

STREAM SEDIMENT GEOCHEMISTRY

W.T. Meyer

Cities Service Company, Tulsa, Oklahoma

P.K. Theobald, Jr.

U.S. Geological Survey, Denver, Colorado

H. Bloom

Colorado School of Mines, Golden, Colorado

Meyer, W.T., Theobald, P.K., Jr., Bloom, H., *Stream Sediment Geochemistry*; in *Geophysics and Geochemistry in the Search for Metallic Ores*; Peter J. Hood, editor; Geological Survey of Canada, Economic Geology Report 31, p. 411-434, 1979.

Abstract

Stream sediments are characterized more by their variability than by their uniformity in composition, grain size, sorting and colour. This variability is a function of the geology, terrain, and climate of the catchment areas sampled by the stream, and it provides the essential ingredient for viable stream sediment surveys. Prospectors have always made use of this fact, initially through observation of mineralized boulders and panning of heavy minerals from the stream bed, and more recently by chemical analysis of the finer fractions of stream sediment. Over the past 25 years, routine application of stream sediment geochemistry has become accepted by government and intergovernmental agencies and the mining industry as the principal method of low-cost reconnaissance exploration in those areas, favoured by the combination of adequate relief and precipitation, where a suitable, integrated drainage system has developed.

At present, surveys that make use of trace analysis of the fine fraction (normally minus-80-mesh) of active sediments, although still the most common, are increasingly being questioned. In areas of extreme climate or where information from the fine sediment is no longer adequate, enhancement of anomalies may require sampling of organic material, of specific coarse fractions of inorganic sediment, of selected mineral groups within the sediment that may be isolated mechanically or chemically, or of a combination of these materials. As a result, variations in sampling and analytical methods have been developed to accommodate regional and climatic differences and differing survey aims (i.e., multi-purpose or strictly prospecting, single or multiple target).

This review outlines the present art with selected examples of surveys by both government and industry. The largest single expense is the sample collection cost, particularly the transportation cost to or between sample sites, and to optimize this investment the tendency is to collect multiple samples at each site and for multi-element analyses. Mathematical and graphical interrelation of all of these components with the geology, geophysics, and physiography of the area under study, usually requiring computer technology, provides a far greater insight into the exploration targets sought today than the single-sample, single-element approach that was so successful in the past.

Résumé

Les sédiments fluviaux manifestent fréquemment un certain degré de variabilité de composition, granulométrie, triage et couleur. Cette variabilité dépend de la géologie, de la nature du terrain et du climat du bassin-versant qui alimente le cours d'eau, et constitue la base d'une prospection sérieuse des sédiments fluviaux. Les prospecteurs ont toujours tenu compte de ce fait: autrefois, ils examinaient les blocs minéralisés et recueillaient par lavage les minéraux lourds se trouvant dans le lit du cours d'eau; de nos jours, ils étudient la composition chimique des plus fines fractions granulométriques des sédiments fluviaux. Depuis 25 ans, les organismes gouvernementaux et intergouvernementaux et l'industrie minière considèrent la prospection géochimique des sédiments fluviaux comme la meilleure manière, et la moins coûteuse, d'explorer les régions dont la topographie, le régime des précipitations et le réseau hydrographique créent des conditions favorables à ce type de prospection.

Actuellement, on doute de plus en plus de la valeur des relevés qui s'appuient sur l'analyse de la fraction granulométrique fine (généralement maille inférieure à 80) des sédiments actifs, bien que ce soit encore la méthode la plus fréquemment utilisée. Dans les zones où le climat est très rigoureux, ou bien dans lesquelles l'analyse de la fraction sédimentaire fine ne suffit plus, il faut parfois, pour mieux déceler les anomalies géochimiques, recueillir dans le sédiment les débris organiques, certaines fractions plus grandes du sédiment inorganique ou certains groupes de minéraux que l'on peut isoler mécaniquement ou chimiquement, ou bien plusieurs de ces matériaux à la fois. Les méthodes d'échantillonnage et d'analyse se sont donc suffisamment diversifiées au cours des années, pour que l'on puisse tenir compte des différences régionales et climatiques, ainsi que des divers objectifs des levés (par exemple, prospection monominérale ou pluriminérale, objectif simple ou multiple).

Le présent article illustre les progrès de la prospection géochimique par des exemples de levés commandés par le gouvernement et l'industrie. L'étape la plus coûteuse des levés est la collecte des échantillons, surtout en raison des frais de transport vers ou entre les sites d'échantillonnage; on s'efforce actuellement de faire plusieurs prélèvements sur un même site, et d'effectuer le dosage de plusieurs éléments à la fois. On s'applique à établir par des méthodes mathématiques et graphiques une relation entre chacun des éléments et les caractères géologiques, géophysiques et physiographiques de la région étudiée; ces méthodes, qui exigent généralement l'emploi d'ordinateurs, nous renseignent bien mieux sur la valeur des objectifs explorés que les anciennes méthodes, qui ont autrefois fait leurs preuves, de collecte d'échantillons isolés et de dosage individuel des éléments.

INTRODUCTION

Stream sediment geochemistry, although an obvious offshoot of the mineralogical study of alluvium, is a relative newcomer amongst the techniques available to the geologist in search of ore. In a recent review of the historical development of modern geochemical prospecting, Hawkes (1976a) traced the first application of stream sediment sampling in North America to Lovering et al. (1950), who described the results of field investigations, conducted in 1947 and 1948, of the downstream dispersion of copper, lead and zinc from the San Manuel deposit in Arizona. Only 30 years have passed since this initial study, but due to the method's obvious advantages in reconnaissance exploration and to the technological improvements in trace analysis and data processing that have occurred during this period, stream sediment surveys have become accepted as one of the most important low-cost reconnaissance tools available to the present day explorationist.

A variety of sampling and analytical methods have been developed to accommodate regional geologic and climatic variations, and these are further modified to suit the aim of the survey, whether it be multi-purpose or strictly for prospecting. This paper reviews the current state-of-the-art in terms of regional development of techniques and provides some examples of recent applications of stream sediment geochemistry.

GENERAL PRINCIPLES

Stream sediments are characterized more by their variability in composition, grain size, sorting and colour than by uniformity in any of these features. This variability is a function of the geology, terrain, and climate of the catchment area sampled by the stream, and it provides the essential ingredient for viable stream sediment surveys. However, the purpose of geochemical prospecting is to isolate that portion of the variability which reflects the presence of mineralization in the catchment area and, to do this, one must understand how sediment composition is affected by lithology, climate, topography, human activity, vegetation and water chemistry. The following provides a brief review of the physical and chemical controls on stream sediment composition that may be of concern to the exploration geochemist.

Mode of Occurrence

A general discussion of the mode of occurrence of trace elements in stream sediments has been given by Rose (1975). Trace elements can be found in stream sediments as major elements in trace minerals, as trace constituents of primary rock-forming minerals or minerals formed during weathering, as ions adsorbed on colloidal particles or in the lattices of clays, and in combination with organic matter. A study of the transportation of transition metals in the Amazon and Yukon rivers (Gibbs, 1977) has shown that most of the metal in suspended sediment is in the form of crystalline particles and hydroxide coatings. To give examples, the element manganese (Fig. 19.1a) is largely present as a coating, and copper (Fig. 19.1b) is predominantly found in the crystalline or mineral phase.

1. Mineral Phase

Trace elements contained within the lattice of rock-forming minerals and within minerals formed during weathering probably make up the greatest proportion of the background variation in most stream sediments. For the purpose of mineral exploration, contrast between anomalous and background concentrations of metal can be maximized through the use of partial chemical extractions which do not remove lattice-held trace metals from the host mineral.

However, study of the efficiency of extraction of metal from minerals using different strengths and combinations of acids (Foster, 1971) has shown that even 5 per cent HNO_3 is capable of extracting appreciable amounts of zinc from pyroxene, limonite, feldspar, biotite, and amphibole (Table 19.1). As the bulk of analytical work on stream sediments is conducted by atomic absorption on hot acid extractions, or by total methods such as emission spectrography and X-ray fluorescence, much of the recorded trace-element variation will be derived from changes in the mineralogical composition of the sediment. This characteristic has been used with some effect in regional reconnaissance to define previously undetected geological units, but in general, geochemical mapping as an aid to geology has been restricted to specific problems in poorly exposed areas (Webb, 1970). It should be noted, however, that trace elements in the lattice of rock-forming minerals (i.e., magnetite and biotite) can provide clues to mineralization, and hence can be anomalous; and that many of the products of weathering are the specific targets (gossans, alteration zones) of the geochemist. Total analysis is often the most effective approach in such cases.

An alternative to partial extraction as a method of suppressing background effects in stream sediment surveys can be provided by multi-element analysis. Rose and Suhr (1971) examined the partition of trace elements among mineral phases of stream sediments in Pennsylvania and found that the most important metal-bearing phases were vermiculite clay (Cu, Zn), iron oxides (Cu, Co, Ni, Zn), and mafic minerals in the sand and silt fraction. Quantitative effects on trace element values resulting from the variation in these major phases were effectively reduced by the application of regression techniques that used the major elements Fe, Mn, Ca, Al, and Mg as predictors of the trace elements. Regression of the values of individual trace elements against R-mode factor scores representing geological and environmental metal associations has also proved useful for background correction of data from varied terrains in Canada (Closs and Nichol, 1975) and Brazil (Meyer, 1977).

Heavy mineral concentrates are being used on a regional scale to mechanically eliminate the effects of dilution by rock-forming minerals. This sample medium greatly enhances anomalies for major metals in trace minerals when the trace minerals have a specific gravity of about 3 gm/cc or more and are resistant to chemical and mechanical destruction in the environment under study. The large initial sample size, often 5 kg or more, reduces sampling error, and the great concentration factor, usually three orders of magnitude or more before analysis, often brings the level of some of the rarer or analytically more difficult elements within easy reach of the analyst. Used in this way, heavy mineral concentrates have perhaps the longest recorded history in prospecting of all stream sediment techniques. Mercury prospecting with heavy mineral concentrates was reported by Theophrastus in about 300 B.C. (Hill, 1746). Application of modern, trace element analytical techniques to heavy mineral concentrates in search of trace minerals dates from at least the early 1950s (Overstreet, 1962), when concentrates from the southeastern United States were routinely screened by semiquantitative spectrographic methods. It is probable that these techniques were in use well before those used in the U.S.S.R. (Sigov, 1939).

Heavy mineral concentrates have been used more recently to upgrade analyses for trace constituents of rock-forming minerals. Magnetite (Theobald and Thompson, 1959a) and biotite (Theobald and Havens, 1960) were the first of these minerals investigated and are probably the most extensively known (see, for example, Parry and Nackowski, 1963, and Jacobs and Parry, 1976). The trace metal content of rock-forming minerals appears to define regional metallographic provinces rather than specific exploration targets,

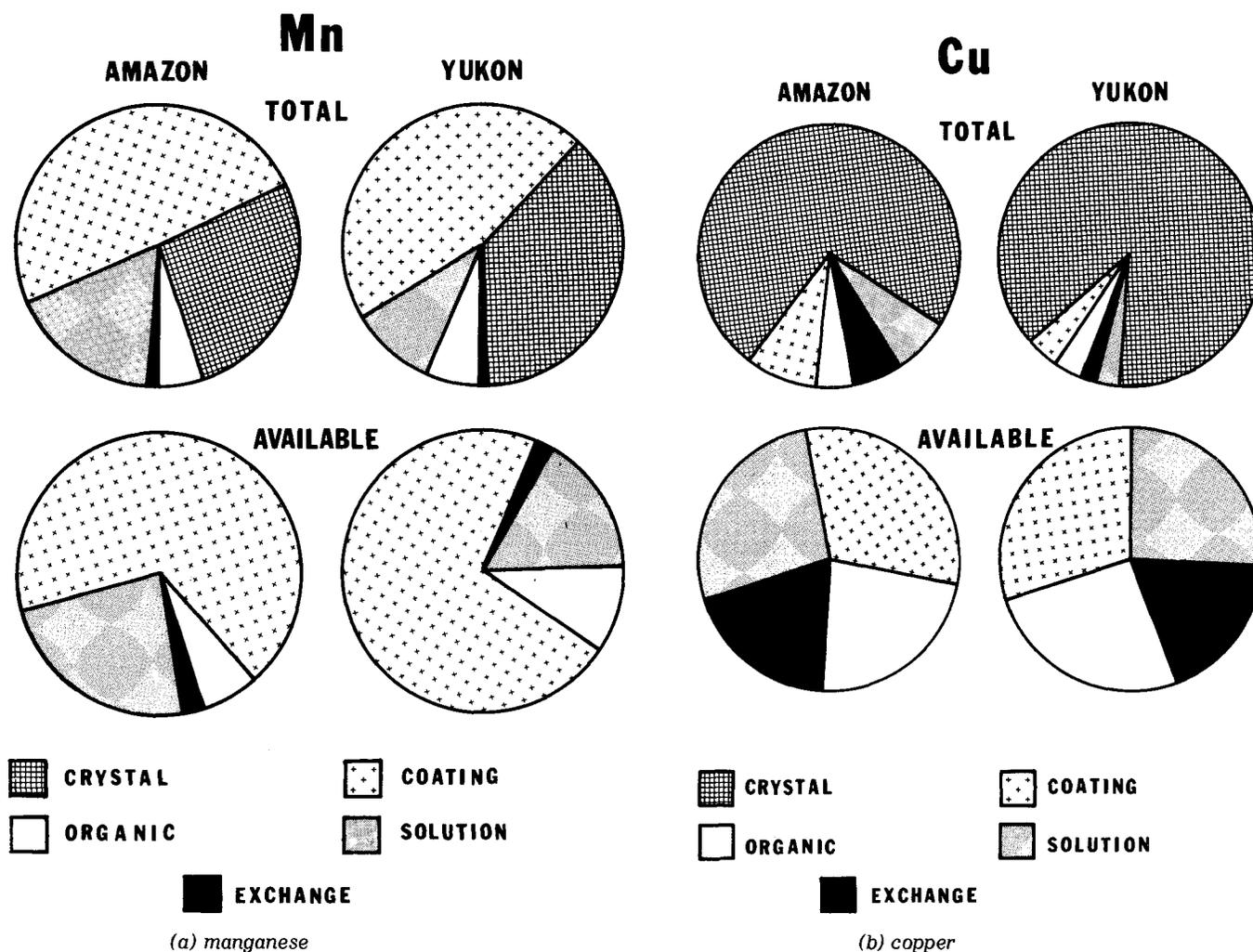


Figure 19.1. Forms in which transition metals are transported by the Amazon and Yukon rivers (after Gibbs, 1977).

hence the technique has been used more by academic or governmental organizations than by the exploration industry. In large virgin areas, multi-element analyses of magnetite concentrates from stream sediment have been used to identify areas most promising for exploration, thus eliminating from the first effort vast areas less likely to contain exploration targets (Theobald, P.K., and Thompson, C.E., unpubl. data).

Separation of the heavy mineral concentrate into several subsamples based on magnetic properties of the minerals leads to far greater enhancement of geochemical patterns than does the analysis of the bulk concentrate. Furthermore, this refinement of the heavy mineral technique often allows the separation of two or more geochemical patterns for a single trace element either in the primary or secondary dispersion of the elements. As shown in the early work on Clear Creek in Colorado, for example, the major part of the tungsten in the bulk concentrate is derived from sporadic scheelite occurrences associated with calc-silicate rocks (Theobald and Thompson, 1959b; Tweto, 1960). None of these are presently known to be economic. The smaller amount of tungsten in the concentrate derived from

huebnerite is from the upper zones of the major molybdenum deposits of the Urad-Henderson porphyry system. The two tungsten sources may be easily separated magnetically.

A more dramatic example is found in the work of Alminas et al. (see, for example, Alminas et al., 1972a, b, c) in southwestern New Mexico where the concentrates are routinely split into three fractions using a Frantz Isodynamic Separator¹: (1) minerals magnetic at 0.2 amp., (2) minerals magnetic between 0.2 and 1 amp., and (3) minerals not magnetic at 1 amp. The third fraction contains most of the common sulphide minerals of the area and direct pseudomorphic alteration products of these. The second fraction contains iron and manganese oxides precipitated from supergene solutions beyond the immediate environs of the deposits, either in host rocks or in post-ore cover. The anomalies are somewhat more subdued in the second than in the third fraction, but the targets are larger in areas where the host rocks are exposed, and frequently anomalies can be identified in areas of thick post-ore cover.

¹ Use of brand names in this report is for descriptive purposes only and does not constitute endorsement by the authors or their institutions.

2. Sorbed Material

Hydromorphic dispersion of metal ions derived from the oxidation of sulphide deposits or from the leaching of oxide ores can result in detectable enrichment of the fine fraction of stream sediments through adsorption of ions on colloidal particles, scavenging by secondary Fe and Mn oxides, ion-exchange reactions with clays, and adsorption and chelation with organic matter (Hawkes and Webb, 1962). Recent work by Hem (1976) has demonstrated the importance of the cation exchange capacity of the fine fraction of stream sediments in controlling the concentration of lead in stream waters. Depending on the cation exchange capacity of the sediment, it was shown that the major portion of ionic lead in river systems falling within the common pH span of 5.7 to 8.5 would be adsorbed on cation exchange sites in the sediment (Fig. 19.2). The high capacity of the fine fraction of stream sediments for metal ion adsorption has been the most important factor contributing to the widespread adoption of silt- and clay-size fractions as the optimum sample material in the search for hydromorphic anomalies. Cold-extractable analytical methods have been particularly useful in isolating the adsorbed metal phase from the fine fraction of sediments.

3. Hydroxide Coatings

In recent years, the ability of iron and manganese oxides to selectively scavenge certain metal ions from surface water has received considerable attention as a means of enhancing contrast between hydromorphic anomalies and background. Scavenging of heavy metals by secondary oxides can take place by any one or a combination of the following mechanisms: coprecipitation, adsorption, surface complex formation; ion exchange, and penetration of the crystal lattice (Chao and Theobald, 1976). Concentration of metals in stream sediments in this manner was demonstrated by Horsnail et al. (1969) in an area where the Eh and pH of groundwaters were substantially lower than those in the

Table 19.1

Extraction of zinc (ppm) from selected minerals using various acids (after Foster, 1971).

Mineral	HClO ₄	HCl	HCl- HNO ₃	HClO ₄ - HNO ₃	HNO ₃	25% HNO ₃	5% HNO ₃	HF- HClO ₄ - HNO ₃
Pyroxene	28	23	31	24	23	28	24	105
Limonite	290	290	285	218	84	58	25	285
Feldspar	8	10	10	8	9	11	11	9
Biotite	265	215	216	246	173	170	84	265
Amphibole	255	156	185	157	109	123	79	260

stream waters, resulting in precipitation of Mn and Fe oxides in the drainage channel. Canney (1966) had previously noted the relationship of enhanced metal values to ferromanganese accumulation, and had cautioned against the possible identification of spurious anomalies if the Fe and Mn scavenging effect was not taken into account during interpretation.

Whitney (1975) has shown that the prevalence and thickness of oxide coatings increases with increasing particle size, and this was also found to be true for suspended material in the Amazon and Yukon rivers (Gibbs, 1977). The presence of a thicker layer of hydroxides on large grains was made use of by Carpenter et al. (1975), who selectively analyzed the black coating of oxides found on stream boulders and pebbles downstream from base metal mineralization in Tennessee and Georgia. This study demonstrated that the anomaly-to-background ratio for base metals was considerably higher in the oxide coatings than in the minus-80-mesh sediment at the same site (Fig. 19.3a, b) for those base metals (Cu, Zn) concentrated in coatings, while minus-80-mesh sediments gave better results for Pb, which was not scavenged by Fe-Mn oxides. The selective scavenging of certain elements by Fe-Mn oxides has been documented by Nowlan (1976) in a multi-element correlation study of stream sediments and oxide coatings from Maine (Table 19.2).

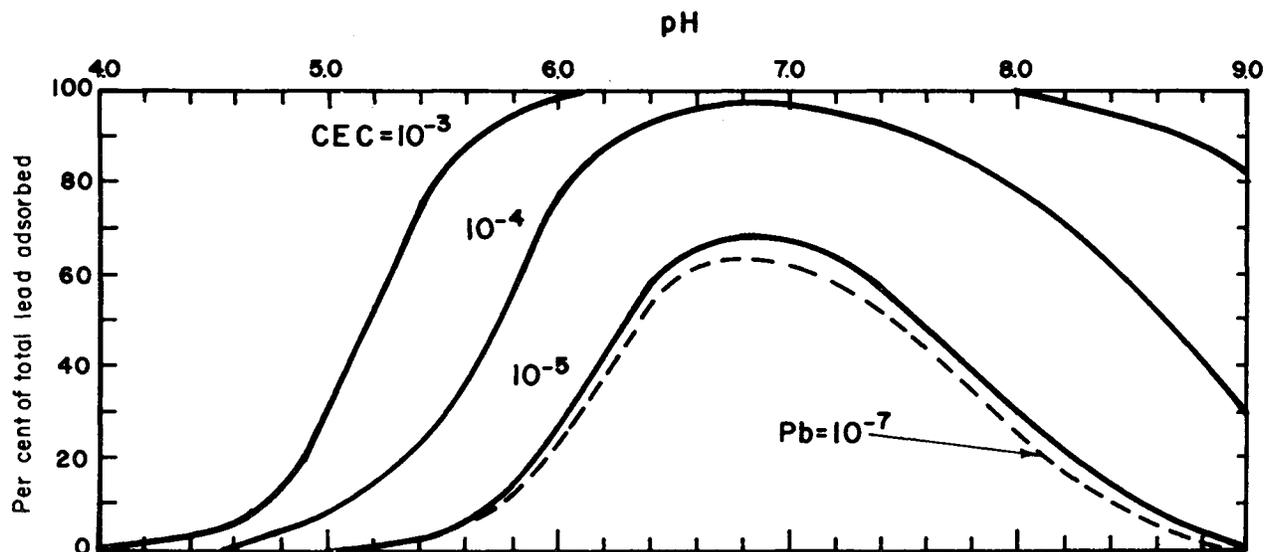


Figure 19.2. Percentage lead absorbed in water-sediment system as a function of pH and cation exchange capacity of sediment. Cation exchange capacity (CEC) indicated in moles/., $[Na^+] = 10^{-4}$, $[Ca^{2+}] = 10^{-4}$, total lead = 10^{-6} (after Hem, 1976).

Table 19.2

Results of investigation of selective scavenging of elements by Mn-Fe oxides in streams of Maine
(after Nowlan, 1976)

Elements not scavenged by oxides	Elements probably not scavenged by oxides	Elements scavenged weakly by oxides	Elements scavenged strongly by Mn oxides	Elements scavenged strongly by Fe oxides
B	Ag	Cu	Ba	As
Cr	Be	Mo	Cd	In
K	Ca	Pb	Co	-
Mg	Ga	Sr	Ni	-
Rb	La	-	Tl	-
Sc	Sb	-	Zn	-
Ti	Y	-	-	-
V	-	-	-	-
Zr	-	-	-	-

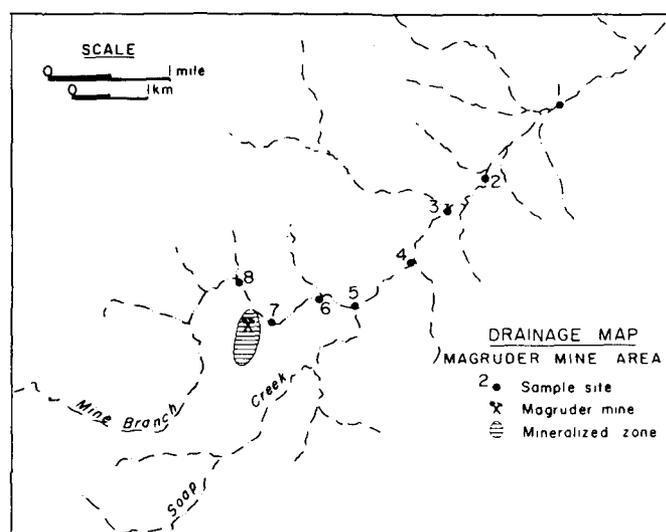


Figure 19.3a. Sample location map for Magruder Mine area, Georgia (after Carpenter et al., 1975).

Selective analysis of Fe and Mn oxides within the fine fraction of stream sediments has also been demonstrated to be efficient in base metal exploration. In a mineral resource assessment of the Tanacross quadrangle, Alaska, Foster et al. (1976) showed that an oxide-specific oxalic acid leach of minus-80-mesh sediment identified base metal occurrences more effectively than total analysis of minus-80-mesh sediment, analysis of heavy minerals, streambank sod, or aquatic bryophytes. Regardless of the size fraction considered, most studies have shown that anomalies are better defined by the ratios of the target metal to Mn or Fe, or to Mn and Fe together. This finding emphasizes the need for analysis of elements not directly related to the desired target in order to interpret the geochemical dispersion of the trace elements under study.

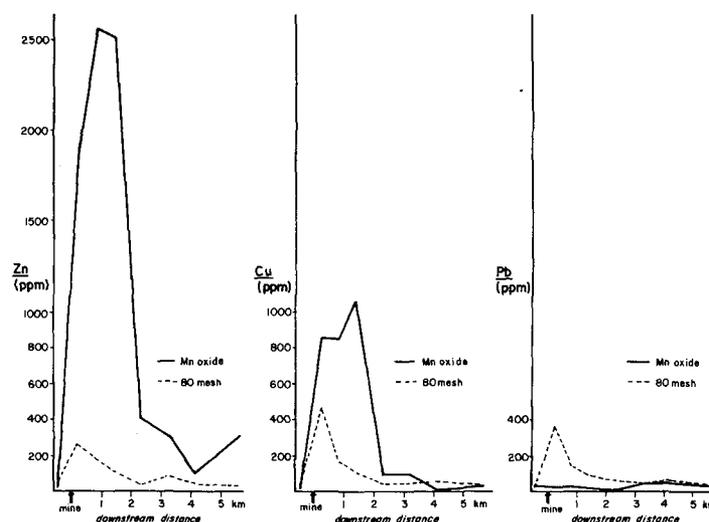


Figure 19.3b. Downstream dispersion for zinc, copper, and lead in minus-80-mesh stream sediments and oxide coatings, Magruder Mine area (after Carpenter et al., 1975).

4. Organic Material

Until recently, organic stream sediments have been carefully avoided in exploration sampling because of the difficulty of analysis and high variability of trace element content that result from the mixing of autochthonous and allochthonous organic matter in the stream bed. However, in cold regions of low relief, such as northern Scandinavia, inorganic stream sediments are not universally present, but organic matter tends to accumulate owing to the low rate of decomposition of vegetation. As a result, sampling and analysis of organic stream sediments has become the accepted mode of regional geochemical prospecting conducted by the Geological Survey of Sweden (Larsson, 1976); the method was adopted after extensive orientation studies were conducted by Brundin and Nairis (1972). Their interpretation of the multi-element analysis of the organic sediments employed multiple regression techniques to eliminate the effects of the environmental variables; content of organic matter, Fe, and Mn.

Table 19.3

Summary of causes of spurious stream sediment anomalies, southern Ontario (after Alther, 1975). Presence of elements are indicated by a cross

Element	Road	Fertilizers	Pesticides	Hogfood	Excreta	Automobile
Pb			X		X	X
Co			X	X	X	
Cu			X	X	X	
Ni			X		X	
Fe		X		X	X	
Mn		X		X	X	
Zn			X	X	X	
Mg				X	X	
Ca	X			X	X	
K		X		X	X	
Na	X			X	X	X

Seasonal Variations

In 1962, Hawkes and Webb indicated that only two studies on seasonal variation of stream sediment composition had been made: firstly, Govett (1958) showed a reduction in the cold extractable copper content of an anomalous stream during the wet season in Zambia; and secondly, a study by Gower and Barr in British Columbia indicated no significant variation in the cold extractable or total copper content within a four-month period in the summer. Most stream sediment surveys are conducted on the assumption that seasonal variation is minimal, but with the current interest in selective analysis of the Fe-Mn oxides this approach may require reconsideration. In a study conducted in Wales, Fanta (1972) determined that seasonal effects were noticeable in those elements subject to coprecipitation by Fe and Mn oxides, indicating that the precipitate phase of the stream sediment was in a state of delicate balance with the chemistry of the stream and the groundwater.

Recent studies in Goias, Central Brazil (Thomson, 1976) have shown no significant variation in the aqua regia and EDTA soluble Cu and Ni content of minus-80-mesh stream sediments collected downstream from the Americano do Brazil Cu-Ni sulphide prospect at the beginning, middle and end of the rainy season. In the contrasting glaciated environment of northwest Maine, Chork (1977) has shown that nitric acid soluble Cu, Pb, Zn, Co, Ni, Mn, and Fe vary only slightly with the seasons, and should not be of concern in routine stream sediment surveys.

Contamination

By definition, the environment will have been polluted to a greater or lesser degree wherever man has been (Webb, 1975). Contamination is a serious problem in geochemical surveys of heavily industrialized countries or areas with a long mining history. This problem has been brought to the fore by the results of a multi-element regional stream sediment survey of England and Wales carried out by the Applied Geochemistry Research Group at Imperial College, London. As an example, this study showed that the high concentration of arsenic in stream sediments from southwest England (Webb, 1975) was derived from the mining and processing of the arsenic-rich tin and base metal ores of the region, where active lode mining has been carried on since the Middle Ages. As yet, no simple method of applying stream

sediment sampling in polluted areas has been developed; therefore, effective exploration in these areas involves time consuming detailed documentation of source areas of potential pollution, often requiring examination of historical mining and industrial records.

Hosking (1971) has provided an excellent review of sources of contamination of drainage due to mining, agricultural, industrial and domestic sources in southwest England. He reports, for instance, that minus-80-mesh stream sediments downstream from the town of Truro contain 400 ppm copper and 600 ppm zinc in an unmineralized area; and that values of 150 to 3000 ppm lead occur in stream sediments for 5 miles below the abandoned mill of the Pengenna mine in northeast Cornwall. While contamination of this degree can be readily recognized, many less spectacular forms of pollution exist in

the vicinity of populated and agricultural areas, and the systematic documentation of these forms would facilitate identification of spurious stream sediment anomalies. One case of agricultural pollution has been documented by Alther (1975). This study of recent contamination due to pig farming in southern Ontario identified enhancement of metal values in stream sediments due to a variety of source materials (Table 19.3).

Spurious anomalies are not always due to human activity. A high content of tin in minus-80-mesh stream sediments (as much as 10 000 ppm, see Fig. 19.4a, 19.4b) from an area in southwest England not known to be mineralized was later traced to redistribution of cassiterite from centres of tin mineralization along shorelines of late Miocene-Pliocene age, presently preserved at an elevation of 400-500 feet (Dunlop and Meyer, 1973).

SAMPLING

Stream sediment geochemistry takes a number of different forms depending on the aim of the survey, and the regional or local constraints of physiography and climate which together make up the landscape. The conventional use of stream sediment surveys to detect anomalous dispersion trains downstream from individual mineral deposits is still the prime mode of application undertaken by most in the mineral exploration industry, but the effectiveness of stream sediment as a sampling medium has led to a broadening of the aims of geochemical reconnaissance to include agricultural, geological, and pollution studies (Webb et al., 1968). The design of stream sediment sampling programs has been influenced by this tendency towards generalization, which is most pronounced in government survey programs that require broad-scale resource assessment, and this factor will be considered in the following sections along with specific programs that have single mineral deposits as the principal target.

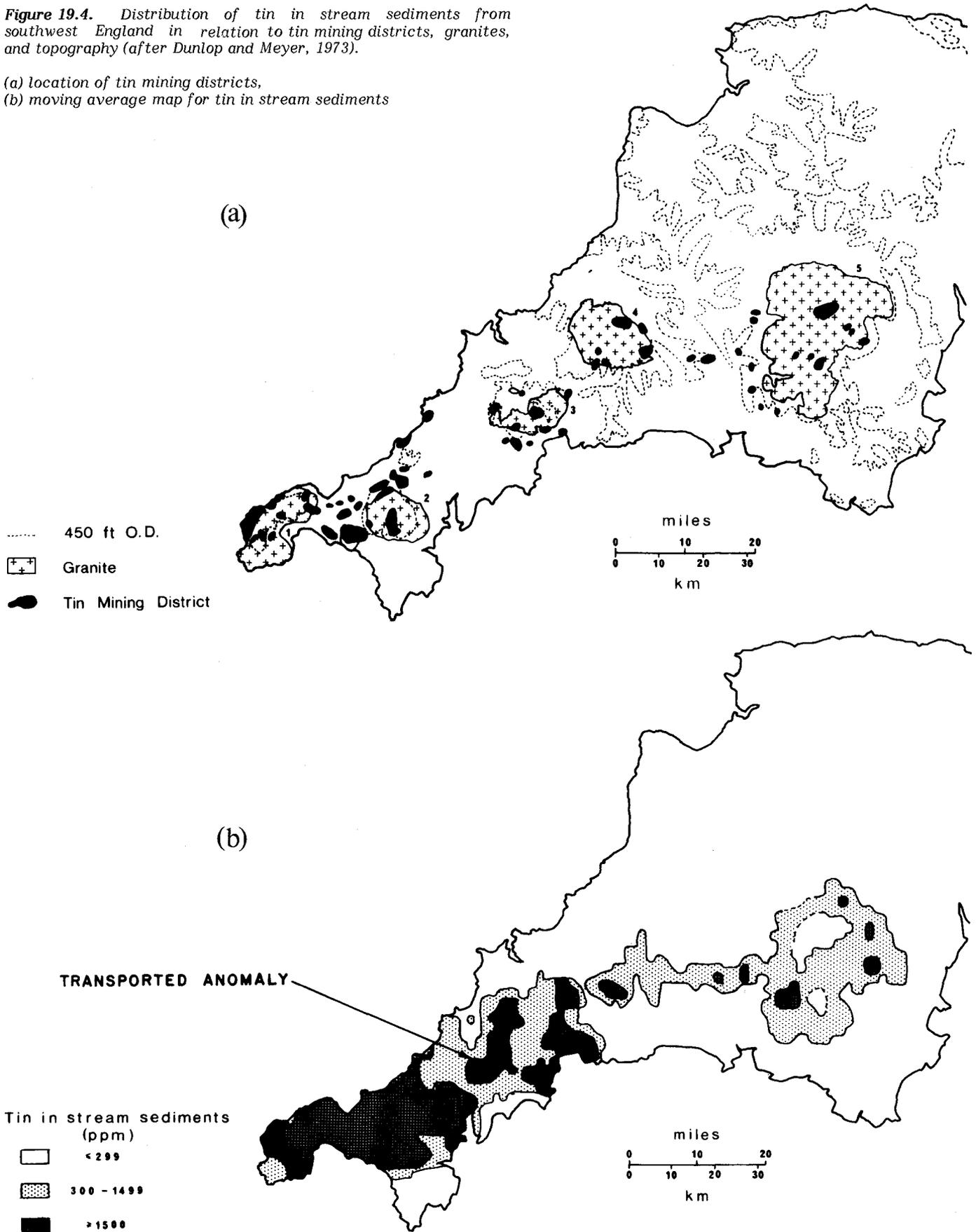
Types of Survey

Low Density Surveys

Widely spaced stream sediment sampling for the detection of metallogenic provinces in relatively unexplored regions has been demonstrated to be an effective method of delineating broad regions of mineral potential (Garrett and Nichol, 1967; Armour-Brown and Nichol, 1970). The aim of

Figure 19.4. Distribution of tin in stream sediments from southwest England in relation to tin mining districts, granites, and topography (after Dunlop and Meyer, 1973).

(a) location of tin mining districts,
 (b) moving average map for tin in stream sediments



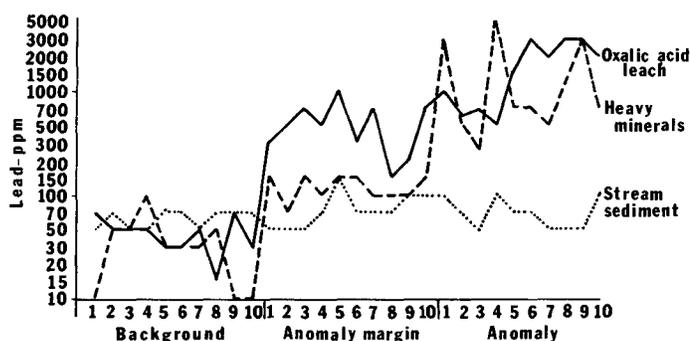


Figure 19.5. Comparison of the lead content of minus-80-mesh stream sediment, the iron-oxide-rich fraction of heavy mineral concentrates, and oxide residue of oxalic acid leachates from minus-80-mesh stream sediment over a suspected buried mineral deposit in the southern San Mateo Mountains, New Mexico. Data contributed by H.V. Alminas and K.C. Watts, U.S. Geological Survey.

this type of survey is not to identify discrete areas of mineralization, but to outline major belts or regions which may warrant further exploration by reconnaissance methods. Sampling density is generally within the range of one sample per 100 to 250 km², over areas of 30 000 to 50 000 km² or greater, although one survey reached continental proportions when a mining company sampled the total area of Australia amenable to drainage sampling (Duff, 1975). Multi-element analysis is the rule in low density surveys because it maximizes the usefulness of samples obtained at high cost per sample and covers the range of mineralization which can be expected within the area covered. Changes in climate, topography, and broad scale geology, which are inevitable in surveys of this size, can be recognized geochemically by use of statistical methods such as R-mode (Armour-Brown and Nichol, 1970) and Q-mode factor analysis. Both of these techniques were applied by Galbraith (1975) in a research study of an area of 36 000 km² in Bahia, Brazil, which delineated geochemical belts or districts on the basis of Cu, Zn, Co, Cr, Ni, Mn, and Ag analysis of samples collected at a density of one sample per 80 to 100 km². He concluded that Q-mode was superior to R-mode factor analysis in the classification of sediment samples related to chromite mineralization in this area. Also in Brazil, a 10-element, 400 000 km², survey over parts of the states of Goias and Minas Gerais has been carried out at a density of approximately one sample per 115 km² by Citco International Minerals Company (W.T. Meyer, unpubl. data).

Regional Reconnaissance

Stream sediment geochemistry excels as an exploration tool in low cost reconnaissance prospecting of large areas for indications of individual mineral deposits, groups of occurrences, or favourable geological environments. Sampling density ranges from one sample per 1 km² to one per 25 km², depending on type of target and drainage characteristics, and inherent in the reconnaissance concept is the need for more detailed sampling to determine the significance of regional anomalies. Much of the exploration and resource assessment carried out by governmental and intergovernmental agencies falls into this category, as does mining company exploration of large concessions and areas being considered for acquisition.

An example of this type of survey currently underway in the United States is the National Uranium Resource Evaluation (NURE) Program, which aims to systematically sample water and sediment collected from streams, lakes,

and wells in order to identify all favourable uranium exploration areas in the United States by 1980 (Dahlem, 1976). Data generated by a program of this scale (a 1977 budget of \$6.1 million was reported by Larson, 1977) could also have a significant impact on exploration for other targets, as the multi-element analytical data from samples collected at an average density of one sample per 10 km² will be made available to industry. One interesting conclusion from orientation surveys carried out in the southern Appalachians prior to NURE sampling was that the minus-100-mesh stream-bottom sediment gave the same or better information than water or suspended solids, was cheaper to collect and analyze, and presented fewer analytical problems (Ferguson and Price, 1976). The conclusion that stream sediments were preferable to water for reconnaissance drainage surveys for uranium was also reached by Rose and Keith (1976) for eastern Pennsylvania. Also within the United States, reconnaissance geochemistry at a density of one sample per 20 km² formed an important part of a survey of the Tanacross quadrangle, Alaska, conducted within the Alaskan Mineral Resource Assessment Program (Foster et al., 1976). This study did not rely on sampling and analysis of the fine fraction of stream sediment alone, but also examined the distribution of trace and major elements in heavy mineral concentrates, stream-bank-sod, aquatic bryophytes, and the soluble oxide fraction of the minus-80-mesh sediment. Results of this survey demonstrated that no one sampling medium or analytical method was effective for all elements in both maturely dissected terrain and mountainous parts of the quadrangle. In the maturely dissected area where hydromorphic dispersion is pronounced, an oxide-selective leach of minus-80-mesh sediment was the most effective medium for locating base metal occurrences, while heavy mineral concentrates were best for detecting tin and tungsten mineralization. Conventional minus-80-mesh stream sediments and heavy mineral concentrates were found to be the most suitable sample media for exploration in the Alaska range, where mechanical weathering is the prevalent destructive process.

A comparison of three of the commonly employed stream sediment techniques is presented in Figure 19.5. In this particular example, a buried, mineralized area in the San Mateo Mountains of New Mexico, the traditional minus-80-mesh stream sediment shows practically no contrast. Over a background of 30 to 50 ppm lead, the maximum value is only 100 ppm. The intermediate-magnetic fraction of the heavy mineral concentrate has a background of 10 to 70 ppm lead, but provides a well defined peripheral zone at 70 to 100 ppm and a distinct, large anomaly of 150 to 5000 ppm lead. This anomaly is attributed to transported, detrital, supergene iron and manganese oxides. The fraction of the sediment soluble in oxalic acid, dominated by iron and manganese oxides but including both the detrital oxides and those precipitated on the sand grains after hydromorphic transport, produces a much broader anomaly. Over a background of 10 to 50 ppm, the intermediate zone is 100 to 700 ppm, and the anomalous zone is 300 to 3000 ppm.

In Canada, more than 90 per cent of the current stream sediment sampling activity of the Geological Survey of Canada is related to the Federal-Provincial Uranium Reconnaissance Program, which commenced in 1975 (R.G. Garrett, pers. comm.). While lake sediments and waters have been adopted as the preferred sampling media in the Canadian Shield (Cameron, 1976), stream sediment sampling was conducted over an area of 75 000 km² in southern British Columbia and the Yukon in 1976. The British Columbia portion of the program covered 46 800 km² at a mean density of one sample per 13 km² (Smee and Ballantyne, 1976), and in the Yukon 2200 stations were sampled over an area of 28 490 km², giving the same degree of coverage. In each

case, the stream sediments were being submitted for multi-element analysis in addition to the uranium determinations required to fulfill the primary goal of the surveys. Gleeson and Brummer (1976) have recently described a regional stream sediment survey carried out in 1970 and 1971 by Occidental Minerals Corporation of Canada over an area of 64 750 km² in the southwestern part of the Yukon Territory. This survey was designed to detect porphyry copper-molybdenum deposits by means of copper, zinc, and molybdenum analysis on the minus-80-mesh fraction of stream sediments collected at a mean density of approximately one sample per 5 km². Moving average smoothing proved to be useful in correlating geochemical patterns with the regional lithology, and automatically plotted residual metal maps were used to define specific follow-up targets.

The first countrywide multi-element regional stream sediment program to be undertaken in the United Kingdom was the survey of Northern Ireland carried out by the Applied Geochemistry Research Group (AGRG) at Imperial College, London, in 1967 (Webb et al., 1973). Nearly 5000 samples, collected at a density of one sample per square mile (one per 2.6 km²) were analyzed for this study. AGRG then sampled England and Wales at the same density in 1969 (Webb, 1975), and collected more than 50 000 samples which have provided the basic data for graduate research on mineral exploration applications (Urquidí-Barrau, 1973; Cruzat, 1973; and Dunlop, 1973), regional geochemistry (Holmes, 1975), data processing, and agricultural and environmental pollution. Regional geochemical sampling by the Institute of Geological Sciences (IGS) commenced in Scotland in 1968. Then, in 1972, under a more detailed mineral reconnaissance program sponsored by the Department of Trade and Industry, stream sediment samples were collected at a density of one per 1.5 km² from an area of 1600 km² in central Wales (Ball and Nutt, 1974). In Scotland, sediments are taken 0.3 m below the stream surface in order to minimize the effects of Fe and Mn oxides. Samples are wet-sieved to <150 microns (minus-100-mesh) and a split is sent for U analysis by delayed neutron activation, while the remainder of the sample is analyzed by atomic absorption and direct-reading emission spectrography. A major long-term project is the compilation of regional geochemical maps made up of raw data plotted at the sample points using a radiating system of vectors, whose azimuth identifies the element and whose length indicates the concentration. Mineral industry regional surveys in the United Kingdom and Ireland naturally cover less area than comparable programs in other part of the world; a typical regional exploration program in Ireland might cover an area of 1300 km² (Horsnail, 1975), with stream sediment samples collected at a density of one sample per 0.85 km².

Regional geochemical surveys of the Precambrian Shield areas of northern Sweden are based on the collection of organic stream sediment samples, supplemented by the sampling of heavy minerals in till. In 1975, a total of 22 000 organic stream sediments were collected. Larsson (1976) has described the results of a survey in the Pajola district, in which more than 10 000 organic sediments were collected from an area of 8000 km². Multi-element analysis of the ashed samples by X-ray fluorescence and emission spectrography was successful in outlining all previously known base metal occurrences in addition to 40 prospective target areas. In southern Norway, regional stream sediment sampling at road-stream intersections has been described by Bjorlykke et al. (1973) of the Geological Survey of Norway. Wet sieving of stream sediments to minus-80-mesh has been adopted by the Norwegian Survey. While this practice results in loss of some fine material in suspension, it eliminates collecting and shipping large quantities of sample (Bolvikén et al., 1976). Both organic and inorganic sediments are collected at an average density of one sample per 1.5 km² during regional surveys by the Geological Survey of Finland.

Analysis is by atomic absorption for Co, Cu, Ni, Pb, Zn, Mn, and Cr (Kauranne, 1975). From 1971 to 1974, a total of 23 179 inorganic and 34 942 organic stream sediments were collected. In 1975 alone, the Finnish Geological Survey collected 9500 organic and 7300 mineral stream sediments, and 1500 organic lake sediments—a grand total of 18 400 samples which together cover an area of 23 000 km² (L.K. Kauranne, pers. comm.).

Geochemical surveys in France are conducted by Bureau de Recherches Géologiques et Minières (BRGM) for base metals, and by Commissariat à l'Énergie Atomique for uranium. More emphasis is placed on water sampling than stream sediments in the search for uranium, a practice that is also followed by the I.G.S. (Ostle et al., 1972) in the United Kingdom.

Regional stream sediment reconnaissance is actively carried out by most government agencies and mining companies in Central and South America. As an example, a description of geochemical reconnaissance studies carried out in Goiás, Brazil, during the pilot phase of the Projeto Geofísico Brasil-Canada has recently been published (Thomson, 1976). The results of these investigations determined the survey parameters for a regional reconnaissance of the State of Goiás, which is being undertaken at a density of one sample per 10 km² with all samples collected from tributary drainages with catchment areas of less than 25 km². Eight elements are being determined by atomic absorption analysis of the portion of the minus-80-mesh fraction that can be extracted using aqua regia. Exploration companies such as Docege also use regional geochemistry extensively, as do State mining companies such as Metago (Goiás) and CPBM (Bahia). Multi-element regional reconnaissance (one sample per 8-10 km²) surveys are carried out by Brazilian subsidiaries of international mining companies (Meyer, 1977). In central Guyana, geochemical reconnaissance was undertaken by the Guyana Geological Survey as part of the Potaro-Mazaruni Project, in which 3000 samples were collected from an area of 6000 km² (Gibbs, 1974). Semiquantitative optical emission spectrography was used as the analytical method in this study.

In Africa, regional and provincial scale geochemical mapping is employed by geologists of the Geological Survey of Zambia engaged in systematic geological mapping. Sample density depends on the scale of mapping, and analyses are for 20 elements by semiquantitative X-ray fluorescence techniques. In Rhodesia, the Institute of Mining Research at the University of Rhodesia has been active in regional geochemical research projects since it was founded in 1969. Recent studies by the Institute include a regional stream sediment reconnaissance of 1350 km² of the Sabi Tribal Trust Land at a density of one sample per km² (Topping, 1976), and a survey of 1664 km² near West Nicholson, Rhodesia, at the same density (Mayfield, 1976). Multi-element analysis was applied in both cases. Most mining companies in southern Africa devote a greater effort to regional soil sampling than to drainage reconnaissance, and Buhlmann et al. (1975) estimated that more than 95 per cent of the samples collected by the major companies in 1973 were taken from soil grids.

A recent survey of stream sediment sampling programs by government agencies in Australia (C.R.M. Butt, pers. comm.) has shown a low level of activity. Only 4250 stream sediments were collected in 1976 and the number is expected to decline in 1977. Government agencies in Australia do not engage in direct exploration, although they occasionally conduct regional or detailed local orientation studies. However, most mineral exploration companies in Australia make regular use of regional stream sediment sampling in the more favourable humid zones; stream sediments are of

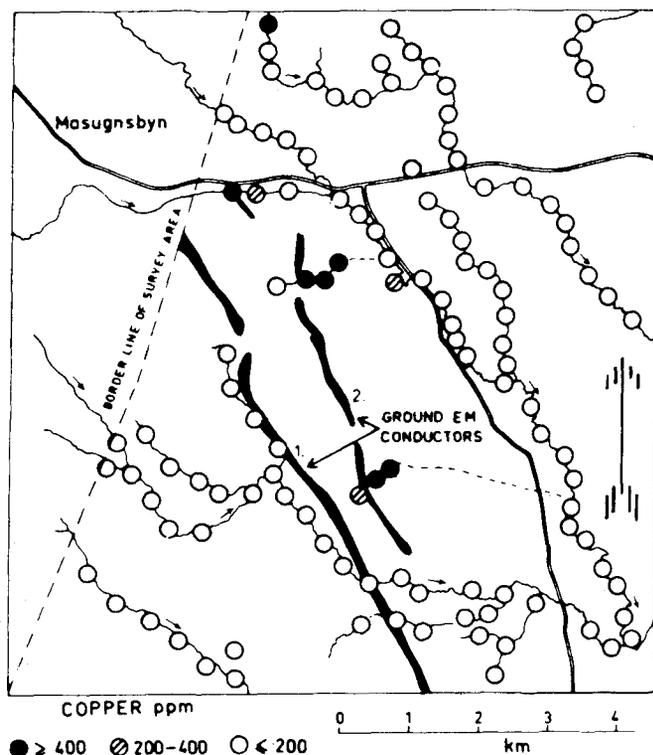


Figure 19.6. Copper content of organic stream sediments in relation to ground electromagnetic conductors, Pajala district, northern Sweden (after Larsson, 1976).

limited use in the more arid areas due to low density of drainage and dilution by wind-blown material. One approach in arid areas has been to use two size fractions, minus-120-mesh and minus-4-plus-16-mesh. The coarse fraction in such studies generally contains gossan fragments and multiple grains cemented by metal-rich iron hydroxides.

Stream sediment surveys have been particularly successful in the Pacific islands of New Guinea, Fiji, Indonesia, and the Philippines in the search for porphyry copper deposits. In Fiji, Leggo (1976) reported the discovery of two porphyry systems on the basis of stream sediment sampling at a density of 2.4 samples per km², with the analysis for Cu, Pb, Zn, and citrate-extractable Cu. The dispersion train from these deposits would have provided two or three anomalous samples if a sampling interval of 1 km had been used. The success of stream sediment surveys in the tropical islands of the Pacific can also be demonstrated by the experience of the Australian exploration company, Conzinc Riotinto of Australia Exploration (CRAE). From 1964 and into the 1970s, CRAE conducted stream-sediment surveys in New Guinea and the Solomon Island chain which resulted in drilling of nine porphyry targets, one of which developed into the highly profitable Panguna mine (MacKenzie, 1977). At Panguna, a weak anomaly could still be recognized 28 km downstream. In almost all cases exploration in this environment has been based on analysis of the minus-80-mesh fraction.

The United Nations Development Program (UNDP) often uses regional stream sediment surveys in its mineral exploration programs in a wide variety of environments. According to Brand (1972), a review of all reconnaissance methods employed by the UNDP indicated that geochemical surveys had been more rewarding than airborne geophysics as prospecting aids to basic geological programs. Among the

notable exploration successes attributed to UN stream sediment surveys are the discoveries of the Mamut deposit in Malaysia, Cerro Petaquilla in Panama, and Chau-Cha in Ecuador – all three are porphyry-copper type deposits.

Detailed Surveys

Detailed stream sediment surveys form the logical sequel to reconnaissance sampling after delineation of regional anomalies; they may be the first phase of exploration in established mining districts; and they are a tool for investigation of targets outlined by geological, geophysical or remote sensing studies. The techniques applied in detailed minus-80-mesh stream sediment sampling are essentially the same as those reviewed in the section on regional reconnaissance. The sampling interval is different, of course, and the detailed surveys can make use of seepage samples, bank sediments, and spring precipitates wherever local drainage conditions permit.

In the shield environment of northern Sweden, where organic sediments are collected in the reconnaissance stage of exploration, Larsson (1976) has described a follow-up technique that makes use of bog-margin samples. An organic stream sediment anomaly for copper (Fig. 19.6) was found to be associated with one of a pair of adjacent electromagnetic conductors, originally considered to represent graphitic horizons within greenstones in the Pajala deposit. Follow-up investigations took the form of sampling along the shallow margins of local bogs (usually less than 0.5 m in depth) in order to detect the enhanced metal content derived from adsorption of metals from groundwater in contact with mineralization. The results of the bog-margin survey confirmed the association of copper with the eastern band of conductors (Fig. 19.7), as copper content of the organic material exceeded 1 per cent close to the geophysical target. This follow-up procedure has the advantage in far northern latitudes of being suitable for winter sampling, and could find wider application in similar terrain.

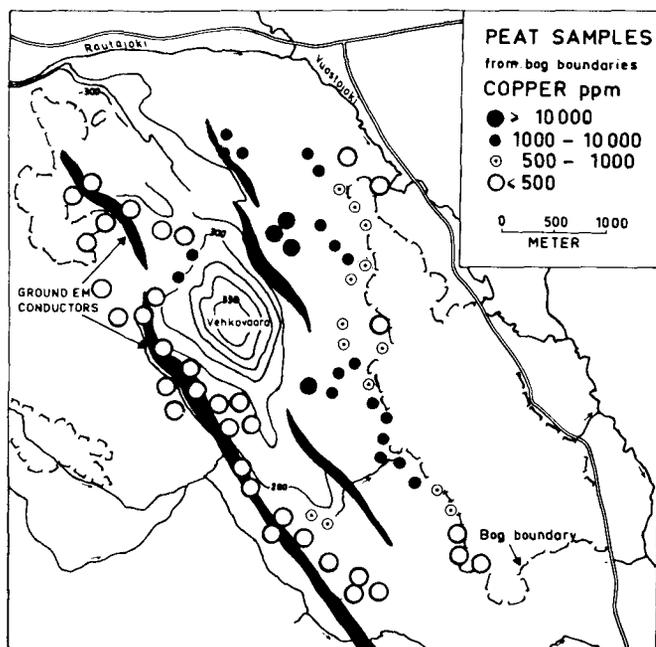


Figure 19.7. Copper in follow-up peat samples from bog margins, Pajala district, northern Sweden (after Larsson, 1976).

A good example of conventional detailed follow-up of a stream sediment anomaly can be found in the investigations of a lead anomaly identified during regional sampling at one sample per 2 km² in southern Norway (Bolviken, 1976). The regional anomaly near Snertingdal was detected in samples containing 160 and 130 ppm Pb (Fig. 19.8); subsequent detailed sampling of the drainage system at 100-m intervals outlined an area of interest of about 5 km², with peak values in excess of 300 ppm. Systematic soil sampling of the favourable area then served to delineate the target area which was found to be related to a 2 km-long mineralized zone of subeconomic disseminated sulphides (Fig. 19.9).

The benefits of sampling seepage areas in the course of detailed sampling are well demonstrated by the dispersion of copper, molybdenum, and zinc in drainage sediments from the Huckleberry Cu-Mo deposit, British Columbia (Sutherland-Brown, 1975). Significantly higher metal values were generally found in seepages when compared with adjacent stream sediments, and copper seepage values exceeded 1500 ppm in close proximity to the mineralization (Fig. 19.10).

Orientation Surveys

Stream sediment orientation surveys are an essential but often neglected operation used in mineral exploration to establish the field and laboratory parameters that maximize the difference between anomaly and background, and provide the data on which to determine a safe sampling interval for detection of the anomalous dispersion train. The most common type of orientation study takes the form of detailed sampling downstream from a known deposit, preferably one which has not been disturbed by mining operations. It is seldom possible to find a suitable undisturbed deposit within the same physiographic and geologic province as the reconnaissance area and, as a result, it is often necessary to accept the compromise of conducting the orientation on a geologically favourable target which has been disturbed to some extent.

An example of this type of orientation survey can be found in a comparative sampling study conducted on the Caridad porphyry copper deposit, in the semi-arid northwest part of the state of Sonora, Mexico (Chaffee et al., 1976). The Caridad deposit was discovered as a result of a

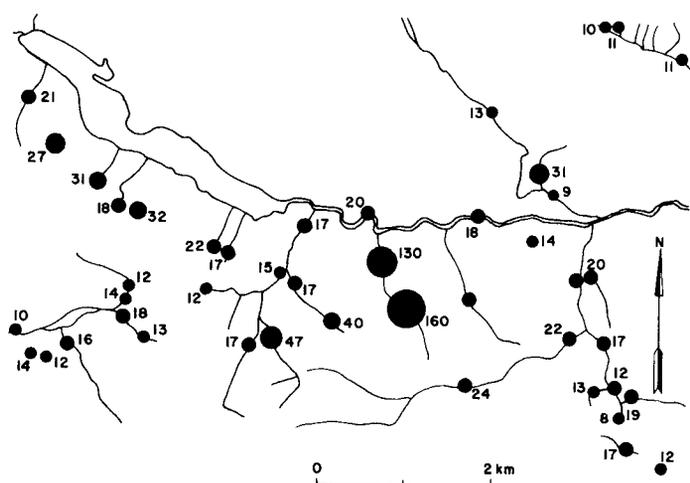


Figure 19.8. Lead content (in ppm) of stream sediments collected at road-stream intersections, Snertingdal area, southern Norway. Area of solid circle is proportional to lead content at each locality (after Bolviken, 1976).

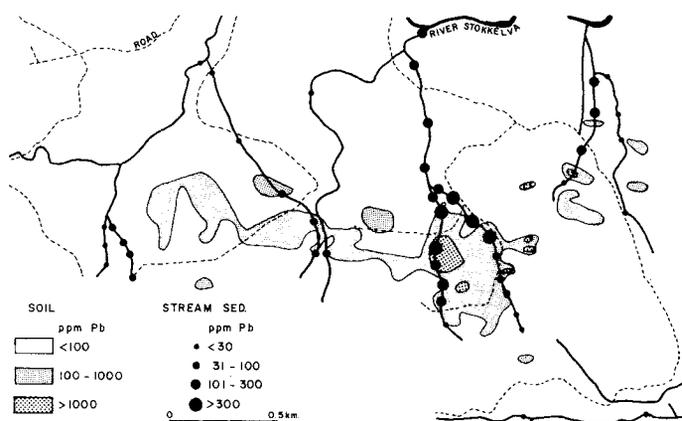


Figure 19.9. Results of detailed follow-up stream sediment and soil sampling of the Snertingdal lead anomaly, southern Norway (after Bolviken, 1976).

reconnaissance stream sediment survey which detected an anomaly 19 km downstream from the mineralized area, but the abandoned small workings in the area may have influenced the size of the anomaly. As part of this pilot study, minus-0.25 mm (minus-60-mesh) stream sediment, heavy mineral concentrates, and trees from arroyos near to and downstream from the deposit were sampled and then analyzed by spectrographic and wet chemical methods for as many as 37 elements. The aim of the study was to determine: (1) which elements other than copper might produce downstream anomalies; (2) the maximum distance at which the deposit could be detected by any sample type; (3) the sample types that would be most effective in revealing the presence of the deposit; and (4) which of the two types of copper analyses, partial or total extraction, would be most effective. Results showed that the porphyry copper deposit at Caridad produced anomalies in stream sediments, heavy mineral concentrates, and two plant species, but that stream sediments gave more useful information than the other sample types investigated. Significant anomalies were detected in molybdenum, zinc, silver, and tungsten in addition to copper. Molybdenum in stream sediments was found to give the longest detectable dispersion train, which extended at least 32 km (Fig. 19.11). Little difference was found between the use of total or cold-extractable copper as a method of locating the Caridad deposit.

Orientation sampling that precedes a regional multi-element survey must be designed to accommodate the aims of the intended survey, i.e. mineral exploration, for a wide variety of targets or multi-purpose geochemical mapping. A good example of an orientation study for a regional geochemical survey is provided by Plant (1971), who studied an area in northern Scotland. She found that grinding of minus-100-mesh stream sediment and collection of samples from second- or third-order streams improved the overall precision, which was a mapping requirement in this area of low geochemical background. Geochemical "noise" produced by coprecipitation of metals with hydrous iron and manganese oxides was reduced by: (1) removal of the fine fraction prior to analysis; (2) grinding of samples; (3) collection of samples beneath the sediment-water interface; and (4) collection of samples from streams greater than first order. This study demonstrates the conflicting requirements of single-target mineral exploration surveys and regional geochemical mapping: an exploration survey for Fe-Mn oxide minerals would seek to amplify the very "noise" that Plant's study tried to minimize, and therefore sampling methods would be completely different.

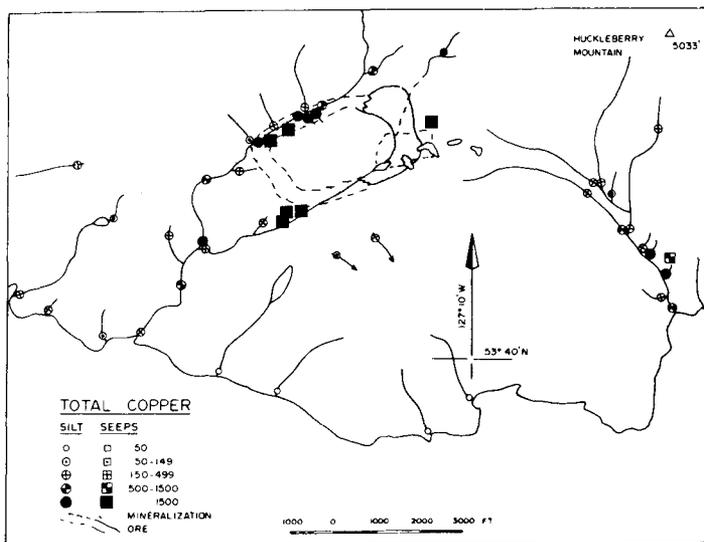


Figure 19.10. Copper in stream sediments and seepages, Huckleberry Cu-Mo deposit, British Columbia (after Sutherland-Brown, 1975).

Large-scale pilot studies are conducted in advance of country wide regional surveys, or where comparisons between new and established methods are required prior to acceptance of modifications of sampling or analytical techniques. The extensive pilot studies recently conducted as part of the Projeto Geofísico Brasil-Canada (PGBC) provided data which facilitated the selection of optimum techniques for both reconnaissance and detailed surveys. This information was obtained through specific orientation studies around known mineral deposits, and the reconnaissance sampling of five relatively large pilot areas (approximately 2500 km² each) at a density of 1 sample per 7-10 km². The study established the validity of stream-sediment sampling in a tropical environment, provided training of survey personnel, and established procedures for systematic sampling of a much larger area (Thomson, 1976). Another pilot study in northern Sweden (Brundin and Nairis, 1972) sampled both organic and inorganic sediments over an area of 400 km² to test the usefulness of organic material in stream sediment surveys.

Field Methods

As alternate sample types and multi-purpose surveys have developed, a greater need has evolved for optimizing sampling design. Miesch (1976) has thoroughly reviewed the statistical basis for optimization of geochemical sampling in general. For practical purposes current stream sediment sampling procedures seldom conform to the unbiased minimum sampling error configuration of the ideal sampling design. Nevertheless, a number of studies of sampling error and survey design (Bolviken and Sinding-Larson, 1973; Howarth and Lowenstein, 1971; Duff, 1975; Sharp and Jones, 1975; and Hawkes, 1976b) have demonstrated a trend towards a more systematic approach to the implementation of stream sediment surveys based on a quantitative assessment of various sampling criteria. In the context of field methods, the present state of the art encompasses the extremes of

haphazard sampling without prior planning, and carefully executed systematic surveys designed to achieve a well conceived goal. Some of the current survey techniques and planning consideration are reviewed in the following sections.

Selection of Sample Sites

While orientation surveys often establish the sampling interval required to obtain at least one or two samples from an anomalous dispersion train, other factors help determine the overall sample spacing for regional surveys. Also considered are the completeness of coverage required, logistics, and the total cost allowed for the survey. Most mining company exploration programs tend to err on the side of caution as far as sample density is concerned, based on the valid assumption that a greater sampling density reduces the probability of missing a mineral deposit. Logistics play an important role in setting sample spacing, particularly if the survey takes place in an area of poor access where labour and transportation costs are high. In this case, the prudent policy requires collection of samples with a closer spacing than that estimated from an orientation survey, even if some samples are not analyzed initially. Evidence of an anomaly can then be verified and more closely defined by analysis of the additional samples without undergoing the expensive alternative of a return to the field area, a practice which can prove particularly important in areas having short periods of access governed by local weather conditions. On the other hand, where access is simplified by the presence of an adequate network of roads crossing the drainage system, the reduction of sampling cost that results through sampling road-stream intersections can provide the overriding factor in determining sample spacing. This was the case in the regional

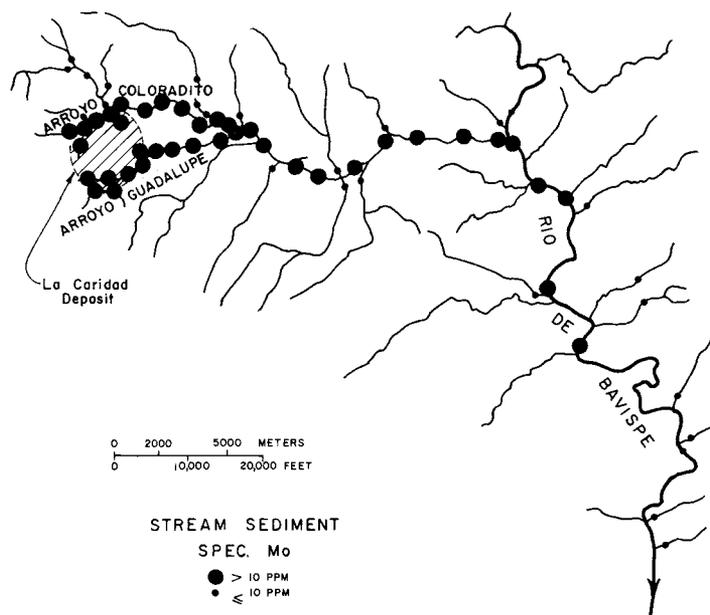


Figure 19.11. Distribution of molybdenum (emission spectrographic analysis) in stream sediments draining the Caridad porphyry copper deposit, Sonora, Mexico (after Chaffee et al., 1976).

sampling undertaken for the Geochemical Atlas of England and Wales (Webb, 1975) and in a reconnaissance survey of 3000 km² in southern Norway (Bolviken and Sindig-Larson, 1973).

In order to quantify the effects of dilution of an anomalous dispersion train and thereby provide a sound basis for establishing sample spacing, and as an aid in interpretation, Hawkes (1976b, c) has developed an empirical formula to relate the composition of sediment samples to the size of the catchment area and the size and grade of the surface expression of the mineralization causing the anomaly. The formula is expressed as:

$$Me_m A_m = A_a (Me_a - Me_b) + A_m Me_b$$

Where Me_m = metal content of mineralized area, Me_a = metal content of anomalous stream sediment, Me_b = metal content of background samples, A_m = surface dimensions of mineralization, and A_a = size of catchment area above anomalous site (see Fig. 19.12 for explanation). For the purpose of establishing a suitable sample spacing, the formula is used to predict the maximum size of drainage basin below which sample collection will result in the detection of an anomaly, assuming the minimum size and grade of an economically acceptable target and the smallest anomaly contrast that can be identified above background levels. For example, if the target is a porphyry copper with an assumed surface area (A_m) of 1 km² and grade (Me_m) of 4000 ppm, a limiting value of 30 ppm would be required if an anomaly contrast of twice background (15 ppm) is adopted.

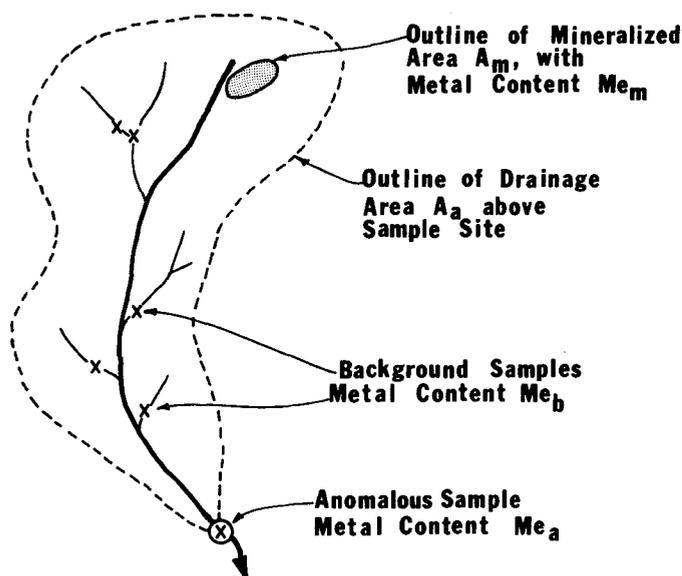


Figure 19.12. Explanation of terms in stream sediment anomaly-dilution formula (after Hawkes, 1976c).

Substituting these values in a rearranged equation, the area above the anomalous sample site can be calculated as follows:

$$A_a = \frac{A_m (Me_m - Me_b)}{Me_a - Me_b} = \frac{1(4000-15)}{30-15} = 266 \text{ km}^2$$

This area would relate to a linear stream distance of about 15 to 20 km, depending on the shape of the drainage basin, and this figure could be used as the limiting distance between samples to assure the location of a porphyry target under the conditions specified.

At best, this procedure will only provide an approximation of the maximum permissible sample spacing owing to the many assumptions that have to be made: namely, those of constant erosion rate, uniform background, minimal sampling and analytical error, stable sediment water chemistry, and absence of contamination. An important factor which is not dealt with in this formula is the relationship of surface size and grade of mineralization to the economic value of a deposit. Depending on erosion level, a large surface anomaly could result from deep weathering to the base of a mineralized system, whereas a relatively "low-grade" anomaly may signify that the land surface lies above a deposit and erosion has not removed a large mass of the mineralized material (e.g. see Beus and Grigoryan, 1977, p. 186).

Sampling Errors

Discussion of error in a sampling process for exploration must be tempered by a consideration of economics. The object is always to get the desired information as cheaply as possible. Hence the need for orientation studies designed to evaluate the relationship of valued information to error, as the process of trying to minimize or eliminate error can be expensive. Such a study was undertaken in five areas peripheral to the Selway-Bitterroot Wilderness Area in Idaho and Montana. Three size fractions of the stream sediment were compared (coarse = -20+30 mesh, medium = -30+80 mesh, fine = -80 mesh). Partial solution techniques were applied to two of these (the medium to fine fractions were treated by the oxalic acid technique described by Alminas and Mosier, 1976), and four magnetic splits were made of the heavy mineral concentrate (sequentially those magnetic at 0.1, 0.5, and 1 amp. on the Frantz Isodynamic Separator and the non-magnetic fraction at 1 amp.). All of the analyses were by optical emission spectroscopy in which 31 elements were sought. The sample design was to pick five areas bordering the Wilderness, one on the west, one on the north, one on the east, and two adjoining each other on the south. These were chosen to reflect a variety of geologic and physiographic environments. Though no significant mineralization is presently known in any of these, clear evidence of low-level mineralization of several types can be seen in the data. Five sites were selected within each area to provide as nearly as possible five adjacent drainage basins of 1-2 km² each. Each site was sampled twice. This plan allows comparison of within-site variance (noise or error) with local variance (between sites, at a scale of a few kilometres) with regional variance (between areas, at a scale of tens of kilometres). The results of the three-level analysis of

Table 19.4

Summary of the results of a nested analysis of variance of analyses of duplicate samples from 25 sites in five areas bordering on the Selway-Bitterroot Wilderness Area in Idaho and Montana. Each sample was analyzed for 31 elements by optical emission spectroscopy.

Sample medium	Number of elements detected	Number of elements showing significant variation		
		Only within site	Between sites	Between areas
Stream sediment -20 + 30 mesh	11	2	16	14
	9	2	17	15
	9	2	18	12
Oxalic acid leach of stream sediment	9	1	7	21
	9	1	11	19
Non-magnetic	7	3	20	12
Heavy-mineral concentrate	9	2	17	16
-0.1 + 0.5 amp.	9	1	18	18
Magnetic	8	1	14	19

variance are summarized in Table 19.4. In each sample type, about nine elements could not be detected. For one to three elements most of the variance was within site; i.e. noise or error. For all sample types, a significant proportion of the variance for 7 to 21 elements was attributable to local and regional factors that should be explainable in geologic terms. It should be noted further that two of the three elements discarded because of large within-site variance in the nonmagnetic fraction of the heavy mineral concentrates are tin (cassiterite) and gold. Both are reported in relatively large quantities in only one sample. The apparent local variance results from tin and gold being major components of a sparse mineral, and the instances where these elements are present constitute legitimate "hits". In geochemical exploration, it is often better to blindly ignore the minor statistical nuisance of sampling and analytical error.

In a similar study covering a wide cross-section of climate and geology in Australia, Duff (1975) studies six field areas (see Fig. 19.13 for location) to determine the sampling technique that would be most effective in low-density regional geochemical mapping. Duplicate samples were collected from a number of localities within each pilot area, and the minus-20, -80, and -140 mesh fractions were analyzed for total Co, Cu, Ni, Pb, Zn, Fe, and Mn by atomic absorption. Analysis of variance methods were used to determine: (1) the minimum number of samples required per locality for regional variation to be significant; (2) the best size fraction for each element, and (3) the major source of error, whether sampling or analytical. The summarized conclusions (Table 19.5) indicating the optimum sampling conditions in each case show some broad trends, such as a tendency towards preferring the coarse grain size in more arid areas, but the best choice of mesh size of sediment and number of samples at each site was found to vary from element to element within areas as well as between areas. This study points out the difficulty in selecting a single size fraction and sampling plan to minimize the sampling error for all elements in multi-element surveys, but it should be noted that it is only in those areas where the regional variability for an element is very low that multiple samples from a single site or multiple analyses on a single sample are required to establish valid geochemical patterns. In Area 2, which is underlain by extensive and fairly uniform Tertiary basalts,

low regional variation of manganese, rather than high sampling and analytical error, explains the need for multiple samples at a site. In most mineral exploration programs, the variability associated with the desired target would probably be large in relation to the sampling error, and the collection of duplicate samples is only routinely adopted as security against loss in shipping, to provide material for later check analyses in cases of contamination or anomalous metal concentrations, and to establish a value for sampling error. In those situations where sampling and analytical error tends to



Figure 19.13. Location of six field areas used in study of the effect of error on low-density regional geochemical mapping in Australia (after Duff, 1975). See Table 19.5 for summary of results.

be high, use of mapping techniques such as moving-average smoothing produces more reliable regional maps of broad scale features (Howarth and Lowenstein, 1971).

The major component of error in working with either heavy mineral concentrates or stream sediments arises from elements that are major components of trace minerals. As noted earlier, this problem is less severe in heavy mineral concentrates because a larger initial sample is taken, thus (1) increasing the probability that the trace mineral will be found in the sample or, more commonly, (2) increasing the number of particles of the trace mineral present in the sample. The first effect is most important for the precious metals, where a single particle of native metal is highly significant. The sampling problem has been clearly defined from the theoretical standpoint by Clifton et al. (1969). From the practical standpoint, a single example from the Hahns Peak district of northwest Colorado may suffice. Millimetre-size gold particles are common in placer deposits surrounding the mining district. During systematic geochemical sampling in and around the district, stream sediment and heavy mineral concentrates from stream sediment were routinely collected. None of the raw stream sediment samples contained chemically detectable gold.

Table 19.5

Summary of optimum particle sizes and number of samples per locality for six areas. Atomic absorption analysis after a hot mixed acid attack. After Duff (1975)

Element	Area 1	Area 2	Area 3 ¹	Area 4	Area 5 ²	Area 6
Co	C 1 A	F 1 A	M 2 A	F 1 A C 2 A	F 1 S	C 1 A F 1 A
Cu	C 1 S	F 1 A	M 1 S	F 1 S C 1 S	F 1 S	F 1 S C 1 S
Ni	C 1 A	F 1 A	M 2 A	C 1 S F 2 A	F 1 S	F 1 S C 1 S
Pb	C 1 A	F 4 A	M 2 A	C 1 A F 2 A	M 2 A F 5 A	M 1 A C 2 A F 5 A
Zn	C 1 S	F 1 A	M 1 S	F 1 S C 1 S	F 1 S	C 2 S F 2 S
Fe	M 1 S C 1 S	F 1 A	M 1 S	C 1 S F 3 S	F 1 S	C 1 S F 3 S
Mn	C 1 S	C 7 S F - S	M 6 S	F 1 (S= A) C 1 (S= A)	F 1 S	F 2 S C 2 A
Key						
First symbol:	Optimum mesh size, C = -20 mesh, M = -80 mesh, F = -140 mesh					
Second symbol:	Minimum recommended number of samples per locality.					
Third symbol:	S or A indicating whether sampling or analytical error is major component of total error.					
Notes:						
1 In Area 3 limited minus-20-mesh data were available.						
2 In Area 5 no minus-20-mesh specimens were collected.						

Visible gold was noted in the field during panning of the heavy mineral concentrates, and the distribution of this gold helped substantially in understanding the geologic history and metal zoning around the district. Only 50 per cent of the concentrates containing visible gold contained chemically detectable gold when a one-half split of the concentrate was analyzed in toto.

More commonly many particles of the trace mineral are present in the large sample taken for heavy mineral separation. Two examples illustrate the extremes of variability encountered in this situation, both involving discrete tungsten minerals. The first example is from north-central Colorado, where a train of fine grained huebnerite extends down Clear Creek for at least 45 miles from the upper zones of the Urad-Henderson porphyry system (Theobald and Thompson, 1959b). At the lower end of this train, the first measured tungsten value on the heavy mineral concentrate was 300 ppm over a background of 40 or less. On two subsequent years this site was reoccupied by students who had one half hour's experience with a gold pan and one day's instruction in the colorimetric analytical procedure (Ward, 1951). The tungsten contents (ppm) of six separate samples collected, prepared, and analyzed by the students are 200, 400, 600, 200, 200, 400. Tungsten is not detectable in the raw stream sediment at this site.

The second example is from the central part of the Precambrian Shield of Saudi Arabia, where stream sediments and heavy mineral concentrates were collected from dry stream beds on a 1-km grid (Theobald and Allcott, 1975). For control, an untrained sampler was asked to collect 25 samples at a single site, and left to accomplish the task. The hope was that this would produce at least a haphazard if not a random sample. The result was a suite of samples collected systematically from the top of the alluvial fill to bedrock, and the last sample was chipped from the bedrock surface. The mineral sought was scheelite, which forms coarse crystals as much as 2 cm long. Nevertheless, the samples were sieved to minus-10-mesh before concentrating. Twenty-two of the 25 samples were run at random among 500 other samples. Though possible sources of error are maximized in this example both by the coarse grain size of the scheelite and by the stratified nature of the samples, the total range of values obtained was 150 (an extreme value at the low end) to 5000 ppm of tungsten. The mean was 2000 ppm, and the coefficient of variation was 80 per cent. Background tungsten from the other 500 samples was less than 100 ppm.

Field Observations and Analysis

With the advent of computers, it has become common practice amongst government surveys and the exploration industry to record field observations in coded form on data sheets such as the familiar Geological Survey of Canada field card (Garrett, 1974). Apart from the essentials of sample number and location (co-ordinates, map, or airphoto reference), data recorded at the field location can be of two types, quantitative values relating to stream dimension, stream order, measured pH, etc., and qualitative information denoting the opinion of the sampler as to the presence of organic material, precipitates, contamination, etc. The first set of numerical data can be readily combined with analytical values for statistical examination of the data. The second set of observations is less amenable to processing, particularly when the data set is made up of information collected by a number of different survey teams, often recruited at the lowest possible level in order to minimize the cost of the survey. During preparation of the regional survey of England and Wales by the Applied Geochemistry Research Group (RSM), it was found that computer plotting of coded field observations made by well trained sampling teams resulted in patterns which coincided with the field areas covered by

different sampling crews. This type of outcome is not uncommon and, as a result, it is probably true that the bulk of the field observations noted in large scale regional surveys are never actually processed. Serious consideration should be given to reducing the number of observations to those items which have proven significance, or which can be reliably quantified. As a general rule, laboratory determination of variables such as content of organic matter and manganese and iron hydroxides provides a more useful measure of sample-site characteristics.

There has been little progress in the development of on-site analytical techniques for stream sediment surveys in recent years. Several field kits are available commercially which enable the sampler to perform colorimetric analysis for Cu, Pb, Zn, or combined heavy metals, largely based on well established methods that use dithizone as the reagent (Bloom, 1955; Holman, 1963; Stanton, 1966) or 2,2' biquinoline for copper (Ward et al., 1963). This type of analysis is particularly useful in the follow-up investigation of base metal anomalies, and can save considerable time in determining the point at which metal enters the stream system, provided the metal occurs in a cold-extractable form. Portable isotope-fluorescence instruments hold promise for an on-site analysis of sediments (Gallagher, 1967; Kunzendorf, 1973), but the poor sensitivity of this method means that field analysis must be restricted to elements which can be concentrated by on-site panning, such as tin in the form of cassiterite.

Laboratory Methods

As analytical methods are reviewed in greater detail elsewhere in this volume, only those procedures related to the preliminary handling of stream sediment samples will be discussed in this section. Included are the methods of sample preparation and the partial extraction techniques most commonly used to evaluate the metal content of selected fractions of the sample.

Sample Preparation

One of the distinct advantages of collecting inorganic stream sediments is the small amount of sample preparation required prior to chemical analysis. In almost all cases, dry sieving through a selected mesh size using noncontaminating screening material (usually nylon or stainless steel mesh) is all that is needed for this type of sample. Sieving can take place at the sample site if the sediments are dry, or if wet-sieving is used (Bolvikken et al., 1976), thus facilitating handling by reducing sample weight. The practice of wet-sieving is generally avoided, as fine grains that may contain substantial amounts of adsorbed trace metal tend to be lost during agitation of the sieve. Except in the case of analysis of a selected coarse fraction, grinding of sediment is seldom carried out before chemical decomposition of the sample. However, Plant (1971) found that grinding to minus-200-mesh improved the analytical precision and reduced preferential volatilization of mineral coatings relative to detrital material in the case of optical emission spectrography.

Preparation of organic samples is generally more complicated. Samples collected by the Geological Survey of Sweden are dried at 110°C, weighted and ashed in an oxidizing atmosphere at 450°C prior to analysis (Larsson, 1976). After reweighing, the organic content is estimated as the loss on ignition. In Finland, organic samples are ashed at 600°C (Kauranne, 1975). For the Tanacross survey in Alaska, stream-bank sod samples were air dried, sieved through a 2-mm stainless steel screen and roasted until ashing was complete. A split of this sample was saved for gold analysis, and the remainder was sieved through 80 mesh and the fine fraction was retained. Moss samples were dried, the

sand and silt was removed, and the samples were pulverized in a Waring blender before ashing in a muffle furnace at a maximum temperature of 500°C (Foster et al., 1976).

Heavy mineral concentrates are among the most difficult to prepare, hence are avoided where a simpler technique is applicable. The accompanying flow sheet (Fig. 19.14) outlines the scheme being used in southwestern New Mexico (H.V. Alminas, written comm., 1975). The similarity of this flow sheet to those presented by Brundin and Bergstrom (1977, p. 4 and 6) for Sweden indicates the general similarity of procedures, and their complexity, now being used in widely separated parts of the world. In general, the procedures include (1) mechanical preconcentration, (2) magnetite separation, (3) laboratory gravity separation, (4) further magnetic or electrostatic separation, and (5) analysis. The goldpan or one of its numerous, regional variants is most commonly used for the initial concentration, though sluices (as in the Swedish scheme), jigs, tables, or combinations of these have been applied. For some problems, this step is sufficient and the rough concentrate may be analyzed directly for the metals or minerals of interest.

Variation in the quantity of magnetite in concentrates collected on a regional basis is often sufficient to control much of the apparent variation in metal content of the rough concentrates (see, for example, Theobald et al., 1967, plate 2F). Further, the high iron content of the magnetite often causes analytical problems. For these reasons, magnetite is usually removed from the concentrate either with a simple hand magnet or a belt or drum magnetic separator. The magnetic concentrate then produced may be analyzed separately if desired. If only the magnetite separate is desired, this may be obtained by direct separation from the stream sediment (Callahan, 1975).

The concentrate remaining after separation of the magnetite may be suitable for direct analysis (Theobald and Thompson, 1959b). Where further separation is desired, the concentrate should be cleaned of light minerals remaining from the rough concentration stage. This is accomplished with a heavy liquid separation usually involving bromoform (specific gravity 2.89) or a similar liquid or sometimes one of the heavier liquids such as methylene iodide (specific gravity 3.3). Heavy liquid separation at this stage serves two purposes: (2) it produces a cleaner final product, minimizing variation due to human or machine variability, and (2) it allows a somewhat rougher and considerably faster initial concentration stage in the field.

Further splitting of the samples is usually accomplished by electromagnetic separation using a Frantz Isodynamic Separator, though strong horseshoe magnets and electrostatic separators have also been used. The number of combinations of properties that may be used to produce subsamples is very large, so some choice of the samples to be analyzed must be made based on the nature of the problem, the physiographic and geologic characteristics of the terrain, and orientation surveys. In the example from New Mexico described earlier, two magnetic splits were analyzed, that not magnetic at 0.1 amp. but magnetic at 1 amp. and that not magnetic at 1 amp. (Alminas et al., 1972a). The magnetite concentrate was isolated but not analyzed. In the Yukon-Tanana upland of Alaska, the electromagnetic separations were made at 0.2 amp. and 0.6 amp. (Tripp et al., 1976). In the Swedish example cited earlier (Brundin and Bergstrom, 1977), the initial sampling plan called for the analysis of six magnetic splits of the concentrate separated by handmagnet and at 0.5, 1, 1.5, and 2 amp. on the Frantz. This was reduced to five splits by using a combination of two heavy liquids, and Frantz separations at 0.7 and 1.3 amp. for different gravity functions.

Selective Extractions

Partial analysis has always been one of the most reliable methods of enhancing the contrast between the metal content of stream sediments related to weathering sulphides and that due to less soluble rock forming minerals. Cold extractions using various buffers (Stanton, 1966) or weak acid attacks (dilute hydrochloric, acetic, EDTA) have been the techniques most frequently used in base metal exploration, but the recent concern over the more precise separation and identification of the form in which metals are present in sediments has led to the use of a far wider range of methods.

Selectivity and effectiveness of the most common extraction techniques have been reviewed by Rose (1975) and Chao and Theobald (1976). The latter authors proposed the following extraction sequence in order to partition the elements into specific fractions, ignoring the small percentage of adsorbed and exchangeable metal:

1. Mn oxides: 0.1 M hydroxylamine hydrochloride in 0.01 M HNO₃ at room temperature, 30 minutes;
2. Fe oxides (amorphous): 0.25 M hydroxylamine in 0.25 M HCl at 70°C, 30 minutes;
3. Fe oxides (crystalline): Sodium dithionate in acetate buffer at pH 4.75 at 50°, 30 minutes;
4. Sulphide minerals: KClO₃ + HCl - 4 N HNO₃, 20 minute boil;
5. Silicate matrix: HF-HNO₃ digestion.

In a similar study, Gibbs (1977) determined the adsorbed metal content of sediments by extraction with 1 N MgCl₂, which was successful in freeing adsorbed ions within a few minutes without affecting the Fe-Mn oxide coatings or organic material in the sample. The selective extraction of organic material is generally accomplished through the use of the oxidizing agents hydrogen peroxide (Rose and Suhr, 1971) or sodium hypochlorite (Gibbs, 1973), but neither is totally specific if sulphides are present.

For many routine exploration purposes less specific extractions can be adopted, and Bradshaw (1975) has outlined a short list of acceptable extractions to be used in orientation surveys, as follows: hot HClO₄ or HClO₄/HNO₃ at reflux temperature for at least 4 hours to give "total" metal; 0.5 N HCl boiling for 20 minutes to give "hot-extractable" metal; and 0.25 per cent EDTA shaken cold for 2 minutes to give "cold-extractable" metal. Other partial extractions in use for Fe-Mn oxides are the oxalic acid digestion (Alminas and Mosier, 1976), and the citrate/hydroxylamine leach (Whitney, 1975).

INTERPRETATION

Interpretation of geochemical stream sediment surveys begins with the presentation of the sample locations and analytical results in map form, followed by examination of the data for anomalous situations which may be due to the presence of mineral deposits. In the case of single-element maps covering small areas, empirical methods are often all that are required to identify abnormal metal concentrations.

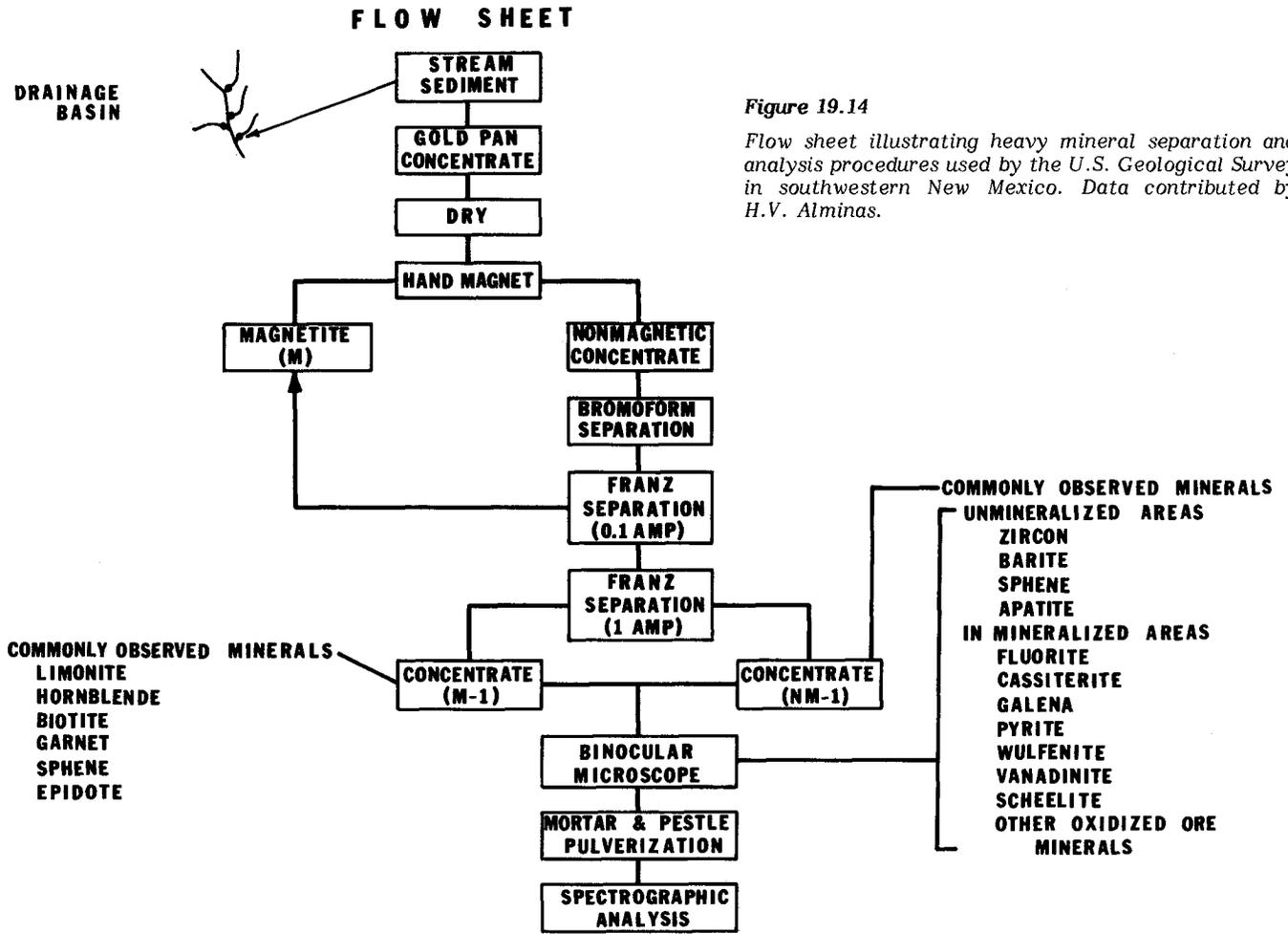


Figure 19.14

Flow sheet illustrating heavy mineral separation and analysis procedures used by the U.S. Geological Survey in southwestern New Mexico. Data contributed by H.V. Alminas.

However, multi-element data are not easy to interpret in two dimensions, even using overlays, unless the values are statistically combined using one of the many techniques available for simplifying data. With the advent of extensive regional surveys and multi-element analytical techniques, computer processing and machine plotting have become important parts of the interpretation procedure. While no attempt will be made to describe the various statistical techniques in detail, some examples of both empirical and statistical interpretation procedures will be outlined in the following paragraphs.

Geochemical Maps

As a first step in making single-element maps, point localities are customarily plotted, whether by hand or machine, giving the analytical value at the map co-ordinates of the sample site, either by recording the numerical concentration or by use of a symbol representing a range of values. Machine plotting of single-element maps can be accomplished symbolically by means of line printer overprinting methods such as Howarth's grey-level mapping program PLTLPI (Howarth, 1971) or the SYMAP program (Dudnick, 1971) favoured by Chapman (1975). Drum or flat-bed plotters are also commonly used for mapping point information, and for contouring metal values. Contouring of stream sediment data from detailed surveys is generally of

limited value due to the displacement of the stream sediment sample downstream from the source area, but the validity of contour maps can be improved by relocating the sample points upstream from the true localities (J. Galbraith, pers. comm.). Regional smoothed data can, however, be effectively represented by machine contouring, and the contoured maps, can, in turn, be converted into three dimensional perspective plots (Fig. 19.15).

In the case of multi-element maps, point-source information presents a more difficult display problem. In an experiment to determine the optimum machine plotting technique for illustrating multi-element stream sediment data as point symbols on a single map, Rhind et al. (1973) investigated symbols such as bar graphs, graduated circles, pie diagrams, and wind roses by considering the amount of information that could be displayed in terms of space and cost. As a result of this study, the wind-rose symbol was selected and has since been adopted for machine plotting of the IGS geochemical maps. Three concentration variables can also be effectively combined using the subtractive colour-mixing technique developed for the laser plotter by Lowenstein and Howarth (1973) and later adapted for line-printer mapping (Howarth and Lowenstein, 1976). This particular method is generally more suited to smoothed regional data having few gaps in the survey coverage.

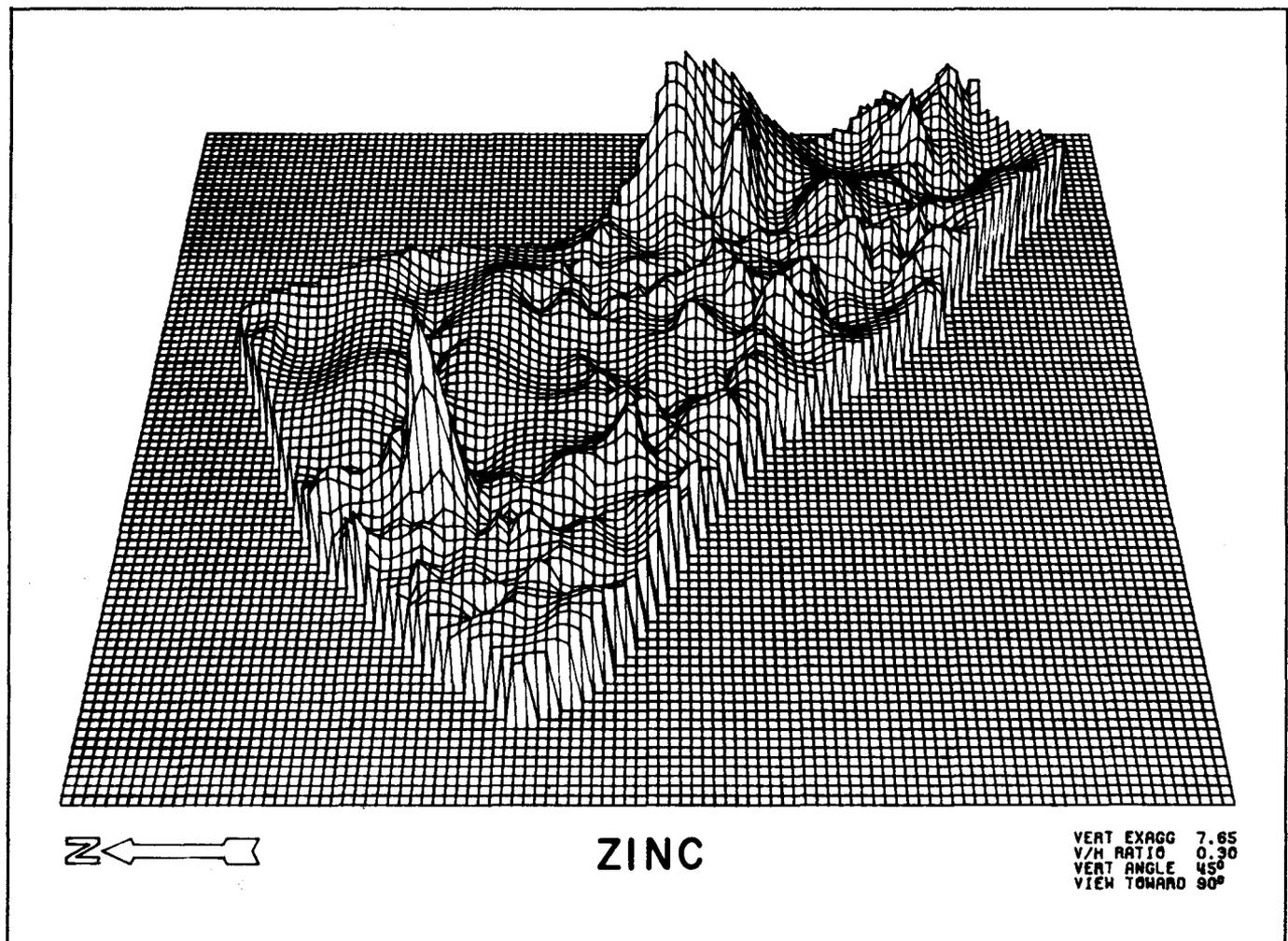


Figure 19.15. Three-dimensional perspective view of zinc distribution in stream sediments from an area of 1100 km² in Central America.

Visual evaluation of mapped stream sediment data, when viewed in combination with geology and topography, can go a long way towards identifying the changes in background resulting from differences in lithology and environment. Grouping of metal values for mapping can be based on log probability plots, percentiles, arithmetic or geometric classes, or multiples of an established background (e.g. 50th percentile). Spatial coincidence of enhanced concentrations of more than one element are often diagnostic of particular types of mineralization (e.g. Cu-Mo with porphyries) and can also be recognized through the examination of overlays or combined element maps, as outlined by Chaffee (1977).

Empirical Methods of Interpretation

Over the years, the experience gained from case studies has led to the development of empirical methods of data analysis for certain exploration situations. An example of this approach can be found in the dilution formula of Hawkes (1976b, c) mentioned earlier in the discussion of sample spacing, and in the method for field interpretation of stream sediment surveys developed by Conzinc Riotinto of Australia Exploration (CRAE) for porphyry copper exploration in tropical terrain (MacKenzie, 1977). This latter method is based on many case histories which indicate that the drainage value is a direct reflection of the average soil value of the catchment. One example that demonstrates this relationship is the Panguna copper deposit on Bougainville Island (Fig. 19.16), where the 2-km² soil anomaly averaging 3100 ppm combined with an 18km² background of 400 ppm results in an overall average of 600 ppm for the 20 km² catchment area. The recorded stream sediment value of 670 ppm at the outlet closely corresponds to the calculated average soil content of 660 ppm. The value of this approach lies in the fact that once the size and tenor of a target has been defined, the required excess copper concentration over background in stream sediments and be calculated, provided that mechanical transportation of soil to stream takes place under tropical weathering conditions similar to those in the pilot areas.

Study of the geochemical distribution of elemental ratios is also of value in a variety of exploration situations. In the case where sampling precision is relatively poor, mapping of metal ratios can be more effective than single-element maps in outlining different lithologies and sources of mineralization. This was found to be true for X-ray fluorescence analysis of heavy mineral concentrates from north Sunderland and the Cheviot Hills (Leake and Aucott, 1973). In any selective analysis procedure making use of secondary oxides of iron and manganese, interpretation is customarily based on the ratios of metal/Mn, metal/Fe, and metal/Mn + Fe in order to reduce the effect of the amount of oxide in each sample (Chao and Theobald, 1976).

Where relatively small numbers of samples and small survey areas are involved, log probability plots can be used to estimate the threshold values which provide the best separation of a population into background and anomalous groups (Tennant and White, 1959; Lepeltier, 1969). This procedure has recently been described in detail, with suitable examples, by Sinclair (1976). However, too much reliance should not be placed on log probability plots as a means of recognizing anomalies in stream sediment data, as this type of frequency distribution study is unrelated to the spatial distribution of the data. As a result, no area should be eliminated from further consideration simply because it shows no indications of an anomalous distribution on a log probability plot; the data should be mapped and examined in detail. Most geochemists have observed the phenomenon described by Chaffee (1977) whereby the log probability plots of large data sets tend to be unimodal, regardless of the presence or absence of anomalies related to ore deposits in the survey area.

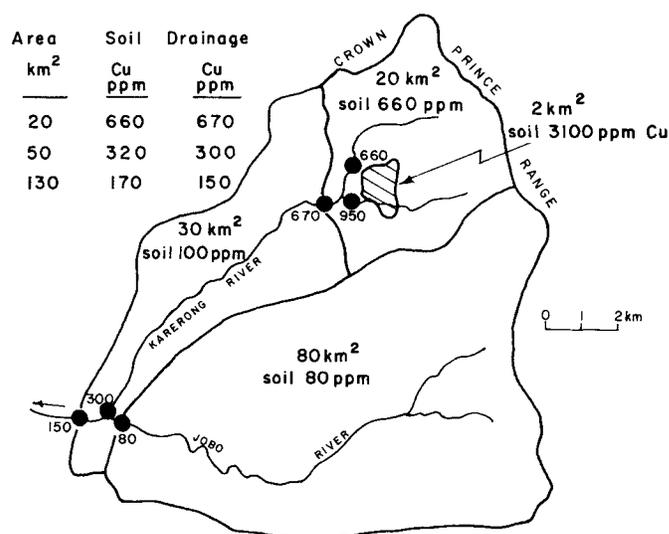


Figure 19.16. Copper in stream sediments and soils in the vicinity of the Panguna deposit, Bougainville Island (after MacKenzie, 1977).

Statistical Methods

Statistical methods of data analysis have become an essential part of regional geochemical reconnaissance using the multi-element approach, and most mining and exploration companies now have access to computing and automatic plotting facilities suitable for handling large data sets. As an example, in the mineral exploration department of Cities Service Company, regional multi-element data are routinely processed via remote-terminal time-sharing operations, which control statistical procedures, and are plotted by line-printer, pen, or electrostatic plotters (Fig. 19.17). Manipulation of contour plots is also carried out by use of an interactive video display system. Statistical programs available include those accessed through standard statistical packages, and log probability plots, trend-surface, empirical discriminant, and Q- and R-mode factor analysis for large sets of data. With these facilities at hand, no difficulty was experienced in processing a recent project involving 40 000 samples with as many as nine analyses per sample.

Historically, statistical methods for interpretation of regional stream sediment data developed from the use of trend-surface, moving-average, and factor analysis, particularly R-mode (Nichol and Webb, 1967). All these methods, together with cluster analysis (Obial and James, 1973), are based on statistical manipulation of the data without prior input of parameters such as known geological or environmental controls. This type of analysis is particularly suited to areas in which the geology is poorly known, as in most "grass-roots" exploration projects. For those regions where the geology is mapped in greater detail, techniques such as discriminant analysis, which requires a prior assignment of training areas, provide an alternate method of interpretation. A recent application of this technique to regional stream sediment data from the U.K. (Castillo-Munoz and Howarth, 1976) gave about a 60 per cent success rate in classifying reconnaissance samples on the basis of small training areas selected as typical of known lithology or mineralization, despite the presence of extensive glacial overburden. The method also served to outline anomalous sample sites related to past smelting or mining activity, and localized areas of manganese scavenging.

Multiple regression has been used with some success to allow for variations in stream sediment matrix due to changes in secondary environment or bedrock composition in the

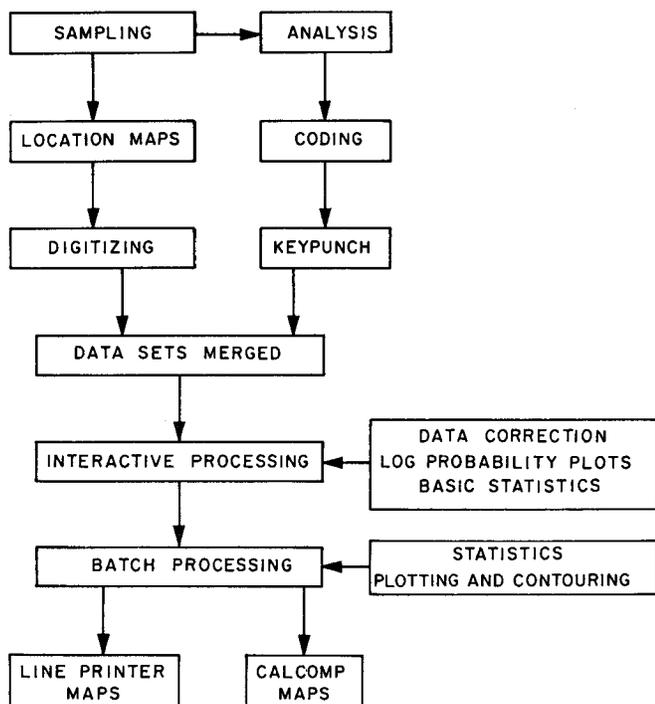


Figure 19.17. Data handling scheme for typical stream sediment survey conducted by Citco International Minerals.

catchment area (Dahlberg, 1968; Rose et al., 1970; Chatupa and Fletcher, 1972), and factor analysis prior to regression has also been used for this purpose (Closs and Nichol, 1975). Attempts have also been made to use multiple regression techniques to predict mineral resources (De Geoffrey and Wignall, 1970), and a variation of this method of combining geological criteria, historical mining records, and regional stream sediment data has been used to estimate the base metal resources of northwest England (Cruzat and Meyer, 1974). Combination of stream sediment results with geophysical and geological variables has also been accomplished by means of discriminant analysis in a study designed to evaluate the potential of the Triassic province in Pennsylvania for magnetite deposits (Rose, 1972).

Computer modelling techniques for interpretation of stream sediment data have recently been described by Culbert (1976). This approach makes use of a terrain and transport model to describe the drainage system, with input in the form of: (1) co-ordinates of sample sites and turning points on streams, (2) catchment areas of creeks, (3) lithology of grid squares, and (4) elevations of grid squares. The program then stimulates the flow pattern and dilution between sequential samples and produces an interpretation similar to the one that would result from the previously mentioned empirical methods involving dilution equations.

DISCUSSION

This review of stream sediment geochemistry in 1977 has emphasized recent changes in routine methods that have been brought about by the application of the technique to environments previously considered to be unfavourable for drainage surveys, and by the wider use of stream sediments for multi-purpose regional mapping. It is likely that these methods will continue to change, not only because new environments are being explored but also because areas formerly prospected by more conventional surveys are being subjected to re-examination using more refined methods.

First-pass regional exploration is rapidly reducing the number of unexplored areas, and future stream sediment surveys will increasingly be devoted to second- or third-pass sampling programs using different sampling, analysis, or interpretation procedures.

While data processing and analytical costs per unit have tended to remain stable or decline in recent years due to technological improvements in instrumentation and transportation, labour costs have increased in line with trends in worldwide inflation. As a result, efficient stream sediment surveys require optimization of sampling and analytical procedures to increase the amount of useful information that can be extracted from each sample. In many situations, this goal is best achieved through the use of multi-element analysis and computer-aided interpretation.

ACKNOWLEDGMENTS

The authors would like to acknowledge the co-operation of Cities Service Company in supplying technical assistance in preparing this review. In particular, the efforts of Travis Brady in the preparation of slides and figures are acknowledged.

REFERENCES

- Alminas, H.V. and Mosier, E.M.
1976: Oxalic acid leaching of rock, soil, and stream-sediment samples as an anomaly-accentuation technique; U.S. Geol. Surv., Open File Rept. 76-275, 25 p.
- Alminas, H.V., Watts, K.C., and Siems, D.L.
1972a: Maps showing lead distribution in the Winston and Chise quadrangles and in the west part of the Priest Tank quadrangle, Sierra County, New Mexico; U.S. Geol. Surv. Misc. Field Studies Map MF 398.
1972b: Maps showing molybdenum distribution in the Winston and Chise quadrangles and in the west part of the Priest Tank quadrangle, Sierra County, New Mexico; U.S. Geol. Surv., Misc. Field Studies Map MF 399.
1972c: Maps showing silver and gold distribution in the Winston and Chise quadrangles and in the west part of the Priest Tank quadrangle, Sierra County, New Mexico; U.S. Geol. Surv., Misc. Field Studies Map MF 400.
- Alther, George R.
1975: Geochemical analysis of stream sediments as a tool for environmental monitoring: A pigyard case study; Geol. Soc. Am. Bull., v. 86, p. 174-176.
- Armour-Brown, A. and Nichol, Ian
1970: Regional geochemical reconnaissance and the location of metallogenic provinces; Econ. Geol., v. 65, p. 312-330.
- Ball, T.K. and Nutt, M.J.C.
1974: Preliminary reconnaissance of central Wales; Inst. Min. Met. Trans., London, Sect. B, v. 83, p. 66-67.
- Beus, A.A. and Grigoryan, S.V.
1977: Geochemical exploration methods for mineral deposits; Applied Publishing Ltd., Illinois, 287 p.
- Bjorlykke, A., Bolviken, B., Eidsvig, P., and Svinndal, S.
1973: Exploration for disseminated lead in southern Norway; in *Prospecting in areas of Glacial Terrain*, Inst. Min. Met., London, p. 111-126.

- Bloom, H.
1955: A field method for the determination of ammonium citrate-soluble heavy metals in soils and alluvium; *Econ. Geol.*, v. 50, p. 533-541.
- Bolviken, B.
1976: Snertingdal: A lead occurrence found by systematic prospecting; *J. Geochem. Explor.*, v. 5, p. 324-331.
- Bolviken, B., Krog, J.R., and Naess, G.
1976: Sampling techniques for stream sediments; *J. Geochem. Explor.*, v. 5, p. 382-383.
- Bolviken, B. and Sindig-Larsen, R.
1973: Total error and other criteria in the interpretation of stream sediment data; in *Geochemical Exploration 1972*, Inst. Min. Met., London, p. 285-295.
- Bradshaw, P.M.D. (ed.)
1975: Conceptual models in exploration geochemistry; *J. Geochem. Explor.*, v. 4, p. 1-213.
- Brand, H.
1972: United Nations mineral survey programs; 24th Int. Geol. Congr., Montreal, Abstr., p. 498.
- Brundin, N.H. and Bergstrom, J.
1977: Regional prospecting for ores based on heavy minerals in glacial till; *J. Geochem. Explor.*, v. 7, no. 1, p. 1-19.
- Brundin, N.H. and Nairis, B.
1972: Alternative sample types in regional geochemical prospecting; *J. Geochem. Explor.*, v. 1, p. 7-46.
- Buhlmann, E., Philpott, D.E., Scott, M.J., and Sanders, R.N.
1975: The status of exploration geochemistry in southern Africa, in *Geochemical Exploration 1974*, Elsevier Publ. Co., Amsterdam, p. 51-64.
- Callahan, J.E.
1975: A rapid field method for extracting the magnetic fraction from stream sediments; *J. Geochem. Explor.*, v. 4, no. 2, p. 265-267.
- Cameron, E.M.
1976: Geochemical reconnaissance for uranium in Canada: Notes on methodology and interpretation of data; in *Report of Activities, Part. C*, Geol. Surv. Can., Paper 76-1C, p. 229-236.
- Canney, F.C.
1966: Hydrous manganese-iron oxide scavenging: Its effect on stream sediment surveys, abstr.; *Geol. Surv. Can.*, Paper 66-54, p. 267.
- Carpenter, R.H., Pope, T.A., and Smith, R.L.
1975: Fe-Mn oxide coatings in stream sediment geochemical surveys; *J. Geochem. Explor.* v. 4, p. 349-363.
- Castillo-Munoz, R. and Howarth, R.J.
1976: Application of the empirical discriminant function to regional geochemical data from the United Kingdom; *Geol. Soc. Am. Bull.*, v. 87, p. 1567-1581.
- Chaffee, M.A.
1977: Some thoughts on the selection of threshold values as practiced in the Branch of Exploration Research of the U.S. Geological Survey; *Assoc. Explor. Geochem.*, Newsletter 21, p. 14-16.
- Chaffee, M.A., Lee-Moreno, J.L., Caire, L.F., Mosier, E.L., and Frisken, J.G.
1976: Results of geochemical investigations comparing samples of stream sediment, panned concentrate, and vegetation in the vicinity of the Caridad porphyry copper deposit, northern Sonora, Mexico; *U.S. Geol. Surv.*, Open File Rept. 76-559, 34 p.
- Chao, T.T. and Theobald, P.K.
1976: The significance of secondary iron and manganese oxides in geochemical exploration; *Econ. Geol.* v. 71, p. 1560-1569.
- Chapman, R.P.
1975: Data processing requirements and visual representation for stream sediment exploration geochemical surveys; *J. Geochem. Explor.*, v. 4, p. 409-423.
- Chatupa, J. and Fletcher, K.W.
1972: Application of regression analysis to the study of background variations in trace metal content of stream sediments; *Econ. Geol.*, v. 67, p. 978-980.
- Chork, C.Y.
1977: Seasonal, sampling and analytical variations in stream sediment surveys; *J. Geochem. Explor.*, v. 7, p. 31-48.
- Clifton, H.E., Hunter, R.E., Swanson, F.J., and Phillips, R.L.
1969: Sample size and meaningful gold analysis; *U.S. Geol. Surv.*, Prof. Paper 625-C, 17 p.
- Closs, L.G. and Nichol, I.
1975: The role of factor and regression analysis in the interpretation of geochemical reconnaissance data; *Can. J. Earth. Sci.*, v. 12, p. 1316-1330
- Cruzat, A.C.E.
1973: Application of regional stream sediment geochemistry in forecasting base metal production, northern England; unpubl. Ph.D. thesis, Univ. London.
- Cruzat, A.C.E. and Meyer, W.T.
1974: Predicted base metal resources of northwest England; *Inst. Min. Met. Trans.*, London, v. 83, Sect. B, p. 131-134.
- Culbert, R.R.
1976: A multivariate approach to mineral exploration; *Can. Min. Metall. Bull.*, v. 69, no. 766, p. 39-52.
- Dahlberg, E.C.
1968: Application of a selective simulation and sampling technique to the interpretation of stream sediment copper anomalies near South Mountain, Penn.; *Econ. Geol.*, v. 63, p. 409-417.
- Dahlem, D.H.
1976: A national hydrogeochemical sampling program for uranium; *Soc. Min. Eng./Am. Inst. Min. Met. Eng.*, Preprint 76-L-38, 22 p.
- De Geoffrey, J. and Wignall, T.K.
1970: Statistical decision in regional exploration: application of regression and Bayesian classification analysis in the southwest Wisconsin zinc area; *Econ. Geol.*, v. 65, p. 769-777.
- Dudnick, E.E.
1971: SYMAP: Users reference manual for synagraphic computer mapping; Rept. 71-1, Dept. Architecture, Univ. Illinois at Chicago Circle, Ill., 114 p.

- Duff, J.R.V.
1975: Sources of error in some geochemical data from Australian stream sediments; unpubl. Ph.D. thesis, Univ. London, 389 p.
- Dunlop, A.C.
1973: Geochemical dispersion of tin in stream sediments and soils in southwest England; unpubl. Ph.D. thesis, Univ. London.
- Dunlop, A.C. and Meyer, W.T.
1973: Influence of late Miocene-Pliocene submergence on regional distribution of tin in stream sediments, southwest England; *Inst. Min. Met. Trans.*, London, Sect. B, v. 82, p. 62-64.
- Fanta, P.
1972: Effects of seasonal variations on iron, manganese and associated metal contents of stream sediments and soils; unpubl. M. Phil. thesis, Univ. London.
- Ferguson, R.B. and Price, V.
1976: National Uranium Resource Evaluation (NURE) program - hydrogeochemical and stream sediment reconnaissance in the eastern United States; *J. Geochem. Explor.*, v. 6, p. 103-118.
- Foster, H.L., Albert, N.R.D., Barnes, D.F., Curtin, G.C., Griscom, A., Singer, D.A., and Smith, J.G.
1976: The Alaskan Mineral Resource Assessment Program: Background information to accompany folio of geologic and mineral resource maps of the Tanacross quadrangle, Alaska; *U.S. Geol. Surv., Circ.* 734, 23 p.
- Foster, J.R.
1971: The reduction of matrix effects in atomic absorption analysis and the efficiency of selected extractions on rock forming minerals; *Can. Inst. Min. Met., Spec. Vol.* 11, p. 554-560.
- Galbraith, J.
1975: Regional stream sediment geochemistry and data analysis in northeast Bahia, Brazil; Ph.D. thesis, Univ. Idaho, 277 p.
- Gallagher, M.J.
1967: Determination of molybdenum, iron, and titanium in ores and rocks by portable radioisotope X-ray fluorescence analyzer; *Inst. Min. Met. Trans.*, London, Sect. B, v. 76, p. 155-164.
- Garrett, R.G.
1974: Field data acquisition methods for applied geochemical surveys at the Geological Survey of Canada; *Geol. Surv. Can., Paper* 74-52, 36 p.
- Garrett, R.G. and Nichol, I.
1967: Regional geochemical reconnaissance in eastern Sierra Leone; *Inst. Min. Met. Trans.*, London, Sect. B, v. 76, p. 97-112.
- Gibbs, A.K.
1974: Regional geochemistry in Guyana; unpubl. M.Sc. thesis, Univ. London, 168 p.
- Gibbs, R.J.
1973: Mechanisms of trace metal transport in rivers; *Science*, v. 156, p. 1734-1737.
1977: Transport phases of transition metals in the Amazon and Yukon Rivers; *Geol. Soc. Am. Bull.*, v. 88, p. 829-843.
- Gleeson, C.F. and Brummer, J.J.
1976: Reconnaissance stream-sediment geochemistry applied to exploration for porphyry Cu-Mo deposits in southwestern Yukon Territory; *Can. Min. Metall. Bull.*, v. 69, no. 769, p. 91-103.
- Govett, G.J.S.
1958: Geochemical prospecting for copper in Northern Rhodesia; unpubl. Ph.D. thesis, Univ. London.
- Hawkes, H.E.
1976a: The early days of exploration geochemistry; *J. Geochem. Explor.*, v. 6, p. 1-12.
1976b: The downstream dilution of stream sediment anomalies; *J. Geochem. Explor.*, v. 6, p. 345-358.
1976c: Selection of sample sites in stream sediment reconnaissance; Preprint 76-L-1, *Am. Inst. Min. Met. Eng.*; Annual Meeting, February 1976.
- Hawkes, H.E. and Webb, J.S.
1962: Geochemistry in mineral exploration; Harper and Row, New York.
- Hem, J.D.
1976: Geochemical controls on lead concentrations in stream water and sediments, *Geochim. Cosmochim. Acta*, v. 40, p. 599-609.
- Hill, John (translator)
1746: History of stones by Theophrastus, 300 B.C., (?) London.
- Holman, R.H.C.
1963: A method for determining readily-soluble copper in soil and alluvium; *Geol. Surv. Can., Paper* 63-7.
- Holmes, R.
1975: The regional distribution of cadmium in England and Wales; unpubl. Ph.D. thesis, Univ. London.
- Horsnail, R.F.
1975: Strategic and tactical geochemical exploration in glaciated terrain: illustrations from Northern Ireland; in *Prospecting in areas of glaciated terrain*, *Inst. Min. Met.*, London, p. 16-31.
- Horsnail, R.F., Nichol, I., and Webb, J.S.
1969: Influence of variations in secondary environment on the metal content of drainage sediments; *Colo. Sch. Mines Q.*, v. 64, p. 307-322.
- Hosking, K.F.G.
1971: Problems associated with the application of geochemical methods of exploration in Cornwall, England; *Can. Inst. Min. Met., Spec. Vol.* 11, p. 176-189.
- Howarth, R.J.
1971: FORTRAN IV Program for grey-level mapping of spatial data; *Mathematical Geol.*, v. 3, no. 2, p. 95-121.
- Howarth, R.J. and Lowenstein, P.L.
1971: Sampling variability of stream sediments in broad-scale regional geochemical reconnaissance; *Inst. Min. Met. Trans.*, London, Sect. B, v. 80, p. 363-372.
1976: Three-component colour maps from lineprinted output; *Inst. Min. Met. Trans.*, London, v. 85, Sect. B, p. 234-237.
- Jacobs, D.C. and Parry, W.T.
1976: A comparison of the geochemistry of biotite from some Basin and Range stocks; *Econ. Geol.*, v. 71, no. 6, p. 1029-1035.

- Kauranne, L.K.
1975: Regional geochemical mapping in Finland; in *Prospecting in areas of glaciated terrain*, Inst. Min. Met., London, p. 71-81.
- Kunzendorf, H.
1973: Non-destructive determination of metals in rocks by radioisotope X-ray fluorescence instrumentation; in *Geochemical Exploration 1972*, Inst. Min. Met., London, p. 401-414.
- Larson, L.T.
1977: *Geochemistry - 1976 Annual Review*; Min. Eng., v. 29, no. 2, p. 57-63.
- Larsson, J.O.
1976: Organic stream sediments in regional geochemical prospecting, Precambrian Pajala district, Sweden; *J. Geochem. Explor.*, v. 6, p. 233-250.
- Leake, R.C. and Aucott, J.W.
1973: Geochemical mapping and prospecting by use of rapid automatic X-ray fluorescence analysis of panned concentrates; in *Geochemical Exploration 1972*, Inst. Min. Met., London, p. 389-400.
- Leggo, M.D.
1976: Contrasting geochemical expressions of copper mineralization at Namosi, Fiji; 25th Int. Geol. Congr., Sydney, Abstr., p. 448-449.
- Lepeltier, C.
1969: A simplified statistical treatment of geochemical data by graphical representation; *Econ. Geol.*, v. 64, p. 538-550.
- Lovering, T.S., Huff, L.C., and Almond, H.
1950: Dispersion of copper from the San Manuel copper deposit, Pinal County, Arizona; *Econ. Geol.*, v. 45, p. 493-514.
- Lowenstein, P.L. and Howarth, R.J.
1973: Automated colour-mapping of three-component systems and its application to regional geochemical reconnaissance; in *Geochemical Exploration 1972*, Inst. Min. Met., London, p. 297-304.
- MacKenzie, D.H.
1977: Empirical assessment of anomalies in tropical terrain; *Assoc. Explor. Geochem., Newsletter* 21, p. 6-10.
- Mayfield, I.
1976: Regional geochemical drainage reconnaissance near west Nicholson; in *Viewing, K.A., 7th Annual Report*, Inst. Mining Res., Univ. Rhodesia, p. 51-53.
- Meyer, W.T.
1977: Regional stream sediment interpretation procedures in a tropical environment, Central Bahia, Brazil (abs.); *Min. Eng.*, v. 29, no. 1, p. 75.
- Miesch, A.T.
1976: Sampling designs for geochemical surveys - syllabus for a short course; *U.S. Geol. Surv., Open File Rept.* 76-772, 128 p.
- Nichol, I. and Webb, J.S.
1967: The application of computerized mathematical and statistical procedures to the interpretation of geochemical data; *Proc. Geol. Soc. London*, no. 1642, p. 186-198.
- Nowlan, G.A.
1976: Concretionary manganese-iron oxides in streams and their usefulness as a sample medium for geochemical prospecting; *J. Geochem. Explor.*, v. 6, p. 193-210.
- Obial, R.C. and James, C.H.
1973: Use of cluster analysis in geochemical prospecting with particular reference to southern Derbyshire, England; in *Geochemical Exploration 1972*, Inst. Min. Met., London, p. 237-257.
- Ostle, D., Coleman, R.F., and Ball, T.K.
1972: Neutron activation analysis as an aid to geochemical prospecting for uranium; in *Uranium Prospecting Handbook*, Inst. Min. Met., London, p. 95-107.
- Overstreet, W.C.
1962: A review of regional heavy-mineral reconnaissance and its application in the southeastern Piedmont; *Southeast. Geol.*, v. 3, no. 3, p. 133-173.
- Parry, W.T. and Nackowski, M.P.
1963: Copper, lead, and zinc in biotites from Basin and Range quartz monzonites; *Econ. Geol.*, v. 58, no. 7, p. 1126-1144.
- Plant, J.
1971: Orientation studies on stream sediment sampling for a regional geochemical survey in northern Scotland; *Inst. Min. Met. Trans.*, London, Sect. B, v. 80, p. 324-345.
- Rhind, D.W., Shaw, M.A., and Howarth, R.J.
1973: Experimental geochemical maps; *J. Brit. Cartographic Soc.*, Dec. 1973, p. 112-118.
- Rose, A.W.
1972: Favorability for Cornwall-type magnetite deposits in Pennsylvania using geological, geochemical and geophysical data in a discriminant function; *J. Geochem. Explor.*, v. 1, p. 181-194.
1975: The mode of occurrence of trace elements in soils and stream sediments applied to geochemical exploration; in *Geochemical Exploration 1974*, Elsevier Publ. Co., Amsterdam, p. 691-705.
- Rose, A.W., Dahlberg, E.C., and Keith, M.L.
1970: A multiple regression technique for adjusting background values in stream sediment geochemistry; *Econ. Geol.*, v. 65, p. 156-165.
- Rose, A.W. and Keith, M.L.
1976: Reconnaissance geochemical techniques for detecting uranium deposits in sandstones of northeastern Pennsylvania; *J. Geochem. Explor.*, v. 6, p. 119-138.
- Rose, A.W. and Suhr, N.H.
1971: Major element content as a means of allowing for background variation in stream-sediment geochemical exploration; *Can. Inst. Min. Met., Spec. Vol.* 11, p. 587-593.
- Sharp, W.E. and Jones, T.L.
1975: A topologically optimum prospecting plan for streams; in *Geochemical Exploration 1975*, Elsevier Publ. Co., Amsterdam, p. 227-235.

- Sigov, A.P.
1939: Shlikovye Izyskaniia (Prospecting by heavy mineral studies); Transactions of the Ural Scientific Research Institute of Geology, Prospecting and Economic Mineralogy and Sverdlovsk Mining Institute, no. 4, 64 p. (Abstracted by H.E. Hawkes, in U.S. Geol. Surv., Open File Rept. issued 1953(?)).
- Sinclair, A.J.
1976: Applications of probability graphs in mineral exploration; Assoc. Explor. Geochem., Spec. Vol. 4, 95 p.
- Smee, B.W. and Ballantyne, S.B.
1976: Examination of some Cordilleran uranium occurrences; in Report of Activities, Part. C, Geol. Surv. Can., Paper 76-1C, p. 255-258.
- Stanton, R.E.
1966: Rapid methods of trace analysis for geochemical application; Edw. Arnold, London.
- Sutherland-Brown, A.
1975: Huckleberry Cu-Mo deposit, British Columbia; in Conceptual Models in Exploration Geochemistry, J. Geochem. Explor., v. 4, no. 1, p. 72-75.
- Tennant, C.B. and White, M.L.
1959: Study of the distribution of some geochemical data; Econ. Geol., v. 54, p. 1281-1290.
- Theobald, P.K. and Allcott, G.H.
1975: Tungsten anomalies in the Uyaijah ring structure, Kushaymiyah igneous complex, Kingdom of Saudi Arabia, section A - geology and geochemistry of the Uyaijah ring structure; Saudi Arabian Project Report 160, U.S. Geol. Surv., Open File Rept. 75-657, 86 p.
- Theobald, P.K., Jr. and Havens, R.G.
1960: Base metals in biotite, magnetite and their alteration products in a hydrothermally altered quartz monzonite porphyry sill, Summit County, Colorado (abs.); Geol. Soc. Am. Bull., v. 71, no. 12, pt. 2, p. 1991.
- Theobald, P.K., Jr., Overstreet, W.C., and Thompson, C.E.
1967: Minor elements in alluvial magnetite from the inner Piedmont belt, North and South Carolina; U.S. Geol. Surv., Prof. Paper 554-A, 34 p.
- Theobald, P.K., Jr. and Thompson, C.E.
1959a: Reconnaissance exploration by analysis of heavy mineral concentrates (abs.); Min. Eng., v. 11, no. 1, p. 40.
1959b: Geochemical prospecting with heavy-mineral concentrates used to locate a tungsten deposit; U.S. Geol. Surv., Circ. 411, p. 1-13.
- Thomson, Ian
1976: Geochemical studies in central-west Brazil; Final report of the pilot phase of the Projeto Geofisico Brasil-Canada, DNPM, Brazil, 258 p.
- Topping, N.J.
1976: Regional geochemical drainage reconnaissance in the tribal trust lands; in Viewing, K.A., 7th Annual Rept., Inst. Min. Res. Univ. Rhodesia, p. 49-51.
- Tripp, R.B., Curtin, G.C., Day, G.W., Karlson, R.C., and Marsh, S.P.
1976: Maps showing mineralogical and geochemical data for heavy-mineral concentrates in the Tanacross quadrangle, Alaska; U.S. Geol. Surv., Misc. Field Studies Map MF-767.
- Tweto, Odgen
1960: Scheelite in the Precambrian gneisses of Colorado; Econ. Geol., v. 55, no. 7, p. 1406-1428.
- Urquidi-Barrau, F.
1973: Regional geochemical variations related to base metal mineralization in Wales; unpubl. Ph.D. thesis, Univ. London.
- Ward, F.N.
1951: A field method for the determination of tungsten in soils; U.S. Geol. Surv., Circ. 119, 4 p.
- Ward, F.N., Lakin, H.W., Canney, F.W. et al.
1963: Analytical methods used in geochemical exploration by the U.S. Geological Survey; U.S. Geol. Surv., Bull. 1152, p. 25.
- Webb, J.S.
1970: Some geological applications of regional geochemical reconnaissance; Proc. Geol. Assoc., v. 81, p. 585-594.
1975: Environmental problems and the exploration geochemist; in Geochemical Exploration 1974, Elsevier Publ. Co., Amsterdam, p. 5-17.
- Webb, J.S., Lowenstein, P.L., Howarth, R.J., Nichol, I., and Foster, R.
1973: Sampling, analytical and data processing techniques (for provisional geochemical atlas of Northern Ireland); Applied Geochem. Research Group, Imperial College, London, Tech. Comm. no. 61.
- Webb, J.S., Nichol, I., and Thornton, I.
1968: The broadening scope of regional geochemical reconnaissance; 23rd. Int. Geol. Cong., Prague, v. 6, p. 131-147.
- Whitney, P.R.
1975: Relationship of manganese-iron oxides and associated heavy metals to grain size in stream sediments; J. Geochem. Explor., v. 4, p. 251-263.