high resolution IR or radar imagery of the earth’s surface, upon which much wealth has been, and is being, expended. This report has endeavoured to demonstrate that a global geochemical database is not only of direct relevance to all life on earth, it is complementary to other global data gathering activities and it is equally attainable. It is needed for the good management of the earth’s resources.

For conclusion, see Executive Summary.

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12 Appendices - supplementary information

12.1 Introduction

The principal purpose of this chapter is to provide supplementary information for readers who do not have easy access to technical literature pertaining to the methods discussed in this report. The information is included to indicate some of the practical considerations and requirements which enter into the design and conduct of geochemical survey activities. Subsequent sections are numbered according to the chapters to which they relate.

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Israel: *Geological Survey of Israel, Jerusalem; (M.Shirav).*
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Scientists in 90 countries, including the above, have requested information about the project.

12.3 Supplement to Chapter 3 Excerpts from research relating to the project

This section contains a selection of short excerpts from a few of the papers published in connection with IGCP 259, to indicate the variety of research and review topics stimulated by the project and to highlight a few of the more interesting conclusions reached by the authors. Quotations have been selected mainly from the following special volume publications (listed below in date order):

Journal of Geochemical Exploration, Special Volume on International Geochemical Mapping, **39**, December 1990, (Eds. A.G.Darnley and R.G. Garrett, 11 papers from 1988 Goldschmidt Conference), 250pp.

IAEA-TECDOC-**566**, 1990, The use of gamma ray data to define the natural radiation environment, Ed. A.Y.Smith, Contributions by members of the Radiometric Committee and others. IAEA, Vienna, 48pp.

Geochemical Mapping of Western Europe towards the year 2000, Pilot Project Report and Proposal, 1990. Ed. B. Bølviken. NGU Report **90-105** (in 2 vols.), Geol. Surv. Norway, 600pp.

Transactions Institution of Mining and Metallurgy, London (Sect.B: Appl. earth sci.),1991. **B100** B47-B147. (Ed. J. Ridgway, 10 papers; selected from International Geochemical Mapping Sessions of 29th International Geological Congress, 1989) 100pp.

Geoanalysis, Journal of Geochemical Exploration, **44**, 1992. (Ed. G.E.M. Hall; 10 review papers from 1990 Geoanalysis Symposium) 349pp.

Journal of Geochemical Exploration, Special Volume on Geochemical Mapping, **49** December 1993. (Ed. P.H. Davenport, selected from 1992 Goldschmidt Conference Sessions, 10 papers), 250pp.

Geochemical mapping — general

Bølviken et al., (1992): The fractal nature of geochemical landscapes.

> *"Geochemical maps and other empirical data from the literature show that significant geochemical dispersion patterns exist for a number of elements at scales from microscopic to continental, indicating that "landscapes" formed by natural geochemical concentrations may have fractal scalings."*

Duval, (1991): Potassium, uranium and thorium geochemical maps of the conterminous USA.

> The largest block of coherent geochemical survey data published to date. A compilation of airborne gamma ray spectrometry data obtained during the NURE program, explaining the levelling methods used.

Friske and Hornbrook, (1991): Canada's National Geochemical Reconnaissance program.

> A description of a national program, with emphasis on the steps required and taken to establish and maintain consistency and quality control.

Xie, (1990): Some problems, strategical and tactical, in International Geochemical Mapping.

> *"...the detection limits for many elements with crustal abundances below 1-2ppm are generally too high, even when highly sophisticated multi-element procedures ...are used."*

Xie and Ren, (1993): A decade of regional geochemistry in China - the National Reconnaissance project.

> A review of a national program covering a variety of terrains, emphasizing standardization of methods and quality control. Demonstrates the rapid rate of progress that is possible.
>
> *"Very low detection limits are set for the determination of elements with very low crustal abundance, such as Au, Ag, Hg, Bi, Cd, Sb, Mo, As and Sn."*

Geochemical provinces and related topics

Bølviken et al., (1990): Geochemical and metallogenic provinces; a discussion initiated by results from geochemical mapping across northern Fennnoscandia.

> *"It is concluded that metallogenic provinces lie within or coincide with a number of geochemical provinces, some of which may have causal relationships with ore deposits."*
>
> *"Regional geochemical maps repeatedly show that the contents of major as well as minor elements in geological material may depict distribution patterns that cross lithologic borders indicated on geological maps."*

McMillan et al., (1990): Tectonic terranes, metallogeny and regional geochemical surveys: an example from northern British Columbia.

> *"This study confirms that mean element concentrations from background populations for certain elements.. collected during regional geochemical surveys from terranes in northern British Columbia are statistically distinctive."*

Steenfelt, (1990): Geochemical patterns related to major tectono-stratigraphic units in the Precambrian of Northern Scandinavia and Greenland.

> *"many large-scale element distribution patterns may be related to major tectono-stratigraphic units. ..information provided by the geochemical data is particularly valuable in Precambrian high-grade gneiss terrains, where the recognition of former boundaries is often difficult due to deformation and metamorphism.."*

Optimization of methods

Simpson et al., (1993): Geochemical mapping of stream water for environmental studies and mineral exploration in the UK. Results are presented for pH, NO_3^-, F^-, Na, Mg, Al, Si, P, SO_4^{2-}, Cl^-, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, Pb and U.

> *“...bedrock geochemistry and mineralisation are the most important variables which influence surface water geochemistry. The primary control by geological parameters is variously modified by secondary influences which include geomorphological factors (especially altitude) atmospheric (climatic and coastal effects), and anthropogenic (agriculture, urban and industrial developments).”*

Davenport, (1990): A comparison of regional geochemical data from lakes and streams in northern Labrador; implications for mixed media geochemical mapping.

> *“Comparing the two types of sediment, most elements show obvious differences in either median content or range or both, indicating that stream and lake sediment are geochemically distinct media, and their element contents cannot be compared directly.”*
>
> *“The implications .... for international geochemical mapping is that geochemical patterns for many elements are strongly dependant upon the sample medium chosen.”*

Dunn, (1991): Assessment of biogeochemical mapping at low sample density.

> *“Various problems, such as seasonal variations in chemistry and the lack of a universal plant, restrict the value of biogeochemistry for mapping large tracts of land.”*
>
> *“The planet can be divided into a few climatic zones, each of which is characterised by one or two common plant genera. If it can be demonstrated that the chemical differences between certain species of a single genus are small- as is suggested by studies of boreal forests — it would be feasible to apply geochemistry as a low-density geochemical mapping tool. The technique could prove particularly useful for assessing the substrate geochemistry of areas of dense forest, rugged terrain and difficult access by employing airborne sampling of trees from helicopters.”*

Garrett et al., (1990): Regional geochemical data compilation and map preparation, Labrador, Canada.

> *“The 25 x 25 km cell median-based maps reflect the major features of the regional geochemistry of labrador. The reduction in data volume is significant ... a 97% reduction. Yet for elements that show high regional contrasts such as Ni and U this ... only results in approximately 30% and 45% reduction of information, respectively.”*

Pirc et al., (1991): Geochemical mapping of carbonate terrains.

> *“...sampling grids and sampling densities can be designed to produce stable geochemical maps of carbonate terrains.’*
>
> *“.. karstic landscape can be sampled by using aquatic moss and sediment from karst springs fed by underground drainage. .. the sediment is typical of the particulate and suspended components of the drainage .. Aquatic moss represents the water-soluble and partly suspended components.”*
>
> *“The capability to characterize the bedrock from drainage samples is good. However, the ability of drainage samples to characterize surficial geochemical processes-either natural or anthropogenic-is quite poor. The availability of suitable karst springs for sampling is problematic.”*
>
> *“Soil characterizes the bedrock in a different way and probably to a lesser extent than drainage sediment. Its geochemical composition depends on a number of exogenic soil-forming factors and is more exposed to the effects of pollution. Although the area of influence of a soil sample is four orders smaller than of a drainage sample, the method seems quite capable of detecting regional geochemical patterns. A great advantage of soil is its availability. Soil is present everywhere, even in the most deeply karstified areas and on high mountains.”*
>
> *“Geochemical mapping based on soil sampling could be performed on any scale, denser sampling grids being preferable.”*

Simpson et al., (1991): Orientation studies in Jamaica for multi-purpose geochemical mapping of Caribbean region.

> *“Studies of sampling and sub-sample preparation methods indicate that soil samples...provide the optimum sampling medium for a regional geochemical survey of Jamaica.” “... unlike stream sediments, showing minimal variation of element concentrations in relation to particle size.”*
>
> *“Soil samples ..provide a robust sample type, with trace-element levels that are unaffected by variations in the proportions of different size fractions arising as a result of operator error, geomorphology, or temporal climatic changes.”*

Ridgway et al., (1991): Variations in regional geochemical patterns-effects of site-selection and data processing algorithms.

> *“...meaningful geochemical maps can be produced from low-density surveys, which is in accordance with the findings of others..”*
>
> *“sampling densities should be chosen on the basis of the scale of the geochemical and geological features to be distinguished and will vary from region to region.”*
>
> *“ ..the low-order streams on which high-density sampling is based are not representative of as large a drainage area as the high order streams sampled in lower-density surveys”*
>
> *“.. sample densities as low as 1/500 km² can yield meaningful results in some areas regardless of the characteristics of the terrain”*

Applications of regional data

Appleton and Ridgway, (1993): Regional geochemical mapping in developing countries and its application to environmental studies.

> *".. application of regional geochemical data for baseline, environmental impact, animal health and land use planning studies illustrated using examples from Bolivia, Kenya, Sumatra and Swaziland."*

Davenport and Nolan, (1991): Definition of large scale zones of hydrothermal alteration by geochemical mapping using organic lake sediment.
[Ed.comment: most of the conclusions could be applied to results obtained in other regions with other media appropriate to the region]

> *"For effective Au exploration it is essential to measure the Au distribution directly."*
>
> *"Major fault systems, by acting as conduits controlling magma emplacement and the flow of fluids, have played a key role in the genesis of a wide variety of ore deposits. ...although major structures provide the regional control, ore deposition typically occurs in only a small proportion of the associated minor structures and therefore the definition of these large geological features is of very limited direct use in mineral exploration. The redistribution of elements by hydrothermal systems can vary in scale from metres to tens of kilometres in extent and geochemical mapping based on surficial materials (typically soils and drainage sediment) can establish local areas of epigenetic mineralisation as well as delineate the broad geochemical framework of hydrothermal activity. The considerable extent of some alteration zones associated with major structures permits their delineation at a reconnaissance level with low-density geochemical surveys."*
>
> *"Geochemical mapping is a unique way of delineating the distribution of elements that are primarily controlled by epigenetic processes. The distributions of these elements on a regional scale are clarified by block averaging, the patterns so obtained being coherent and very extensive. This suggests that they are controlled by major structural features, the full significance of which is not yet clear. The size of these geochemical features and their coherence permit their recognition in some elements from low-density, reconnaissance surveys."*
>
> *"The overall arrangement of epigenetic geochemical patterns with respect to the geological framework of Newfoundland implies that the island's geological fabric has been pervasively altered by very broad-scale regional, structurally controlled hydrothermal systems. The effect of these processes - and their ubiquity - is only obvious from the results of systematic geochemical mapping."*
>
> *"Low-density drainage geochemical surveys can map broad geochemical patterns in a reconnaissance fashion. These patterns would include those which reflect primary lithological contrasts of regional extent, such as in Ni, and also broad epigenetic geochemical patterns, such as in As. The resolution of these patterns requires that they be laterally consistent and extensive and that the random sampling and analytical errors be small in relation to overall data variance. The interpretation of such broad-scale patterns for mineral exploration will be limited both by their very large extent and by the reliability of the theoretical metallogenetic framework that is used to link regional epigenetic enrichment patterns to mineralisation."*

Garrett and Geddes, (1991): Studies of regional drainage geochemistry in Jamaica.

> *"The ...survey was successful in recognising all the previously known mineral occurrences of significance in Jamaica, in outlining areas not previously believed to have mineral potential and in stimulating fresh appraisals of old occurrences in terms of their potential for new commodities."*
>
> *"An additional study .... indicated a possible link between the incidence of kwashiorkor in children and background levels of Se."*

Plant et al., (1991): Regional distribution of As Sb and Bi in the Grampian Highlands of Scotland and the English Lake District: implications for gold metallogeny.

> *"The data presented...support a model whereby gold and its pathfinders were initially concentrated in volcano-sedimentary sequences in rapidly subsiding tectonically controlled basins.. Remobilization and mineralization occurred subsequently...with the influx of granite magmas ..... and the establishment of hydrothermal convective circulation systems."*

12.4 Supplement to Chapter 4 Global sample collection

Care should be taken to use sampling equipment which does not contaminate the samples. Each sample should be placed in a strong plastic bag or a water-resistant paper bag in the field. A coarse-pointed, acetone-based (waterproof), black felt-tip marker pen is used to mark numbers on sample bags. Narrow-tipped waterproof pens should be used to plot sample sites on maps.

Each sample site should be plotted on a base map, where possible more detailed than 1:100 000. Data recording is made on field sheets distributed by the international coordinators of the project. National coordinates and projection as well as latitude and longitude should be recorded for each sample. To obtain the latter quickly and easily consideration should be given to using Global Positioning System (GPS) receivers, which are compact, lightweight and reliable and are now (1994) relatively low-cost. Sample and site documentation should follow the recommendations given in Chapter 5 (Field methods).

12.4.1 Sample identification

Prior to sampling, sites of global composite samples are allocated sequential numbers (starting with 1 in each country). The identification code of samples should consist of data fields which are separated by dashes and which hold some important information on the sample (see also Chapter 8, Data management). The numbering system should be checked by the regional coordinator before work begins because it is essential that there should be no confusion or overlap. The following system is recommended:

> Country ID / year of sampling / cell number / sample number / sample medium / average depth (cm) of sample (when appropriate), / D for duplicate samples. The following codes are suggested for the sample media:
>
> Drainage samples:
> - SS stream; LS lake sediment
> - W river/lake water
>
> Regolith (A_{25}, alluvial):
> - FS floodplain, OS overbank sediment (label optional samples from lower horizon, FSL, OSL)
>
> Regolith (residual, non-alluvial):
> - RU upper (A_{25}) horizon; RC lower (C) horizon
>
> Humus: H

Example: FIN/1992/11/2/OSL/230/D is a Finnish duplicate sample of overbank sediment collected in 1992 in the global sampling cell No. 11 at site No. 2 at an average depth of 230 cm.

A general description of the physiography and geology is given for the area of the global composite sample. A similar but more detailed description is given for each sampling site which, if possible, is photographed or video recorded. If possible, a close-up of the soil profile in each pit of sampling should be photographed or recorded on a video film. Identification of personnel involved in sampling a site should be recorded. Each national agency compiles a report on relevant data after completion of a sampling program.

12.5 Supplement to Chapter 5 Drainage and soil sampling procedures for temperate; humid tropical; seasonally humid tropical regions

The following description of sampling procedures, as used by the British Geological Survey in different parts of the world, primarily as an aid to mineral exploration, is included to provide supplementary operational information. Where there are minor procedural differences (as with respect to water sampling) between this section and recommendations in the main body of the report, the recommendations in Chapters 1 to 8 should be followed. Note that the sieve size (<150 micron) is within the broader sieve size range quoted in Chapters 4 and 5.

12.5.1 Drainage samples

12.5.1.1 Introduction

The geochemical sampling procedure is based primarily upon collection of sieved <150 micron active stream sediment, from randomly distributed stream sites. For temperate regions, the method has been described by Plant (1971); Plant and Moore (1979); Plant et al. (1988), and in the BGS regional geochemical atlas series.

The methods for seasonally humid and humid tropical regions are essentially the same as those described for temperate regions, with modifications to allow for the different conditions which may be encountered in tropical regions.

Heavy mineral concentrate sample procedures are based on the method described by Leake and Aucott (1973). The chemometric procedures have been described by Plant (1973) and Plant et al.(1975). Studies of seasonal variation in temperate climatic zones have been made by Chork (1977) and Bolviken et al. (1979); and in Australia by Ishak and Dunlop (1985). Temporal variations in the chemistry of stream sediments are a potential difficulty in seasonally humid tropical regions (Ridgway and Dunkley, 1988) and in humid tropical regions (Ridgway and Midobatu, 1991). In humid tropical regions, sampling should be restricted to the dry season, when conditions are at their most stable. In seasonally humid tropical regions, particular care should be exercised in areas with strongly seasonal rainfall or where periodic catastrophic events, such as cyclones, are common.

In both types of region, a series of regularly sampled monitoring stations should be considered for regional programmes which will span several years. This will allow any major seasonal variations in stream sediment chemistry to be recognized and taken into account in the interpretation and presentation stage of a geochemical mapping programme.

Many humid tropical terrains present logistical difficulties for sampling teams because of their remote and/or rugged nature and attainment of the ideal sampling programme, in terms of sampling density or pattern and amount of material collected, may not be feasible. Problems of location in rain forest areas are discussed in Appleton and Ridgway (1994) and the use of modern satellite-based global positioning systems may be advantageous in some terrains.

12.5.1.2 Site selection

The sampling pattern is designed to meet the following criteria:

(1) The sampling pattern should be at as high a density as is consistent with the main aims of the survey (global mapping, reconnaissance, detailed etc.) and should aim to give uniform coverage from evenly distributed sample sites. Wherever possible sample sites should be marked, unnumbered, on field copies of topographic maps before going into the field.

(2) In accordance with the main aims of the program as identified in (1) above, each sample should be collected from as low an order tributary as possible and sufficiently far upstream of the confluence with a higher order stream to avoid taking sediment resulting from mixing of material from the two channels during flood flow.

(3) Ideally samples are collected at regular intervals along stream courses. Sample sites are pre-selected using topographic maps and aerial photographs to ensure an even distribution of data and that sources of contamination are avoided as far as possible. The field sites are selected to within +/- 50 metres of the recommended point by the sampling team and the sample number is entered onto field copies of topographic maps.

The factors involved in selecting the optimum site for the collection of drainage samples are:
(1) Absence of obvious sources of contamination, for example, sample sites are never located below road/stream intersections, and are always a minimum of 100 metres upstream of habitation.
(2) (a) In rugged terrain the collapse of bank material into the channel is common. Samples should be collected as near to the centre of the stream as possible to avoid sampling bank-slip material.
(b) In areas of subdued relief, active sediment in the centre of channels may be enriched in quartz and depleted in clays and other fine particles. In these circumstances material deposited along stream margins during flooding may locally be finer-grained and more suitable for a geochemical survey, although channel sediments will be better for the collection of heavy mineral samples (Tosiani and Tapia, 1993).
(3) Avoidance of well sorted gravel areas and areas of limited sediment accumulation.

Wherever possible, a suite of geochemical samples, comprising a <150 micron active stream sediment, a <2 mm panned heavy mineral concentrate, and both filtered and unfiltered water samples should be collected. Conditions in the seasonally humid tropical terrains may be suitable for wet sieving or dry sieving, but in many instances neither technique may be feasible and sediment samples may have to be collected in bulk for later processing in the laboratory. Thus in some cases it may not be possible to collect any of the samples on site, while in others only the most recently active stream sediment sample will be able to be taken.

12.5.1.3 Water samples

Note comment under 12.5. Where streams are flowing, three 30 ml unfiltered water samples are collected at each site for pH, fluoride ion and uranium determination together with one 250 ml sample for total alkalinity determination. Two water samples filtered through 0.45 micron are also collected. One of these is acidified at field base for later ICP-AES analysis, the other for chloride/nitrate analysis, is collected in a pre-rinsed sterile polycarbonate 30 ml bottle. Sample containers are thoroughly rinsed in unfiltered and filtered water as appropriate, prior to filling using plastic syringes and 25 mm diameter cellulose filters. All water samples are collected in midstream flow conditions, below the surface, before the stream bed is disturbed.

12.5.1.4 Stream sediment sample

(1) A sieve nest is used comprising two circular wooden frames (approx. 45 x 15 cm), with 2 mm and 150 micron aperture nylon sieve cloth in the upper and lower sieves respectively and mounted on a Malaysian-style ‘dulang’ pan. The sieves and pans are washed in the stream immediately prior to sampling if water is present.
(2) No matter what the state of flow in the stream, material should be collected from 5 sites over a 50 m stretch of the stream bed to produce a representative composite sample.
(3) The top 10-20 cm of sediment, which can contain high concentrations of secondary Fe and Mn oxides and surface contaminants, is first removed using a mild steel trenching tool or polyethylene implement.
(4) (a) Flowing streams - coarse sediment, preferably from beneath the surface redox barrier, is loaded into the top sieve with the minimum input of water. Care is taken to remove large clasts from the sediment by hand. The material in the top sieve is rubbed through by the collector wearing rubber gloves. The top sieve is then removed and the material in the lower (150 micron) sieve repeatedly washed and shaken through to the pan below using small amounts of water only. The final dry weight of fine sediment required is 100 g and sieving of coarse material through the top sieve should continue until a sufficient amount of the final sample has been produced. It is very important at this stage that coarse material, which would bias the sample, does not enter the pan. This can be avoided by carefully washing down the outside of the sieves before shaking. The pan containing the sediment is left undisturbed for as long as is feasible (up to 20-25 minutes), to allow the suspended material to settle.
(b) Totally dry streams - the procedure is similar to the foregoing except that the sediment is sieved dry and brushed through the sieve cloth using a soft nylon or bristle brush until sufficient <150 micron material has been accumulated.
(c) Dry streams with damp sediment - in this circumstance there is no alternative to the collection of material in bulk for later laboratory processing. Sieving using 2 mm cloth (or possibly 500 micron) to eliminate the coarsest grains will reduce the amount of material which need to be taken in order to ensure that sufficient <150 micron sediment is available after processing. The use of pools of standing water to facilitate wet sieving is not recommended because of the dangers of contamination from animal and human use and organic matter.
(5) (a) Flowing streams - excess water is then slowly decanted to leave a final sample volume of 200-250 ml. This is then homogenised by gentle agitation and carefully decanted into a 10 x 20 cm Kraft sample bag using a clean polypropylene funnel. The sealed Kraft bag is placed in a 15 x 40 cm polythene bag and secured with a loose knot and then placed upright in a plastic sample box for transportation to the field base. This prevents loss or cross contamination during transport.
(b) Totally dry streams - the dry sample material is placed in an 8 x 13 cm Kraft envelope.
(c) Dry streams with damp sediment - the damp, partially sieved sediment is placed in several 10 x 20 cm Kraft bags. The number of bags of material necessary to yield 100 g of <150 micron after later drying and sieving should be determined during an orientation survey.
(6) For 5 (a) and (c) Heavy duty rubber gloves must be worn throughout the sampling process in order to protect samplers and prevent contamination from jewellery, first aid dressings etc.
In the case of 5 (b), gloves are not necessary, but polyethylene implements should be used and care should be taken to ensure that jewellery, first aid dressings etc. do not come into contact with the sediment.
(7) (a) Flowing streams - after sampling all equipment is thoroughly washed in the stream before being packed away.
(b) Totally dry streams - equipment is brushed clean and the first sediment to pass through the sieves at the next site should be discarded.

(c) Dry streams with damp sediment - only the coarser sieve will have been used. This should be dry by the time that the next site is reached and can be brushed clean and the first pass of new sediment discarded.

In circumstances where samples may need to be carried by the field party for several days, wet Kraft bags may disintegrate. The alternatives are:
(1) To collect the sieved samples in contaminant-free polythene bottles for transport and decant into Kraft bags as soon as possible for drying.
(2) To collect several Kraft bags of well-drained < 2 mm (or < 500 micron) sediment for later drying and laboratory sieving.

12.5.1.5 Heavy mineral concentrate sample

As with stream sediments, slightly different approaches are required according to stream conditions:
(1) Flowing streams - a further 3-5 kg of wet < 2 mm fraction sediment, recovered from as deeply as possible within the sediment profile at 5 sites, is collected in the pan using large quantities of water to aid sieving. Further material is dug as necessary, rubbed through the 2 mm sieve, to make up the pan to approximately 60-70% full. The panning procedure then involves three discrete steps:

> (a) Removal of clay and organic material by repeated washingand stirring.
> (b) Formation of a heavy mineral bed by vigorous shaking with ample water for a minimum of two minutes.
> (c) Selective removal of the less dense fraction by circulating the pan on the surface of the water in an elliptical motion to yield a 20-40 g concentrate, depending on initial sample volume.

In order to enhance the reproducibility of results, every effort should be made to standardize both the initial and final volumes of material. The final concentrate is examined with a hand lens for visible gold, sulphides and other heavy minerals before being transferred to a labelled 8 × 13 cm Kraft envelope which is then placed in a plastic bag secured with a loose knot.
(2) Totally dry streams - sediment is sieved to < 2 mm and collected in bulk (4-5 kg) for laboratory processing.
(3) Dry streams with damp sediment - sediment is either collected in bulk as in (2) or, if standing water is present, processed on site using the same procedure as in (1).

12.5.1.6 Field observations and data recording

The same instructions apply to all stream conditions. Prenumbered field data cards, randomised in blocks of 100 numbers, are issued daily to the sampling teams, normally in batches of 10-12. At each site the appropriate number is transferred to all the sample containers and to the field map. Site locality description, grid reference and a wide range of observations such as sediment composition, colloids, clasts, precipitates, contamination, land use, clast/bedrock lithology and heavy mineral identification are recorded on the data card. Recent aerial photographs can be used to locate major sources of contamination (e.g. from mining), which should be recorded on the data card.

Where several teams of samplers are employed without direct supervision, the development of potentially bad sampling practices may be minimized by changing the composition of the teams on a daily basis.

12.5.2 Soil samples

Sampling techniques are similar in almost all terrains despite the wide variety in soil types which may be encountered (Butt and Zeegers, 1992). Ultimately, after appropriate sample preparation, the fine (<150 micron) fraction of the soil should be used to help preserve compatibility of geochemical data with those from stream sediment samples. In addition a coarser fraction of < 2 mm should be obtained for environmental studies.

12.5.2.1 Site selection

Site selections should conform to the following criteria:
(1) As with stream sediments, the sampling pattern should be as dense as is consistent with the main aims of the survey (global mapping, reconnaissance, detailed etc.) and aim to provide uniform coverage from evenly distributed sites. Consideration of the geological environment is of prime importance and soil sampling is normally carried out on a regular grid pattern at right angles to the strike, using cut lines where undergrowth is thick. Where a totally regular grid is not used, sample spacing should be closer across the strike than along it.
(2) For mineral exploration purposes, only residual soils (i.e. those developed above bedrock) should be sampled. For environmental purposes, sampling of other soil types, e.g., overbank and floodplain alluvium, is also necessary.

12.5.2.2 Sampling method

(1) In order to minimize local inhomogeneities, it advisable to collect several sub-samples at each nominal sample location. One technique is to take a central sample at the nominal location and four further samples, each at a distance of 5-10 m from the centre, at the corners of a square. These samples are then composited to form one bulk sample for later laboratory processing.
(2) At each of the five sites a small pit is dug using a trenching tool or similar implement. A hole of 20-25 cm depth will normally be sufficient, but the depth is less important than sampling a consistent soil horizon. The B horizon, which occurs below the organic rich and leached A horizons is normally sampled, but in areas of very thin soil development the whole profile may be used. Soil containing large quantities of organic material or rich in Fe or Mn oxides should be avoided if at all possible. For a description of different soil horizons and sampling techniques see standard geochemical exploration texts such as Levinson (1980) and Rose et al. (1979).
(3) Where dry conditions are encountered the soil can be sieved to <150 micron on site using the same equipment and techniques as recommended for dry stream sediment sampling. In damp conditions coarse material can be separated out by the use of a 2 mm (or if feasible 500 micron) nylon sieve, but care must be taken to ensure that contamination of subsequent samples by dirty sieve cloth does not occur.
(4) Material sieved to <150 micron can be placed in an 8 × 13 cm Kraft envelope, while damp partially sieved sediment should be transferred to 10 × 20 cm Kraft sample bags using a polyethylene scoop or rubber glove to prevent contamination from jewellery, first aid dressings etc.. The amount of sample necessary to yield 100 g of <150 micron material should be determined by an initial

orientation survey. A second sample of < 2 mm soil will provide a useful link to data obtained for agricultural purposes.
(5) Equipment is brushed clean and the first sediment to pass through the sieves at the next site should be discarded.

12.5.2.3 Field observations and data recording

The field data card will contain a variety of information including grid coordinates, landscape description, site topography, vegetation, presence and nature of overburden, bedrock, sample texture, soil horizon, thickness of sampling interval, colour, fragment content and possible contamination etc.

12.6 Supplement to Chapter 6 Geoanalytical methods

12.6.1 Examples of analytical schemes used as part of national mapping programs

12.6.1.1 Multi-element analytical system used in China

China's national geochemical mapping program, known as the "Regional Geochemistry National Reconnaissance (RGNR) Project," was initiated in 1978. A joint project for developing analytical methods to be used in the RGNR Project was recommended in 1979 by many laboratories undertaking analytical work for the RGNR Project. The general guidelines along which all the research works were to follow are: (1) a method and instrument with multi-element analysis capability should be used as the backbone in order to scan a large number of elements simultaneously; (2) elements with low crustal abundance should be dealt with separately by whatever method which could achieve the detection limits required.

A variety of methods and combinations of methods were developed by different laboratories. But after 6-8 years of practice and "natural selection", the system and even the analytical procedures have been gradually unified and standardized. This system has been arranged to determine 39 elements. They are all included in the list of "essential" elements which we recommend for international geochemical mapping (see Fig.6-1). The other 10 elements in the list of essential elements but not included in China's RGNR Project are LOI, S, Ga, Sc, Rb, Cs, Ce, Se, I and Cl which could easily be incorporated into the existing system used in China's RGNR Project. We would like to recommend this system to be used in this geochemical mapping project, because (1) it was established based on about 12 years experience of 1 million sample analyses, and (2) it is particularly suitable for developing countries, because relatively unsophisticated analytical instruments are employed which are available in many laboratories. In the suggested multi-element analytical system based on China's experience, the 49 essential elements will be grouped into 6 packages to be determined with a variety of analytical methods successively (see Fig.6-2). **Package 1** consists of 10 rock forming elements Si, Al, Fe, Ca, Mg, K, Na, Mn, Ti, P which can be determined simultaneously in the same sample by XRF. **Package 2** consists of 19 minor and trace elements Cu, Pb, Zn, Cr, Ni, Co, Sr, Ba, Rb, Cs, Sc, Y, La, Zr, V, Nb, Th, Ce, S, which can also be determined simultaneously in the same sample with rock-forming elements by XRF. **Package 3** consists of the remaining 20 essential elements that must be determined on a more individual basis by a variety of methods: As, Sb, Bi, Hg, Se by AFS; W, Mo by POL, Sn, B, Be by AES; Ag, Cd, Li, Cs by AAS; U by LF; Au by CP-AES or GF-AAS; F by ISE; I and Cl by IC; and LOI by GR. In **Packages 4, 5 and 6** are the 20 non-essential elements that can be determined in a flexible way, either determined together with the essential elements, or determined in a later stage, or determined selectively. Package 4 consists of the 12 rare-earth elements that can be determined by ICP-AES. Package 5 consists of Pt and Pd that can be determined by AES after preconcentration and Package 6 consists of other 6 non-essential elements N (as NO_2), Hf, Ta, In, Tl, Te that might be handled in separate groups. Although the rare earth and platinum elements were not included in RGNR Project in the past, they may be added to the list of elements in later stages of the project. Some provincial central laboratories have already begun to determine these elements extensively using the newly developed ICP-AES methods for rare-earths (after preconcentration) and for Pt and Pd which have proven very successful.

12.6.1.2 Multi-element scheme used in Finland for till analysis

Part 2 of "The Geochemical Atlas of Finland" (Koljonen, 1992) describes the results of a till survey in Finland, at a low sample density of one per 300 km^2 . Both ICP-AES and INAA were used to analyse the 1057 samples, collected from the upper part of the C-horizon and sieved to < 60 micron. Two acid attacks were employed to dissolve the sample prior to analysis by ICP-AES: the first based on HF and oxidising acids to reflect the near total amount of element present; and an aqua regia digestion to provide information pertinent to the weathering and migration probabilities of the elements. For the "total" element result, 3 ml of HF were added to 0.1 g of sample, left in contact for 12 h, and 0.5 ml of HCl and 0.5 ml of HNO_3 were subsequently added. The digestion was continued by heating at 80 °C for 1 h after which 50 ml of boric acid were added (to complex HF) and the solution made up to 100 ml. This method brings into solution most of the elements incorporated in silicates, carbonates, sulphides and phosphates. However, Al-rich minerals and oxides (e.g. hematite, chromite) dissolve only sparingly; typically over 98 % of the sample was dissolved in the Finnish set of tills. For the partial leach, 3 ml of aqua regia were added to 0.15 g of sample and heated at 80 °C for 1 h. After cooling, the solution was made up to 15 ml and analysed; the dilution factor of 100, tenfold smaller than that in the "total" method, results in superior detection capability for the "partial" amount of the element. While sulphides, carbonates and phosphates are largely completely dissolved in aqua regia, most silicates and some oxides are not.

The elements determined by ICP-AES following the two decompositions are: Ag, Al, (As), (B), Ba, Ca, (Cd), Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, (Sb), Sc, Si, Sr, (Th), Ti, (U), V, (W), Y, (Yb), Zn and Zr. The elements in parentheses were not presented as maps (inadequate detection limits and/or decomposition). INAA was employed as a supplementary method to acquire data on those elements not intrinsically sensitive by ICP-AES. The sample weighing 0.1 - 1.0 g was irradiated for 25 h in an epithermal flux and the resulting gamma-ray activities measured after a 4-6 day decay period. The elements determined by INAA are: (Ag), As, (Au), (Ba), Br, (Co), (Cr), Cs, (Fe), La, Lu, Mo, (Na), (Ni), Rb, Sr, (Sc), Sm, (Sn), Ta, Th, U, W and (Zn). Where elements were determined by more than one technique, only the most reliable was reported in the Atlas. The near total results by HF-HCl-HNO_3 / ICP-AES generally agreed well with those by INAA. Detection limits for the elements determined by both analytical techniques are given in Table 2.1 of Koljonen (1992).

In addition to the elements determined by ICP-AES and INAA, S, Au, and Pd were also reported. Sulphur was measured by the conventional `leco' method where SO_2 is volatilised from a 950 mg sample by inductive heating at 1000°C and then quantified by infrared spectrometry to yield a detection limit of 20 ppm S. Gold and Pd were determined to limits of 0.3 and 1.5 ppb, respectively, by GFAAS following digestion at room temperature of a 1 g sample in 2.5 ml of HCl and 0.5 ml of HNO_3 for 14 h. Preconcentration was effected by reductive coprecipitation with Hg and stannous chloride; the Hg precipitate is then dissolved in HCl and H_2O_2 for analysis.

12.6.2 Additional background information concerning geoanalytical methods

12.6.2.1 Acid digestion

HF is most effective in breaking up the Si-O bond to form SiF_4 which volatilises upon heating. Fluorides of As, B, Ti, Nb, Ta, Ge and Sb may be lost to varying extents upon heating. HCl, a strong acid, is effective in the dissolution of carbonates, phosphates, borates and sulphates (except barite) and has become an almost universal solvent suitable for most techniques (possible exception of ICP-MS due to the formation of Cl-molecular species). Its capacity to attack Fe and Mn oxides is superior to that of HNO_3 due to its reducing and complexing properties. Pyrite is only slightly soluble in HCl while pyrrhotite, sphalerite and marmatite dissolve completely. Hot, concentrated HNO_3 is used to decompose sulphides, selenides, tellurides, arsenides, sulphoarsenides and phosphates through oxidative degradation (S is oxidised to SO_4). HNO_3 dissolves the majority of metals occurring in nature, with the exception of Au and the PGEs. Iron sulphides and molybdenite dissolve easily. Practically all O-containing primary U minerals are decomposed with conc. HNO_3. The powerful oxidising and dehydrating properties of hot, conc. $HClO_4$ are effective in decomposing sulphides and organic matter, but care must be taken to avoid an explosive hazard with samples high in organic matter. Its high boiling point makes it useful in driving off HF and more volatile acids. Although H_2SO_4 has similar properties, it has not found such widespread application probably due to the interference effects created by SO_4 in AAS and to the low solubility of alkaline earth and Pb sulphates.

HF is customarily used with mineral acids to effect decomposition of oxides and sulphides as well as silicates. Fluoride is usually removed by evaporation with $HClO_4$ thereby preventing the precipitation of insoluble fluorides (e.g., Ca, REEs) later in the digestion. Teflon or Pt dishes are employed and the absence of HF in the analyte solution makes it suitable for passage through glass nebulisers, spray chambers and torches. HNO_3 is added to moderate the action of $HClO_4$ on organic material which could be explosive. There are many variations on the procedure but normally the mixed acids are evaporated to dryness and the residue dissolved in HCl (0.5-1 M) for analysis.

The less rigorous digestion - aqua regia - is employed more frequently than HF-$HClO_4$-HNO_3 in geochemical exploration when the elements of interest (e.g., Cu, Pb, Zn) are sorbed onto clay minerals or in other readily decomposed phases. Some laboratories also add HF to attack the silicates. The mixture of 3 parts HCl to 1 part HNO_3 (aqua regia) has a strong oxidising power due to the formation of nascent chlorine and nitrosyl chloride. [The Lefort digestion is the reverse mixture of these acids]. Hot aqua regia is an efficient solvent for numerous sulphides (e.g., those of As, Se, Te, Bi, Fe, Mo), arsenides, selenides, tellurides, sulphosalts, and native Au, Pt and Pd. The minerals belonging to the group of simple oxides and their hydrates (e.g., Fe-Mn) are completely decomposed with aqua regia. Natural U oxides, Ca phosphates and most sulphates (except barite) are solubilised, as are some silicates such as the zeolites. The oxidising strength of aqua regia can be enhanced by adding bromine. In Canadian laboratories, there has been a trend away from employing the $HClO_4$-HNO_3 attack, requiring special fume hoods, for the decomposition of organic- and sulphide-bearing material in favour of the simpler aqua regia procedure. Evaporation to dryness with conc. HCl converts salts to chlorides, ready for final solubilization in dilute (0.5-1 M) mineral acid which is compatible with the analytical technique. Aqua regia digestion for As, Sb, Bi, Se and Te should not be taken to dryness to avoid loss of analytes via volatilisation. Strong oxidising acid mixtures are required to convert all forms of Hg to Hg^{2+}.

The effectiveness of extraction naturally depends upon the temperature, pressure and time of sample/acid contact. More complete decomposition is achieved by closed rather than open system digestion where increased temperature and pressure conditions prevail. Various types of vessels are available such as PTFE crucibles encased in metal ("bombs") and all Teflon vessels of different shapes. Polypropylene and polycarbonate bottles can be used up to 130°C while PTFE-lined vessels can withstand temperatures of 150-250°C. Pressure decomposition with mixed acids may attack certain refractory minerals (e.g., beryl, pyrite) not completely solubilised in open digestion. Unlike most of these vessels, screwcapped Teflon vials of 15 ml volume or greater are inexpensive enough to be applicable to large scale decomposition schemes. Closed system digestion is increasingly being used with the energy source being microwave radiation rather than heat. The advantages include more complete dissolution in much less time, lower volume of acids required and less exposure to toxic fumes. Adaptation to high production has been slow due to the manipulations involved but newer designs are addressing this issue.

12.6.2.2 Fusions

Although classical methods of silicate analysis relied heavily upon the Na_2CO_3 flux, borate fusion, particularly $LiBO_2$ rather than $Li_2B_4O_7$, now dominates in geoanalysis due to its widespread applicability and effectiveness at low flux:sample ratios (3:1 or greater). Flux and sample are simply mixed together in a graphite or Pt crucible, fused at 1000°C for 30 min. with gentle swirling, allowed to cool and the melt dissolved in HNO_3 or HCl. This fusion is employed for major and minor element determination as well as for traces where a dilution factor of ca. 500 suffices. More work is needed in designing automated preconcentration schemes so that this efficient method of decomposition can cover a wide range of trace elements using various analytical techniques.

Boron is often determined after a Na_2CO_3-$NaNO_3$ fusion; other oxyanion forming elements such as Cr, V, Mo and W can be determined simultaneously. Potassium pyrosulphate is useful in decomposing some refractory oxides such as rutile and ilmenite as well as oxides of Nb and Ta whereas silicates are not effectively attacked. Ammonium iodide is considered to be specific to convert cassiterite-Sn to SnI_4, thus providing a method to classify Sn-binding ($LiBO_2$ fusion would represent total Sn). Fusion with Na_2O_2 is effective for the decomposition of sulphides, arsenides, REE phosphates, W, Nb and Ta minerals, vanadates, chromite and zircon.

A combination of acid attack and fusion, as a way of ensuring total dissolution of all minerals while retaining a low dilution factor of ca. 100, has been described by Thompson and Walsh (1989). The residue remaining after an HF-$HClO_4$-HNO_3 digestion is fused with a small amount of $LiBO_2$, dissolved in acid and the two extracts combined for analysis. Decomposition methods for Au and the PGEs involve specific procedures.

12.6.2.3 Atomic Absorption Spectrometry (AAS)

Elements which can normally be determined by flame AAS include the majors and minors Si, Ca, Mg, Na, K, Al, Fe, Ti, Mn and the traces Ba, Be, Co, Cr, Li, Ni, Pb, Rb, Sr, V and Zn. Other geochemically important trace elements require a preconcentration step which improves detection capability for such elements as Ag, Bi, Cd, Pb, Mo, Sb, As, Ga, In, Tl and Se. Cold-vapour (CV) AAS remains the analytical technique of choice for the determination of Hg.

Graphite furnace (GF) AAS enjoys superior sensitivity over F-AAS by 1-3 orders of magnitude but suffers from more complex interferences and lower productivity. Elements requiring the sensitivity of GF-AAS include Ag, Cd, In, Sn, Tl and Pb. Probably the greatest need for GF-AAS lies in the determination of Au, Pt, Pd and Rh. The elements annotated in the Periodic Table (Fig.12-1) can, for the most part, be determined easily by AAS to crustal abundance levels with different degrees of complexity reflecting the relative cost and productivity of analysis. The detection capability of GF-AAS is rivalled only by the much more expensive and sophisticated technique of ICP-MS.

12.6.2.4 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Solutions presented to the ICP can be derived from fusions or acid attacks. Lithium metaborate is in common use for total decomposition and is suitable for major and minor element determination but the necessity to incorporate a dilution factor of ca. 500 to keep the total salt content below 1% degrades detection limits for traces. The ease with which the $LiBO_2$ fusion can be carried out coupled with the capability of ICP-AES has made this the method of choice for major and minor element determination, replacing the older method of fused disc/XRF in many geoanalytical laboratories. However, the precision obtained by ICP-AES (+/-1% relative) is inferior to that of XRF, especially for Si and to a lesser extent Al. The suite normally reported comprises SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, Fe_2O_3, MnO, Cr_2O_3, P_2O_5, TiO_2 (and LOI). These elements, with the exception of Si, are also determined following an HF-$HClO_4$-HNO_3-HCl attack but decomposition is not necessarily complete.

Acid digestions in commercial laboratories fall mainly into 2 categories: aqua regia (HCl-HNO_3) and HF-$HClO_4$-HNO_3-HCl. The latter is often referred to as "total" but it must be remembered that resistant minerals such as chromite, zircon, sphene and cassiterite are only partially attacked. Dilution factors following acid attack range from 20 to 100, compatible with the determination of about 30 elements at their crustal abundance.

Table 12-1 lists the determination limits quoted by four large commercial laboratories using an acid digestion for trace elements together with those published by Thompson and Walsh (1989). The latter are significantly higher than the values arrived at by multiplying the 3σ ICP-AES detection limit for ideal, "clean" solutions by a typical dilution factor in order to account for

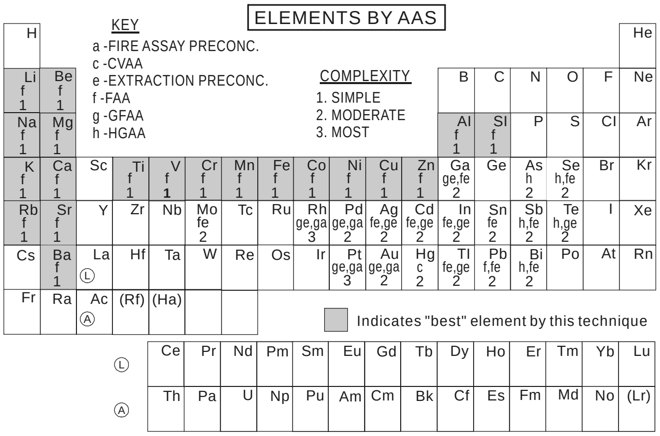


Figure 12-1 *Elements which can be determined by AAS*
from Hall, 1991

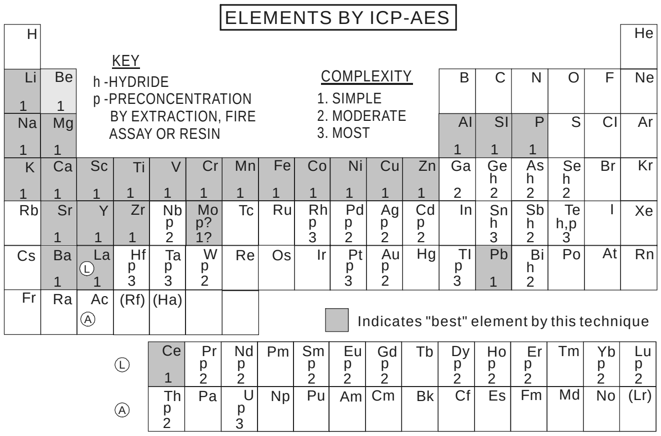
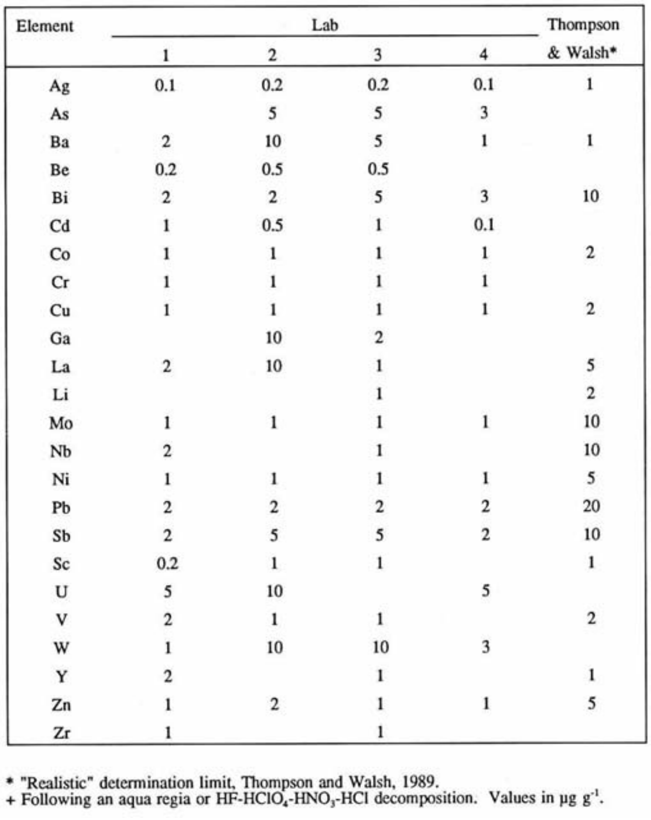


Figure 12-2 *Elements which can be determined by ICP-AES*
from Hall, 1991



Element	Lab 1	2	3	4	Thompson & Walsh*
Ag	0.1	0.2	0.2	0.1	1
As		5	5	3	
Ba	2	10	5	1	1
Be	0.2	0.5	0.5		
Bi	2	2	5	3	10
Cd	1	0.5	1	0.1	
Co	1	1	1	1	2
Cr	1	1	1	1	
Cu	1	1	1	1	2
Ga		10	2		
La	2	10	1		5
Li			1		2
Mo	1	1	1	1	10
Nb	2		1		10
Ni	1	1	1	1	5
Pb	2	2	2	2	20
Sb	2	5	5	2	10
Sc	0.2	1	1		1
U	5	10		5	
V	2	1	1		2
W	1	10	10	3	
Y	2		1		1
Zn	1	2	1	1	5
Zr	1		1		

* "Realistic" determination limit, Thompson and Walsh, 1989.
\+ Following an aqua regia or HF-$HClO_4$-HNO_3-HCl decomposition. Values in μg g^{-1}.

Table 12-1 *Determination limits quoted by four commercial laboratories for trace elements analysed by ICP-AES*

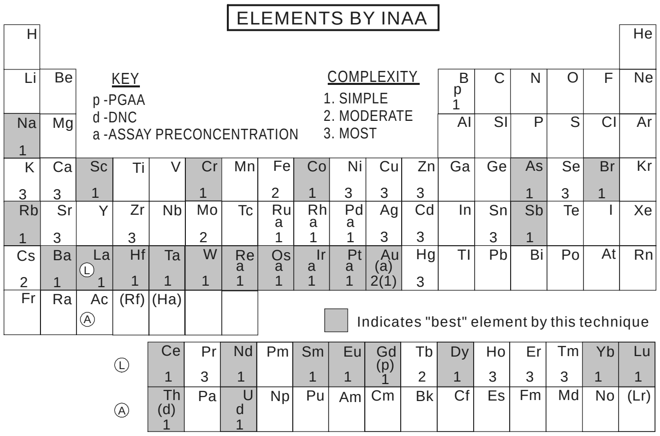
variability introduced by the digestion (contamination, sample processing etc.) and the uncertainty encountered in applying correction procedures when analyzing real solutions.

The terms "determination" limit and "quantitation" limit are generally defined to represent 6σ and 10σ, respectively. Of the elements listed in Table 12-1, those with determination limits at or near crustal abundances comprise Ba, Be, Co, Cr, Cu, Ga, La, Li, Mo, Ni, Pb, Sc, Sr, V, Y, Zn and Zr. Of these, low results due to incomplete digestion may arise for Ba, Be, Cr, Sr and Zr.

Elements frequently determined by ICP-AES are shown in the Periodic Table, (Fig. 12-2). Straightforward analysis of an acid or fusion leachate is appropriate for the elements labelled "1" while preconcentration is generally required for those with a "2" unless a survey is intended to depict only "highs". A substantial improvement in sensitivity is needed to reach abundance levels for those labelled with a "3" and consequently costs can be significant.

12.6.2.5 Instrumental Neutron Activation Analysis (INAA)

INAA is remarkably free of interferences as matrix effects are small. Self-shielding of neutrons occurs during irradiation when a sample contains high concentrations of an isotope having a high neutron capture cross-section. The worst offenders in this regard are elements such as Gd, Eu and B which fortunately are not major constituents of geological materials.



ELEMENTS BY INAA

KEY
p -PGAA
d -DNC
a -ASSAY PRECONCENTRATION

COMPLEXITY
1. SIMPLE
2. MODERATE
3. MOST

▨ Indicates "best" element by this technique

H																	He
Li	Be											B p 1	C	N	O	F	Ne
▨ Na 1	Mg											Al	Si	P	S	Cl	Ar
K 3	Ca 3	▨ Sc 1	Ti	V	▨ Cr 1	Mn	Fe 2	▨ Co 1	Ni 3	Cu 3	Zn 3	Ga	Ge	▨ As 1	Se 3	▨ Br 1	Kr
▨ Rb 1	Sr 3	Y	Zr 3	Nb	Mo 2	Tc	Ru a 1	Rh a 1	Pd a 1	Ag 3	Cd 3	In	Sn 3	▨ Sb 1	Te	I	Xe
Cs 2	▨ Ba 1	▨ La Ⓛ 1	▨ Hf 1	▨ Ta 1	▨ W 1	▨ Re a 1	▨ Os a 1	▨ Ir a 1	▨ Pt a 1	▨ Au (a) 2(1)	Hg 3	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac Ⓐ	(Rf)	(Ha)													
		Ⓛ	▨ Ce 1	Pr 3	▨ Nd 1	Pm	▨ Sm 1	▨ Eu 1	▨ Gd (p) 1	Tb 2	▨ Dy 1	Ho 3	Er 3	Tm 3	▨ Yb 1	▨ Lu 1	
		Ⓐ	▨ Th (d) 1	Pa	▨ U d 1	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	(Lr)	

Figure 12-3 *Elements which can be determined by INAA*
from Hall, 1991

A major application of INAA is the determination of the REEs and other elements of importance in petrogenetic and tectonic studies such as Sc, Hf, Ta, Th and U. The precision of INAA is excellent, aided greatly by the minimum sample manipulation required. Contamination is not of the concern it is in other techniques and any introduced after irradiation would not be measured in any case. The determination of Au by INAA is particularly advantageous in light of the fact that the common aqua regia attack employed for solution based techniques can be partial (matrix dependent), as can Pb fire assay if precautions are not taken for certain matrices. Furthermore, 30 g of sample can be accommodated. Only recently has INAA been rivalled (by ICP-MS) in its ability to determine the PGEs, following a preconcentration and separation procedure.

INAA has advantages for the analysis of vegetation and humus. This matrix is ideal because of the insensitivity to such elements as C, N, H and O, thus creating a low background. Besides being an inexpensive, accurate and productive method of analyzing vegetation, INAA avoids ashing where volatiles can be lost and the considerable problems of dissolving copious amounts of organic matter are negated. Elements such as Pb, Cu, Ni and Cd are not well served owing to lack of sensitivity.

The ability of INAA to determine the REEs, Au, As, Sb, Hf and Ta and the other elements shown in Figure 12-3 clearly demonstrates that it is a technique complementary to others such as ICP-AES and XRF whose strength lies in analysis for the majors and base metals.

12.6.2.6 X-Ray Fluorescence Spectrometry (XRF)

Analysis of silicates and carbonates by ICP-AES following $LiBO_2$ fusion does not yet rival the precision obtained by fused disc XRF for the major elements.

All XRF measurements on bulk samples are subject to non-linear effects resulting from the attenuation, or infrequently enhancement, of fluorescence X-ray intensities by interaction with the sample matrix. These effects comprise mainly: (1) attenuation as the beam penetrates the sample, dependent upon photon energy (low suffers more) and matrix composition (greater for high atomic number); and, (2) attenuation of the fluorescence photons emerging from the sample. Many mathematical models, based either on fundamental principles or empirically determined, have been developed to account for these matrix effects. There is a critical depth below the surface of a sample beyond which fluorescent X-ray photons are effectively absorbed. The magnitude of this critical penetration depth depends on the photon energy and on the mean mass attenuation coefficient of the sample. For example, for the Kα lines of Na and La in a silicate powder they are estimated to be 0.005 mm and 10.6 mm, respectively. Thus, for a powder sieved to pass 60 μm, the fluorescence signals from the lightest elements (Na Kα to Ca Kα) will be derived from a single monolayer. It is unlikely that this mass of sample would adequately represent the bulk and distortions may arise from heterogeneity along the surface of a compressed powder. Heavier elements are much less effected as the signal is acquired from a greater thickness of material. Hence the heavier trace elements may be determined in samples prepared as pressed pellets while for the majors it is essential that the mineralogical constituents of the sample are broken down.

Powder pellets are prepared by mixing the sample (having been sieved to pass a 200 mesh screen) with a suitable binder, compressing and forming a disc. Most fluxes used to prepare glass discs are based on lithium tetra- and/or meta-borate which are not normally detected by XRF. Problems arise in the fusion of mineralized samples. Elements such as As, Sb, Se, Te, Hg, Cd and S as sulphide are likely to be volatilised, but this can be partially overcome. The fusion based method is normally reserved for the "whole rock" analysis of silicates and to a lesser extent carbonates, chromites and barites. It is general practice to calibrate with as many SRMs as possible, although other calibration schemes are also used.

The typical classical "whole rock" package available from commercial laboratories comprises the determination of: (1) SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, Fe_2O_3, MnO, Cr_2O_3, P_2O_5, TiO_2 to 0.01 %; (2) Ba, Nb, Rb, Sr, Y and Zr to 10 μg g^{-1}; and, (3) at extra cost Cu, Zn, Pb, Ni, Co, Mo, U and Th to 10 μg g^{-1}. Detection limits for the trace elements improve in the pressed powder package (see Fig.12-4).

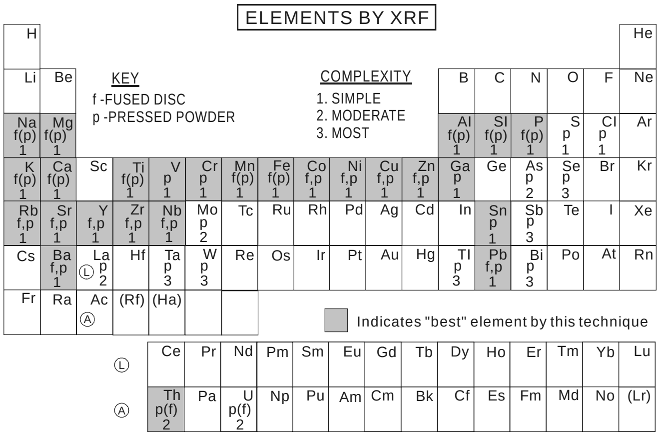


Figure 12-4 *Elements which can be determined by XRF*

from Hall, 1991

12.6.2.7 Methods for Au and the PGEs

Renewed interest in exploration for Au, Pt and Pd in the 1980s stimulated research into improving analytical methods for these elements, both in the area of decomposition/separation and instrumental measurement. This illustrates that if the need exists, methods can be devised. The low abundance of Au and the PGEs requires the use of sensitive analytical techniques. A number of options are available in selecting the method by which Au is to be determined, the choice being governed by the sample matrix, mineralogy, representative weight and detection limit required to meet objectives. Because of the "nugget" effect, a much larger weight than suffices for other trace elements is taken for analysis.

12.6.2.8 Methods for waters

This set of notes is concerned with methods where groups of elements are determined cost-effectively in a manner appropriate for geochemical surveys. "Packages" of elements are listed below according to the recommended analytical technique and any sample preparation required to attain detection limits *below* natural abundance ranges. These suggestions are based on experience in the analysis of lake and stream waters from Newfoundland, remote from industrial sources of pollution. There are considerable differences in sensitivity (and robustness) between mass spectrometers. These recommendations could change slightly depending upon the instruments available.

12.6.2.9 Elements by direct nebulisation ICP-ES:

Na, Mg, Si, P, S, Sr, K, Ca, Mn, Ba, Fe, Zn. About 10 ml of sample are needed for simultaneous determination.

Note: Flame AAS could be used for these elements except P and S, with less efficiency (throughput) than a simultaneous ICP-ES.

12.6.2.10 Elements by direct nebulisation ICP-MS:

B, Al, Ti, V, Mn, Co (?), Ni (?), Cu (?), Zn, As, Rb, Y (?), Mo (?), Cd (?), Sb (?), I, Cs (?), La, Ce, Pb (?), U (?). About 10 ml are needed but flow injection facilities will decrease this volume requirement.

Note: Both techniques above would improve in sensitivity by a factor 5-10 with sample introduction using ultrasonic rather than conventional pneumatic nebulisation. This modification is ideal for waters of low dissolved salts content - other more complex matrices would not benefit so much as interferences, especially in ICP-MS, would negate the improvement in sensitivity due to the higher percentage of solution transferred to the ICP. The efficiency of sample introduction using conventional nebulisation is only in the order of 2-4 %. Ultrasonic nebulisers have become much easier to operate and maintain and those elements listed above with question marks attached would be well served by USN-ICP-MS.

12.6.2.11 Elements by chelation/ICP-MS:

Al, Ti, V, Co, Ni, Cu, Y, Cd, In, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb, U. Fifty ml is currently used for a 10 times preconcentration factor.

Note: The above is based on a Chelex-100 type of preconcentration, using a factor of 10 (50 ml to 5 ml) which can be changed easily to decrease detection below 1 ppt (ng/l). A Dionex chromatography system is fully automated so that operator attendance is not needed.

The labile form of the element is being determined here; metal-organic bonds, if present, would require breakdown by UV irradiation or chemical oxidation. To date this has not been investigated.

12.6.2.12 Elements by hydride ICP-MS:

Se, Sb, Te (?), Bi (?), Sn (?), Ge (?). Different acid conditions are needed for generation of Sn and Ge hydrides as opposed to the others.

Note: Those elements with ? marks require detection limits below 1 ppt and thus preconcentration is needed, perhaps by simple evaporation prior to analysis. This method determines inorganically bound hydride elements. By using different acid strengths, we can differentiate between, say, Sb (III) and Sb (V). Organically bound species must be liberated by oxidation prior to analysis.

12.6.2.13 Elements by charcoal adsorption ICP-MS:

Au, Pt, Pd

Note: About 1 l is required to reach a detection limit of ca. 0.5-1 ppt; a decade improvement is required for Pt and Pd. Au can also be determined by GFAAS with adequate sensitivity.

12.6.2.14 Vapour generation ICP-MS:

Hg. Yet to be investigated, but should reach 1 ppt relatively easily. Similar to established vapour generation quartz tube AAS methodology.

12.6.2.15 Ion chromatography:

F, Cl, Br, NO_3, NO_2, PO_4, SO_4. All detected to 10-50 ppb (ng/ml) as a package.

Note: It is preferable to determine F by the ion-selective electrode as low molecular weight organics interfere in the IC method.

12.6.2.16 Miscellaneous methods

Other analytical techniques in use which have not been discussed in this review are electrochemical techniques such as anodic stripping voltametry (ASV) and detection by an ion selective electrode (ISE) which are employed for specific purposes. Fluoride is measured by ISE, directly in waters or in a leachate following an alkaline fusion. Alternatively, it can be determined together with Cl and S by ion chromatography (IC). IC is used routinely to determine F, Cl, S, Br, P and N species in waters.

12.7 Supplement to Chapter 7 Additional information on airborne gamma radiation data collection and data reduction

12.7.1 Summary of IAEA Technical Report No. 323 (1991)

The contents of this report, which illustrate the various considerations which enter into the execution of the method are as follows. Following a short introduction (Section 1), Section 2 provides an outline of the physics of gamma rays and the instrumentation used to detect them. The emphasis is on aspects relevant to the practicalities of airborne gamma ray spectrometry. Section 3 deals with airborne survey parameters such as flight line direction and spacing, detector volume, and with operational procedures during fieldwork. It also covers ancillary equipment necessary for the conduct of the surveys. Section 4 deals with all aspects of data reduction that are required to convert airborne measurements to ground concentrations of potassium, uranium and thorium. The various topics covered include: calibration of radar altimeter and barometric pressure transducer, determination of equipment dead-time, determination of cosmic, aircraft and radon backgrounds, determination of stripping ratios and height attenuation coefficients, and finally determination of system sensitivities.

The quality control procedures are described in Section 5, mainly as they apply to spectrometric mapping of the distribution of natural radioelements or of fallout. Three types of variables requiring monitoring to ensure high quality radiometric data are discussed: instrumental, operational and environmental. Section 6 discusses processing requirements and procedures for natural radioelement mapping. Products from natural radioelement mapping by airborne gamma ray spectrometry are discussed in Section 7. These include profiles and profile maps, gridded contour maps, the digital data archive and reports. Section 8 is devoted to the use of airborne gamma ray spectrometry for environmental monitoring. The mapping of the Chernobyl fallout in Sweden is briefly described, followed by a discussion of the instrumental, calibration, processing and output requirements for environmental and emergency response monitoring. Section 9 describes briefly the use of airborne gamma ray spectrometer surveying methods to locate lost radioactive objects and sources. Several cases are described, including the search in northern Canada for the radioactive debris from the Soviet satellite Cosmos 954, which was complicated by the high levels of natural background radiation.

Appendices provide a model of detailed specifications for contracting an airborne gamma ray spectrometer survey, both for data acquisition and data processing. Specifications for an airborne magnetometer survey are also included since this can be conducted simultaneously. A selected bibliography lists the most important literature relating to the various aspects of airborne gamma spectrometry covered in the manual.

An abbreviated version (with minor amendments and additions), of key sections of IAEA Technical Report 323 most relevant to users of AGRS data, is given below.

12.7.2 Important considerations in the conduct of airborne surveys

12.7.2.1 Equipment and operational considerations

Detector volume and aircraft groundspeed

From the point of view of optimum AGRS system performance, detector volume and aircraft ground speed are interrelated factors.

In order to obtain high quality data it is necessary to minimize the statistical uncertainty inherent in measurements involving natural radioactivity, which arise because of low count rates. In order to maximize sensitivity and minimize the errors involved in applying the essential corrections it is necessary to accumulate as many counts per unit distance as possible. This is achieved by carrying as large a detector volume as possible and flying as slowly as possible. The ratio of detector volume (in litres) to ground speed (km/h) provides a comparative index of the performance of different systems for a given terrain clearance. The most sensitive AGRS systems employed for regional surveys carry a detector volume of 50l at 200 k/h; their performance index is thus 0.25. A value less than 0.2 is unsatisfactory.

Commonly 33 to 50 litres have been employed for fixed wing surveys and 17 to 33 litres for helicopter surveys. The latter tend to be flown slower and at lower elevations, but this has the consequences discussed below.

Accumulation time and sampling rate

Data acquisition should be arranged so that the accumulation of the spectral data is a continuous process. While the data from one sample are being processed, new data are being acquired in the next sample interval. Sample intervals are therefore contiguous, with no “dead-time” while data are being processed. Normally, data are sampled once per second.

Because the aircraft moves forward during the accumulation time, the area of ground sampled is elongated. A rule of thumb gives 60 - 70% of the counts originating in an oval of width twice the flying height and length twice the flying height plus the distance travelled during accumulation. For a helicopter survey, at height 120 m, speed 140 k/h (39 m/s) and accumulation time 1 second, the area represented by each sample is about 240 m by 280 m.

Flight line direction

For natural radioelement mapping the flight line direction should be at right angles to the geological structures of interest, usually the geological strike, if this is known. For large scale reconnaissance surveys covering areas of variable strike an arbitrary direction is chosen, often north-south or east-west. If aeromagnetic data are being recorded in addition to the radiometric measurements and the survey area is very close to the geomagnetic equator, then lines should be approximately north-south. In severe mountain terrain where regular grid flying is dangerous or impossible, flying may be carried out at constant elevation following topographic contours.

Flying height

Spectrometer surveys are flown at an approximately constant height above ground level (AGL). Gamma rays are attenuated by air in an exponential fashion. For an infinite slab source, the amplitude decreases by approximately half for every 100 m of height. The amplitude at 125 m is therefore only about 35% of the ground level amplitude. For a point source the fall-off is much greater. A lower flying height provides a stronger signal and can reduce signal-to-noise problems such as those associated with atmospheric radon. However, the area of ground sampled is reduced by the lower ground clearance and the flying becomes more hazardous.

For natural radioelement mapping using fixed wing aircraft, flying height above ground level has been generally standardized at 125 m (400 ft). In flat terrain, e.g. Finland, heights as low as 30 - 50 m have been used, mainly to enable electromagnetic methods to be operated simultaneously.

Aircraft selection and ancillary equipment

Aircraft selection:
An unsuitable aircraft can substantially reduce the quality of an otherwise well equipped survey. Because of the importance of achieving the highest possible count rates in order to maximize sensitivity, and the fact that the weight and cost of a large detector volume can be a practical limiting factor in equipment installation, it is advantageous to select an aircraft which can carry an adequate detector volume at low speed. Excess speed will reduce sensitivity and/or spatial resolution. As speed increases it becomes more difficult to maintain a constant ground clearance. Because most aircraft are optimized to fly fast, careful selection is important. Slow-flying fixed-wing aircraft are more economical than helicopters and are suitable for surveys over flat terrain, or hills with low gradients. Where gradients are steep, as in mountainous regions or in regions with deep narrow canyons, helicopters must be employed.

Navigation systems:
In most past surveys, navigation has been by a combination of visual methods, using maps or photomosaics marked with the intended flight line positions, and an electronic method such as doppler radar, inertial position fixing, GPS satellite fixing or radio triangulation. The electronic fixes are digitally recorded with the spectrometric data for use in plotting the true flight track. A tracking video or film is also made during flying to cross check the electronic system. GPS satellite navigation and positioning is rapidly becoming established as the standard method because of its simplicity (in terms of aircraft instrumentation), ubiquity of the signal and reliability.

Other equipment:
A precision radar altimeter, accurate to about 2 m, is essential for height keeping since attenuation corrections must be applied to the data. Temperature and pressure sensors are needed to convert the radar altitude to an effective height at Standard Temperature and Pressure (STP). The pressure sensor may be a barometric transducer or a barometric altimeter.

On natural radioelement mapping surveys, other geophysical instruments such as magnetometers and EM instruments may be carried, and their data are recorded along with the spectrometric data.

The data from the spectrometer, navigation system and other instruments are formatted by an on-board computer or data acquisition system and digitally recorded on tape or some other medium. The computer also controls the sampling sequence of the instruments and supplies a sequence of numbers (fiducials) on the tracking video which corresponds to numbers on the data tape.

12.7.2.2 Corrections and calibration for natural radioelement mapping

Airborne gamma ray spectrometry can produce a quantitative estimate of mean surface radioelement concentration provided that data collection is performed with high quality equipment, the data are subjected to the requisite corrections and the equipment has been properly calibrated. The procedures involved are fully described in reports published by the International Atomic Energy Agency (IAEA) and so details are not given here beyond listing the factors which must be taken into account:

(1) Radar altimeter calibration.
(2) Calibration of barometric pressure transducer.
(3) Determination of equipment dead-time.
(4) Determination of cosmic and aircraft backgrounds.
(5) Determination of radon background.
(6) Determination of stripping ratios.
(7) Determination of height attenuation coefficients.
(8) Determination of system sensitivities.

With the application of corrections and calibration appropriate to the system being used, data can be presented as per cent K, ppm eU, ppm eTh. The prefix e (equivalent) is used for U and Th measurement by gamma ray spectrometry as a reminder of the fact that the determinations are based on daughter products, ^{214}Bi and ^{208}Tl respectively, and the assumption is made that the ^{238}U and ^{232}Th decay series are in equilibrium. Each measurement in AGRS is based on a large volume of material (of the order of 50×10^3 m^3), so disequilibrium is only a significant factor under conditions of extreme chemical weathering.The radiation associated with the radioelements can also be expressed (and displayed) in terms of dose-rate.

1 per cent K = 13.1 nGy h^{-1} (old units 1.505 μR/hr)
1 ppm eU = 5.43 nGy h^{-1} (old units 0.653 μR/hr)
1 ppm eTh = 2.69 nGy h^{-1} (old units 0.287 μR/hr)

12.7.2.3 Products from natural radioelement mapping

Products from natural radioelement mapping may consist of profiles along each flight line are usually produced as multi-parameter plots on paper. The plots are drawn to a true linear scale, e.g. 1:50 000 or 1:100 000, with the horizontal axis annotated with the fiducial numbers. Plots are typically 0.5 to 1 m wide and show K%, eU, eTh and exposure rate with effective ground clearance, barometric height, magnetometer and other geophysical data if available. These plots are sometimes called “stacked profiles”, but this name is ambiguous as it is used by some to denote profile maps of the type described below.

Profile Maps

Maps on which the data are plotted as profiles along horizontal axes formed by each flight line provide a quick and useful means of viewing the results of a survey. They can fairly easily be produced on a field computer. Sometimes features can be seen on these maps which do not survive the subsampling and smoothing implicit in gridding and contouring operations.

Gridding

Most map products require the data to be interpolated onto a regular grid. There are many ways for this to be done. Many of the standard gridding algorithms are unsuited to radiometric data, because of the inherent statistical variations. A suitable gridding algorithm is one which takes the average of all data points lying within a circular area, weighted for distance from the grid point.

Contour Maps

Contour maps in one form or another are still the most widely used product of most airborne spectrometer surveys. The choice of gridding algorithm, contour interval and style will normally be made after some experimentation, in consultation with the end-user of the data, but will generally involve a minimum of smoothing to respect the raw data as closely as possible.

Use of computer produced colour contour maps is now widespread. Again, the gridding algorithm, colour palette and other variables are usually determined after some tests and experiments. These maps are a very effective means of displaying the data and should be regarded as the main map product for regional surveys.

Another effective map presentation is the colour ternary map, on which each radioelement is represented by one of the three primary colours, with intensity varying according to the radioelement concentration. There are several different ways to produce these maps, which give informative and semi- quantitative results.

Ternary maps are produced most easily using image processing software. In this case the additive primary colours, red, green and blue are used. The intensity of each colour depends on the concentration of the radioelement: black represents low concentrations of all three. The appearance of the image is optimized using interactive contrast-stretching. This method gives visually satisfying images quickly and easily, but they are essentially qualitative as the quantitative information is largely lost in the optimization process. The final product is a photographic image which can be enlarged to the map scale required.

Electrostatic or ink jet plotters can also be used to produce ternary maps. In this case the subtractive primary colours yellow, magenta and cyan are used to represent the three radioelements and the lowest concentrations of all three are shown as white. With care and some experimentation, colour intensity scales can be chosen which give a map that is both visually satisfying and quantitative, so that a particular colour denotes a known combination of concentration values. Choice of colour scales can often be made easier by making use of a cumulative probability plot of the data for each radioelement.

In a simpler form of map, the colours are distributed on a triangular diagram according to the relative proportions of the elements, with respect to their sum. Pure magenta signifies very high potassium with negligible uranium and thorium; yellow signifies high thorium with negligible uranium and potassium and cyan represents high uranium with no potassium or thorium. This type of map is essentially a ratio map, since the colours depict the relative concentrations of the radioelements.

Notes on production of ternary maps

Ternary maps are produced most easily using image processing software. In this case the additive primary colours, red, green and blue are used. The intensity of each colour depends on the concentration of the radioelement: black represents low concentrations of all three. The appearance of the image is optimized using interactive contrast-stretching. This method gives visually satisfying images quickly and easily, but they are essentially qualitative as the quantitative information is largely lost in the optimization process. The final product is a photographic image which can be enlarged to the map scale required.

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Digital Archive

In addition to the field tapes carrying the raw data, the digital archive contains processed records of both flight line data and gridded data. The flight line data should have, for each sample, the fiducial number, the line number, map coordinates, the apparent radioelement concentrations, exposure rate, effective height AGL and the corrected values of magnetic field and any other geophysical data. The raw values of the potassium, uranium and thorium, total count, cosmic and upward uranium windows, temperature, pressure and radar altitude can also be included. Each tape should have a header text file with descriptions of the format and contents. Grid data tapes need header information specifying the grid origin and orientation, x and y spacing and numbers of x and y points. Half-inch, 1600 bpi tapes coded in ASCII or EBCIDIC are still the normal and the preferred medium for digital archives.

Reports

Complete technical reports covering survey operations, calibrations and processing are a necessary part of every airborne gamma ray survey, but are often overlooked. A list of the topics which should be covered is given in the sample specifications in IAEA Technical Report 323.

12.8 Supplement to Chapter 8 Data management

12.8.1 Databases

The data fields are normally of character type even if the data are numeric and needed for arithmetic computations--character fields can be transformed to numeric when needed within a database application. The length of the fields indicates the internal length in the database, not the display length. Fields matching the WEGS data description are typed *italic* in the descriptions below.

12.8.2 Index Database

The purpose of the *index database* is to hold administrative and methodological information about national geochemical surveys that are relevant to international geochemical mapping (Table 12-2).

12.8.3 Block Database

Each block corresponds to a node in a grid of meridians and parallels spaced at ½° from each other. The block areas vary from about 3080 to 53 km^2 when moving from the equator to the 89:th latitude – north or south. The most northern and southern blocks delimited by the 89.5:th and -89.5:th latitudes respectively, consist of the spherical triangles containing the poles. The northing index of blocks runs from the south pole to north from -180 to 180. The easting index runs west from Greenwich from 360 to 1 and east from Greenwich from 361 to 720. For efficient searches in the network of blocks a single integer, the Morton number, is recommended to point to blocks directly. The Morton number is an index running from 1 to 129,600 on the Northern hemisphere and from -1 to -129,600 on the Southern Hemisphere. The Morton numbers are signed according to the latitude and thus are consistent with the UTM convention for zone numbers. Medians of the concentrations are the preferred estimators for the block averages. The medians are more resistant to the influence of extremely high and low values (up to 50% outliers). In light of the large number of samples falling in any block the loss in efficiency of the median vs. the mean is far outweighed by the advantages of using a robust, outlier resistant, estimator to determine average regional geochemical background levels.

The recommended structure of the database is relational with an internal index to link each block value to its parent survey, location (Morton number), and unique variable (element/anion), sampling media, size fraction and analytical method (total, extractable, radiometric) combination (Fig.12-5). Compared with purely flat sequential structures, indexed tables are easily expandable with new data or unique variable, sample media, size fraction and analytical method combinations. Such relational tables and indexes can be constructed with most database management software even if they do not fully facilitate relational tools. The following description of data types does not show indices associating block values to attributes (Table 12-3).

The data descriptor table is built by the database software and contains every existing combination of measured variable (element/anion), sampling media, size fraction analysed and analytical method described in the Index Database. By using this approach with a Block Data table there are no empty fields; this reduces the amount of disk storage required for the data, and avoids the necessity of finding a satisfactory “missing data” code that will work across all computing platforms.

A large index is maintained by the database software that provides the linkages between survey data source, location, and measured variable details. It is this index that permits rapid and specific retrievals to be made.

FIELD CONTENT	DATA TYPE	LENGTH IN CHARACTERS	RANGE OF DATA
Identification number of survey	integer	5	a unique ID-number entered by the database manager
Level of survey	character	1	I for international (e.g. Nordkalott project) N for national
Survey objective	character	1	1 exploration 2 environment 3 multipurpose 4 other
Survey status	character	1	1 under planning 2 ongoing 3 completed 0 unknown
Location information:			
Country	character	20	valid name of country
Name of region(s)	character	20	name of region
Corners of a polygon including the survey area (max 10 corners) expressed either in UTM or geographic coordinates			
1. UTM boundaries			
Zone number	character	3	a valid 2-digit zone number (1,...,60) and the sign in the UTM-system
Easting	character	6	measured in m
Northing	character	7	measured in m
2. Geographic boundaries			
Latitude	character	5 (1)	degrees (-90.0, ..., 90.0) to 1 decimal precision, + northern and - southern latitudes
Longitude	character	6 (1)	degrees (-180, ..., 180) to 1 decimal precision, + east and - west from Greenwich
Size of area	integer	8	measured in km^2, 0 unknown
Morton indices of blocks within survey area	integer array	max 60 integers (60 x 8 = 480)	see section 5.2.2 for Morton numbers
Characteristics of the region:			
Topography	character	1	0 unknown 1 low plateau 2 high plateau 3 very variable
Degree of pollution	character	1	0 unknown 1 unpolluted 2 polluted by agriculture 3 polluted by industry 4 polluted by various sources
Samples and analyses:			
Sampling medium	character	12	one of the strings: GROUNDWAT LAKESED LAKEWAT MOSSES OVERBANK ROCK ROOTS SOIL STREAMSED STREAMWAT TILL

Table 12-2 *Index database*

FIELD CONTENT	DATA TYPE	LENGTH IN CHARACTERS	RANGE OF DATA
Samples and analyses (cont.):			
Grain size (µm)	character	12	any string indicating one or two integer bounds in µm; if only one bound entered then it should be preceded by a character "<" meaning "finer than"; or ">" meaning "coarser than"; if two values are entered then the first one is the lower and the second one the upper bound for grain size
Heavy mineral fraction	character	1	Y yes, N no, U unknown
Number of samples	integer	8	any integer < 10 million
Approx. sample density (samples / km^2)	real	8 (2)	any positive real value with two decimals precision
Composite samples	character	1	Y yes, N no, U unknown
Replicate samples	character	1	Y yes, N no, U unknown
Elements determined:			
Total	character	max 600 (= 6 x 100)	a string of element or anion names (max 6 characters)
Extractable	character	max 600 (= 6 x 100)	a string of element or anion names (max 6 characters)
Replicate analyses	character	1	Y yes, N no, U unknown
Radiometric surveys	character	1	Y yes, N no, U unknown
Other information:			
Years of collection	character	9	a string indicating one year *yyyy* or an interval of years *yyyy - yyyy*
Organization responsible	character	20	abbreviated name of organization
Contact person responsible	character	30	name of person
Bibliographic reference(s)	integer	max 40 (= 4 x 10)	integer pointers to the Bibliographic Database
Availability of digital data:			
Available	character	1	Y yes, N no, U unknown
Charge	character	5	price in ECU, 0 meaning free
Comments	character	30	free text for comments on availability
Contact person:			
Name	character	30	name of person
Address	character	40	address
Phone	character	20	international phone number
Fax	character	20	international fax number
e-mail	character	30	e-mail address

Table 12-2 *Index database (continued)*

FIELD CONTENT	DATA TYPE	LENGTH IN CHARACTERS	RANGE OF DATA
Availability of sample archives:			
Available	character	1	Y yes, N no, U unknown
Charge	character	5	price in ECU, 0 meaning free
Comments	character	30	free text
Contact person:			
Name	character	30	name of person
Address	character	40	address
Phone	character	20	international phone number
Fax	character	20	international fax number
e-mail	character	30	e-mail address
Total characters / record		max 2261	

Table 12-2 *Index database (continued)*

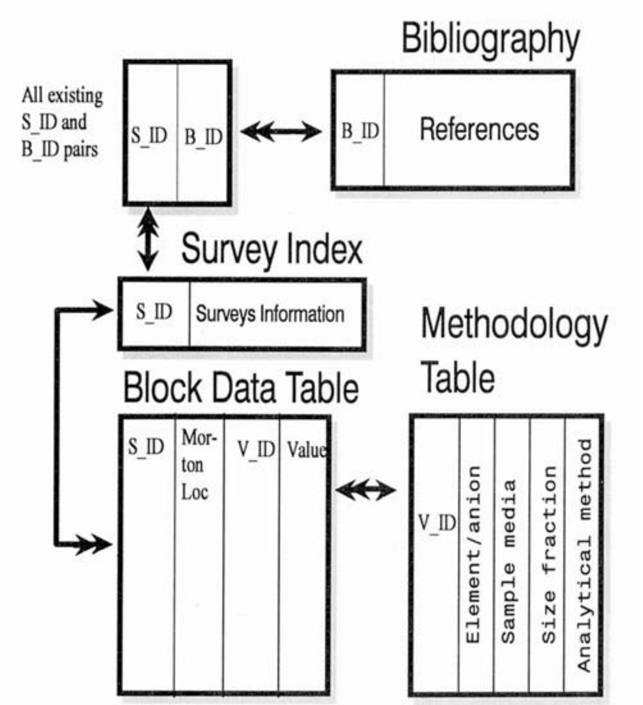

Figure 12-5 *Relational structure of the block database*

12.8.4 Bibliographic Database

The Bibliographic and Index Databases are interlinked by the unique survey ID numbers and the bibliographic reference ID numbers. The structure of this database is simple sequential. As a single reference may relate to several surveys and a single survey may be described in several references, a table of all valid survey-reference ID pairs is maintained as a relational table built by the database software (Table 12-4).

12.10 Supplement to Chapter 10 Implementation

12.10.1 Training facilities available to developing countries

Training programs relating to some aspects of the science and technology covered in this report may be available through the International Atomic Energy Agency, Vienna. In general the Agency does not perform the training directly, but may make the necessary arrangements with universities, government agencies, or other scientific institutions. Some government-to-government technical assistance programs provided by the European Community and individual countries such as Canada, Czech Republic, Finland, France, Germany, United Kingdom, USA and others may be willing to consider appropriate training, particularly where application is made by a group representing more than one country.

12.10.2 Cost factors in geochemical surveys

12.10.2.1 Field sampling considerations

A primary aim of the International Geochemical Mapping project is to establish a geochemical reference network as rapidly as possible, so with this objective in view sampling should not be delayed until such time as national mapping programs commence work in an area. National programs will collect many samples and normally progress slowly, so that many years could elapse before all parts of a country are reached. It is desirable that a single team should be responsible for the collection of all reference samples in a region so that identical criteria and procedures are applied at all sites. Collection should take place over as short a time span as possible to minimize seasonal variations caused by marked

FIELD CONTENT	DATA TYPE	LENGTH IN CHARACTERS	RANGE OF DATA
Block data values:			
Unique survey identification number	integer	5	Same as the Index Database
Morton number of occupied block	integer	7	(-129,600 to 129,000)
Unique ID for the variable, sample media, size fraction and analytical method	integer	5	assigned by database software
Element / anion median value	real	8	any appropriate real value
Number of samples for the median	integer	5	the number of samples that the median is based upon
Fill proportion	integer	1	An integer in the range 1 to 3 indicating the proportion of the spherical rectangle covered by the survey area: 1 for < 1/3 2 for > 1/3 and < 2/3 3 for > 2/3
Lower and upper quartiles associated with the median	2 reals	10	two real values computed from the same distribution as the median
Total characters / record		41	

Table 12-3 *Block data values*

FIELD CONTENT	DATA TYPE	LENGTH IN CHARACTERS	RANGE OF DATA
Data descriptors:			
Unique ID for the variable, sample media, size fraction and analytical method	integer	5	assigned by database software
Names of elements / anions	character	6	as per the Index Database
Sampling medium	character	12	as per the Index Database
Size fraction	character	12	as per the Index Database
Analytical method	character	12	one of: TOTAL EXTRACTABLE RADIOMETRIC
Total characters / record		47	

Table 12-3 *Data descriptors*

FIELD CONTENT	DATA TYPE	LENGTH IN CHARACTERS	RANGE OF DATA
Bibliographic data:			
Bibliographic reference ID	integer	4	same as the bibliographic reference number in the Index Database
Author(s)	character	160	name(s)
Title	character	160	title of paper, report etc.
Year of publication	character	4	4 digit year *yyyy*
Publication	character	80	name of journal or series as appropriate
Journal	character	40	name of journal
Publisher	character	40	organization name
ID numbers of surveys in the Index Database which the reference describes	integer vector	max 50 (= 5x10)	no more than 10 5-digit ID numbers per publication

Table 12-4 *Contents of bibliographic data file*

differences in stream flow, water-table elevation or soil moisture (affecting *in situ* gamma-ray measurements). Also, it is desirable that all samples from a region should go through the analytical process during a known time period. Therefore, reference network sample collection should be planned and costed as a stand-alone project.

12.10.2.2 Geographic regions

Ideally the world should be divided into regions of similar physiography, climate and infrastructure and similar approaches devised for all the countries within each region. In practice it will be necessary to obtain administrative and/or institutional approval and cooperation in each country, possibly at more than one level, and this will influence the lead-time and logistical arrangements. It could also add to the time required to prepare and conduct sampling operations and hence add significantly to costs. If Regional Coordination Centres can be set up (see 10.2.3 above) this should greatly facilitate planning and implementation.

12.10.2.3 Sample spacing

Experience in many countries with the conduct of geochemical surveys has shown that in all but developed urban/suburban areas where there is a dense road network the cost of sample collection has exceeded the cost of sample preparation and analysis. (It should be recognized that in part this has been due to the limited amount of analytical work performed on each sample). The greater the distance between sample sites the greater the unit cost of collection because sampling teams have more unproductive time. Thus there is an argument for collecting additional samples en route between network sites if no significant distance is added, but it would involve slowing-down the operation, resulting in more samples to be carried and processed. This should be costed for each region.

12.10.2.4 Costs of sampling/field transportation

In regions with a good road network, vehicle based sampling parties can operate cheaply and relatively rapidly. Boats could be used in a few regions. Helicopters, although more expensive, provide the most rapid and secure access in undeveloped countries and can provide the only means of access to remote areas. Because of the rate of coverage which is possible with a helicopter, fewer sample collection teams are required which simplifies supervision and standardization of procedures. The cost of field sampling is the sum of the size of team and their expenses, travel time between sites, cost of vehicle(s) and fuel, time required to collect, dry and prepare samples, cost of packing and labelling samples, cost of shipping samples, cost of site documentation and record keeping.

12.10.2.5 Team training and supervision

Quality control at all stages of the work is essential, and this applies particularly to the first (sample collection) stage of the operation where it might seem economical to employ casual labour with minimum training. Each stage of an operations must take place under close professional supervision, and thorough training must be given to all involved. There must be complete confidence that samples are collected as and where intended. A minimum of 2 people should go to each field sampling site. The total number in a field party will vary according to the region, mode of transport and logistic arrangements. It is strongly recommended that each sampling team should be instructed by a regional coordinator who will first meet with coordinators from neighbouring regions before training begins. Regional co-ordinators should be assigned responsibility for supervising project operations in their own regions.

12.10.2.6 Costs of analytical methods

Analytical arrangements for the reference network samples hinge on the participation of a number of leading international geoanalytical laboratories which have yet to be approached officially. Therefore it is not possible to say on what basis work will be done, whether for a nominal cost or at a commercial rate. In normal practice, analytical costs are minimized and results improved by guaranteeing to submit a large number of prepared samples in an orderly flow over a period of time. If the time period is too extended costs will rise. Provision must be made for clean dry storage of samples whilst work is in progress, and subsequent archiving. Cross contamination must be avoided during handling and shipping. Unique permanent labelling of all samples is essential.

As an indication of order-of-magnitude costs, enquiries made in Canada in September 1992 indicate that a total analysis for 73 elements in a solid sample, using the most sensitive methods commercially available, could be obtained for about $175 per sample if ordered in large numbers (e.g. in batches of 10 000). Not all methods are available in any single laboratory, and preparation costs are approximately $10 per sample.

The cost of analytical reference materials, which must be obtained from approved sources, is the responsibility of individual laboratories and will be factored into their analytical prices.

12.10.2.7 Data verification and compilation

Data verification (quality control) should be undertaken independently of the sample collection and analytical processes and costed separately. It is most appropriately performed by those responsible for data compilation.

12.10.2.8 Costs of airborne gamma-ray spectrometry

As with many services, if purchased as a long-term contract airborne surveys can be substantially cheaper than if purchased in small units. Assuming that an experienced commercial contractor is selected, with high-sensitivity equipment calibrated according to IAEA recommendations (see Chapter 7), it is suggested that in order to minimize the initial mobilization costs, work should be planned which will combine the requirements of several neighbouring countries so as to occupy a 4 to 5 month period. In this way costs could be in the range of $15 to $35 per line-km of data delivered.

Key word Index

(Excludes entries in Summaries and Bibliography)

We know that the surface of the earth – rock, soil, water, air – and the living things on it contain all 92 chemical elements. What we lack is detailed information about their distribution and the quantities present. Natural processes and human activities are continuously modifying the chemical composition of our environment, and in order to monitor and measure the global changes that are occurring we need access to high-quality, global geochemical baselines. It was in this context that the multi-stage International Geochemical Mapping (IGM) project was established.

This book stems from a component of the IGM, an International Geological Correlation Programme (IGCP) project, and is the result of a comprehensive review of methods of regional and national geochemical mapping and of an examination of the results obtained. Its recommendations are directed towards geochemists and all those institutions which have a mandate for providing earth science and/or environmental databases. The recommendations provide for a recognized, global, quantitative base on which local investigations can be built to answer particular environmental and economic problems concerning animal and human health, soil fertility, agriculture, forestry, water supply and irrigation, waste disposal, mineral exploration and mining, industrial pollution and land use in general.

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