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Problems Associated with the Application of Geochemical Methods of Exploration in Cornwall, England

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ABSTRACT

In recent years, during the resurgence of interest in the mineral potential of Cornwall, geochemical methods of exploration have been applied with varying degrees of success in the county. From over 600 mines, one or more of the elements Sn, Cu, W, Pb, Zn, U, As, Fe, Sb and Mn have been recovered in economically important amounts, and cassiterite and wolframite have been won from many placers. Contamination, due to mining, mineral beneficiation and smelting operations, is widespread, and further contamination results from the presence of domestic and factory waste in the rivers, and the employment of metal-bearing fungicides by farmers.

Intensive investigations into the nature and origin of any contamination likely to occur in an area selected for exploration is necessary before decisions are reached concerning the feasibility of applying geochemical methods and, if feasible, the best program to adopt.

However, despite the magnitude of the contamination problem in Cornwall, geochemical methods, particularly those involving soil analysis, have, when prudently applied, facilitated the search for parallel lodes, permitted the extensions of known lodes and vein systems to be rapidly delineated, and pointed to a possible mineral potential in areas that had been neglected in the past.

Finally, on occasion, contamination due to mining has aided exploration. The local inversion of placers during past mining operations sometimes permits the parent lodes to be located with comparative ease by geochemical methods. Similarly, geochemical and allied studies of old mine dumps have revealed information concerning the lodes from which the discarded material came, which is very broadly equivalent to that which might be obtained from diamond drill cores.

> "But by skill we can also investigate hidden and concealed veins, by observing in the first place the bubbling waters of springs . . .: secondly, by examining the fragments of the veins which the torrents break off from the earth, . . . The soil also should be considered . . ."
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> (Agricola, p. 37)

INTRODUCTION

OF RECENT YEARS, there has been a resurgence of interest in the mineral potential of the Southwest of England, and particularly of the county of Cornwall, in which more than 600 underground mines have operated, largely within a belt about 75 miles long and 10 miles wide. From these mines, economically important amounts of tin, tungsten, copper, lead, zinc, uranium, arsenic, iron, antimony, silver and manganese have been recovered, together with occasional small 'parcels' of bismuth, nickel and cobalt ores. In addition, cassiterite and wolframite have been won from scores of fossil placers, and rivers receiving the tailings from tin mines have been the sites of numerous 'stream works' in which 'tailings cassiterite' was extracted from the active stream sediments and in which, on occasion, copper was recovered by the cementation process. Locally, from the water of adits of copper mines, in particular that from the County Adit (a plexus of 30 miles of tunnels draining the St. Day field), copper was recovered by the cementation process and ochre, for paint, was collected in settling pits. Finally, concentrations of cassiterite occurring in the uppermost horizons of certain beach deposits and in the neighbouring offshore active sediments, which have been developed by the reworking of mine tailings by marine agents, have been exploited to a limited extent.

The above ungarnished facts alone will serve to indicate that the applied geochemist is likely to be faced with a multitude of problems when he attempts to work in this metallogenic province. However, a broad picture of the geology of the Southwest (which is presented immediately below) is a necessary prelude to a full appreciation of the nature and magnitude of each of the problems posed by past mining and other industrial activities.

GENERAL GEOLOGY

Cornwall is a peninsula, about 75 miles long and with an average width of about 20 miles, which is fringed along the southeast by the Lizard and Dodman peninsulas and from these separated by what are probably exposed parts of a single thrust.

Ignoring the fringing peninsulas, the geology of which is complex, and which are unlikely to attract exploration groups (although a few unprofitable attempts to mine the native copper which occurs sporadically in the Lizard serpentine have been made in the last century), the region is composed of Devonian and Carboniferous, essentially non-calcareous, intensely folded and faulted regionally metamorphosed sedimentary rocks (the 'killas') which are often devoid of fossils and commonly lack 'marker horizons', and contemporaneous basic and ultrabasic intrusives and effusives (collectively termed 'greenstones') into which were intruded, in Permo-Carboniferous times, a high-level granitic batholith and related minor acid dikes and veins, and minettes. Aureoles of thermal metamorphism are clearly defined around the exposed granitic masses.

A phase of hydrothermal mineralization commenced before the last of the 'granite' had been emplaced and resulted first in the development of swarms of greisen-bordered veins in the apices of granitic cusps and mineralogically and structurally similar swarms in the metasediments overlying buried cusps. Individual veins of these bodies are narrow, often not more than a few inches in width, and of limited strike length. Their structure is commonly simple, although it may be surprisingly complex. The cassiterite and wolframite content of the swarms has made them of some economic interest, although this has never been very great because the grade of ore is low and mineralization is limited to a zone only a few hundreds of feet thick. The veins of the swarms may contain only a few mineral species, but the number present is often quite impressive. Arsenopyrite almost always occurs, and stannite and sphalerite are far from rare. The strike of these veins commonly parallels that of the associated granite ridges, of which the cusps are but high-spots, and in this they are similar to the mineralogically and structurally complex lodes from which the bulk of Cornwall's hardrock tin, tungsten, arsenic and copper ores have been obtained. Such lodes, which are usually steeply dipping and may be locally as much as 50 feet in width, although a width of a few feet is much more usual, may extend for several miles along the strike. Mineralization, of economic importance, may be traced down the dip for over 3,000 feet, although commonly the figure is considerably less. Primary zoning, in which high-temperature zinc and copper mineralization gives way in depth to tin, may be clearly defined in some lodes (as in the Main Lode of the Dolcoath mine), but telescoping is an equally important feature.

In due course, hypothermal mineralization gave way to mesothermal. On occasion, mesothermal species (galena, low-temperature sphalerite, siderite, etc.) were deposited in late-reopened hypothermal lodes and veins, and in places they developed along fault fissures striking parallel to neighbouring hypothermal lodes, but more commonly they were deposited in and along faults which trend approximately at right angles to the early lodes of the district.

During the Mesozoic, it is probable that most of the region was land and the higher parts of the granite were uncovered; then some of the orebodies must have been oxidized and eroded. Radiogenic dates indicate that at least incipient mesothermal-type mineralization occurred during both the Mesozoic and the Tertiary eras, and the presence of hot, chloride-rich springs in some of the mines may be taken as an indication that perhaps incipient mineralization is still taking place. Following the Alpine (Miocene) storm, all the land below the present 420-foot contour was probably submerged. This submergence was followed by emergence in stages during Pliocene time, a process which resulted in the formation of a series of marine platforms of which the so-called 400-ft one is by far the most extensive and, indeed, occupies much of the Peninsula.

Elevation continued into Pleistocene time, with the further development of at least three more platforms.

At this time, Cornwall was not far removed from the southern limit of the ice sheet and was subject to permafrost conditions. Temporarily during the Pleistocene, and again toward the end of the period, the climate became more temperate, and the melting of the snow and ice caused frost-shattered surface debris to migrate to lower levels. The result of this was that large quantities of boulders set in a matrix of sand and clay (which, beyond doubt, contained considerable quantities of cassiterite in the vicinity of tin-lode areas) were deposited in the valleys and locally on some of the platforms. This periglacial solifluction product is termed 'head of rubble' or simply 'head'.

Elevation continued into Recent times, probably raising the land a further 30 feet above the height it had attained during the Pleistocene. During this time, the climate was a very wet one and consequently the rejuvenated rivers carried large volumes of water, which enabled them to deepen their channels rapidly and at the same time wash and sort the debris in their valleys so that any cassiterite present tended to be concentrated immediately above the bedrock.

Following this stage was one in which forests flourished, and the debris from these accumulated on the 'low-level' gravels. This was succeeded by a period of depression which lowered the beds of the rivers at their mouths to as much as 40 ft below the present O.D. At the same time, the low-level gravels, already covered by the 'forest bed' and peat, were further buried beneath estuarine and marine deposits, and low-lying forests were submerged.

Finally, sand dunes developed where the cliffs were low, the beach gently shelving and rich in sand, and the shore exposed to strong onshore winds.

RELATION BETWEEN THE GEOLOGY AND THE SURFACE GEOCHEMICAL EXPLORATION PROGRAM

If complications due to contamination are ignored, the following facts, of importance when planning a geochemical exploration program in Cornwall, emerge from a consideration of its geology.

(i) — The county is well covered with rivers and hence the establishment of patterns of appropriate metals in the active stream sediments should facilitate the search for hardrock mineral deposits both on a regional and local scale and particularly during the reconnaissance stages of exploration.

This has, in fact, been well substantiated in Cornwall and it has also been established that, although in the case of tin a better contrast may, on occasion, be obtained if the minus-20-mesh (B.S.S.) fraction, rather than the minus-80-mesh one, is analyzed, in no case known to the writer would an anomaly have been missed had the finer fraction been employed and, furthermore, analysis of the finer fraction yields satisfactory results when investigating the distribution patterns of all the other metallic elements of economic interest in the county.

(ii) — Much of Cornwall possesses a thin residual soil cover and hence analyses of appropriately chosen samples of it usually reveal with great clarity the presence of sub-outcropping mineral deposits. In all studies made by the writer, the analyses of the minus-80-mesh (B.S.S.) fraction of samples from the B horizon yield perfectly satisfactory results.

When deciding whether or not a geochemical soil survey is likely to prove rewarding, the topography and height above sea level of the area must be given consideration. High-level basins within the granite are filled with a non-residual, and often quite thick, cover. Also, the 420-ft contour approximates the Pliocene strand line: below this line the ground is often comparatively flat; above it, the land often rises comparatively steeply due in part to the fact that the remnants of the Pliocene cliffs occur there. It follows, therefore, that immediately below the 420-ft contour the superficial cover may be composed locally of Pliocene littoral deposits on which rests head-of-rubble. Such deposits must be much more common than the literature indicates, and exploration at Pendarves, near Camborne, a few years ago, demonstrated that such deposits were locally of the order of 100 feet thick.

The lower-level platforms are all largely covered with raised beach material which is locally overlain by head-of-rubble and, in places, also by dune sand. These platforms, however, are all extremely narrow and do not, therefore, constitute a serious obstacle during exploration. Several mineralized areas are, however, covered by sand dunes, and the most important of these are in the Gwithian-Hayle area and at Perranporth. No satisfactory geochemical method has been devised for locating lodes beneath these features, although the distribution of zinc and copper in the calcareous hard-pan of the Perranporth dunes possibly reflects, in a very diffuse way, some of the underlying lodes (Hosking and Pisarski, unpublished studies). However, mining activities in the neighbourhood might have been partly responsible for the results obtained during these geochemical investigations.

(iii) — The characteristics of the lodes and veins dictate the sample interval, the distance between sample points on a given soil traverse line, the distance between traverse lines, the optimum bearing of the traverse lines and the metals to be determined.

Because the lodes and veins are narrow features, the distance between consecutive sample points on a given traverse must be modest. Most of the exploration work has been directed toward the discovery of further primary tin deposits and, because most of the tin in these occurs as the inert cassiterite, which is mechanically dispersed in the soil, experience has shown that whether one is attempting to trace a single lode or a vein swarm, it is usually unwise to have a sample interval greater than 25 feet and probably better to limit it, when prospecting for lodes, to 20 feet.

Although the strike lengths of lodes and vein swarms are subject to great variation, 200 feet constitutes a safe initial interval between consecutive traverse lines. At a later phase in the exploration it may, however, be wise to sample locally along intermediate traverses. In any given area, because the strikes of both lodes and vein swarms tend to parallel each other and those of associated granitic ridges and porphyry dikes, establishment of the optimum soil-traverse bearing (which, of course, is at right angles to the strike of these various features) is usually simple. However, in Cornwall, lodes with distinctly anomalous strikes do occasionally occur, so it is always important to analyze the results of a geochemical soil survey in an unbiased way.

Difficulties in locating and tracing tin lodes also stem from the following facts:

(a) A lode (such as the Dolcoath Main Lode) may contain rich deposits of cassiterite at depth and yet nearer the surface it may consist essentially of sphalerite and copper-bearing sulphides together with the products of their oxidation. Thus, although the soil over such a lode may contain distinctly anomalous concentrations of copper and zinc, its tin content is unlikely to be more than slightly anomalous.

(b) The width of a given lode may be subject to very marked variation along the strike. The great Flat Lode, near Camborne, for example, varies in width from several feet to a small fraction of an inch. It is self-evident that the tin content of soil samples from points along this major tin lode would also be subject to wide variation.

(c) The cassiterite in a lode may be essentially confined to shoots which are separated by tin-poor material, although this material may contain appreciable quantities of other 'ore' minerals. This constitutes part of the reason for determining not only tin but also certain associated lode metals when prospecting for primary tin deposits.

Experience has shown that, generally, the most useful pathfinder elements are arsenic, copper and zinc.

(iv) — The present climate and topography indicate that springs should be plentiful and hence the analysis of spring waters for 'heavy metals' might enable the presence of oxidizing ore deposits to be established. That this is, indeed, the case has been established in mid-Cornwall (Hosking, Derici and Lwin, 1962), but in the region under review it is unlikely to have any real value as a prospecting tool.

The common presence of marine caves also suggests that analysis of the efflorescences occurring in them might indicate the presence of oxidizing orebodies in the vicinity. That this is so has been established along the Hayle - St. Agnes coastal section (Hosking, unpublished studies), but this exploration technique is also likely to be of little or no importance in Cornwall.

THE CONTAMINATION PROBLEM

If Cornwall were a virgin piece of country, there is no doubt that geological methods would play a major role in the search for sub-outcropping deposits there, and there is no doubt that many discoveries would be largely due to its use, for what, after all, could be a better terrain for the applied geochemist than one which is well drained and, for the most part, covered by a thin residual soil. However, this happy state of affairs has been sadly altered by man's activities. These activities, the nature of the contamination accruing from them and the problems arising from them, which are of concern to the applied geochemist, are now discussed.

For the purpose of this paper, it is convenient to treat the problem under review under the following headings:—

1. Contamination due to mining and allied activities.
2. Contamination due to agricultural activities.
3. Contamination due to industries other than those covered by 1 and 2.
4. Contamination due to domestic and allied activities.

Contamination due to Mining and Allied Activities

This topic may be further broken down into the following the sub-sections:

(i) contamination due to mineral exploration;
(ii) contamination due to mining and quarrying;
(iii) contamination due to mineral beneficiation; and
(iv) contamination due to smelting.

Contamination due to Mineral Exploration

Particularly in the past, in Cornwall, the prospector looked for visible signs of mineralization such as lodes in cliff exposures and gossans. It is said that on occasion he located ore because of the smell of arsenious oxide during the burning of moorland vegetation and the deposition of visible arsenious oxide on the ground after the fire had burnt itself out. It is also claimed that sub-outcropping ore was found by dowsing and that, on occasion, the presence of 'lode lights' (Will-'o-the-Wisp?) guided the searcher to hitherto unknown deposits. Indeed, there is documented evidence in support of the fact that an old woman directed the mine captains of the Basset mines to a site beneath which a major copper orebody was subsequently discovered, and she claimed that it was the lode lights which drew her attention to the spot (Jenkin, 1927).

Cliff exposures were investigated by adits, and gossans and other linear indications of possible lodes were examined by pitting and trenching along lines both transverse to and along the strike of the features of interest. It is important to note that the spoil from each pit was piled just beyond the lip of the excavation, and it is clear that the prospectors were unable to differentiate between, say, a gossan due solely to pyrite and one which was derived from copper-bearing sulphides. These observations will be returned to later. It is sufficient to note here that they have been confirmed in the Nangiles Mine area.

The prospector was also interested in locating extensions of lodes, and on occasion he attempted to do this, when surface clues were lacking, by sinking a line of shafts, from which limited cross-cutting was done, across the strip of land in which he thought the lodes should run. An excellent example of this occurs to the west of Camborne: these workings were established in an attempt to locate the westward extensions of the great Dolcoath Main Lode together with less important parallel orebodies. Clearly, many of these prospect shafts, which are common in Cornwall, are surrounded solely by dumps of completely barren rock waste.

Contamination due to Mining and Quarrying

In the past, most of Cornwall's hardrock deposits were mined by underground methods, although there were a few notable opencast mines. The underground methods involved the sinking of numerous shafts on the line of the lodes and the spoil was accumulated around these shafts and now forms the so-called mine dumps. Drainage of the superficial parts of the mines was effected, whenever possible, by adits with portals opening either in valleys or in the cliff face. These adits often constituted very extensive underground drainage systems, the most notable being the so-called County Adit which drained the St. Day copper field and which was composed of an underground system of tunnels in all some 30 miles in length.

Within the Cornish mining field, there are literally thousands of mine dumps and, clearly, material from these centers may contaminate adjacent soil together with the water and sediments of neighbouring drainage systems.

Obviously, the nature and amount of contamination due to these dumps is dependent on many factors. The metals liberated from the dumps will, clearly, depend on the composition of the latter. As indicated earlier, many of the smaller dumps are memorials to ancient abortive prospects in barren terrain, and so no contamination, either of the drainage or of the adjacent soil, will occur near them. The quantity of a given 'heavy' metal leached from a dump will depend, among other things, not only on the absolute amount of the metal in the dump but also on its mode of occurrence, the various soluble species present, the relative amounts of the species present and the spatial relationships existing between the species. Thus, for example, chalcopyrite disseminated in a quartz matrix is much less easily attacked by 'surface agents' than liberated fragments of the sulphide. Chalcopyrite closely associated with abundant pyrite or marcasite will be decomposed much more readily than would be the case were it the sole sulphide present. When chalcopyrite is associated with, say, pyrite together with considerable arsenopyrite, much of the copper released during weathering is likely to be rapidly fixed as an insoluble arsenate. Furthermore, the copper in ore from the zone of oxidation is largely present as insoluble crystals of secondary minerals and so is much less readily mobilized than that occurring in the form of sulphides.

The amount of leaching which takes place in a given time must also be dependent on the physical characteristics of the dump components and on the morphology of the dump. Thus, if the dump is composed largely of large blocks of rock, water can penetrate readily through it; if, on the other hand, the dump contains a high percentage of clayey material it may be practically impermeable. Furthermore, the ease with which rain can penetrate a dump may be a function of the shape of its components, particularly when they are large. Clearly, slate slabs are likely to behave as a roof over the dump, whereas the much more equidimensional granite masses will permit ready access of rain. The amount of leaching must also depend, to some extent, on the shape of the dump — other things being equal, it is likely to decrease as the slope of the dump increases. It is probable, also, that assuming constant climatic conditions, the amount of heavy metals removed from the dump during any given year will often depend on its age. Maximum removal is to be expected during, and immediately after, the accumulation of the dump, as then the unstable minerals will be least protected by oxidized coatings and the dump will be in the most permeable state. Later, many of the unstable species will be protected from further sub-aerial attack by coatings of relatively impermeable secondary species, and the compaction of the dump by gravity, as well as the blocking of channels by the washing in of finer material from higher horizons, will tend to decrease losses by leaching. Furthermore, leaching of the superficial parts of the dump, and the concomitant accumulation of clay and other fine rock particles in run-off channels, will often initiate conditions amenable to plant growth, and in their turn the plants will reduce the amount of rain water entering the core of the dump.

Although the degree of contamination due to a mine dump depends, to a large extent, on the factors noted above, it is also partly governed by the nature of the terrain. It is obvious, for example, that whereas the zone of contaminated soil might be quite limited on flat ground, as was found to be the case in the vicinity of a copper-rich dump at Wheal Alfred, near Hayle (Hosking, 1955-56, p. 61), an extensive contamination fan might well be found below a dump on a steep hill- or valley-side. It is also clear that when a dump is situated on the banks of a river, components removed from it by leaching, sheet-wash and slumping will contaminate the associated drainage system, albeit in an erratic way, depending to no small extent on the distribution, duration and intensity of the rainfall, for an indefinite period of time.

From what has been noted earlier, it will be seen that wherever there has been mining in Cornwall the river water is likely to be seriously contaminated by the mine water — often heavily charged with copper, zinc, etc. — which emanates from adits. Interesting examples of heavy-metal contamination of stream water due to additions of adit water are found in the Perranporth area, and the extent of the contamination is shown in *Figure 1* (after Hosking and Pisarski, unpublished studies.) An extreme example is afforded by the waters of the Carnon river (West Cornwall), which are heavily contaminated by copper-rich waters emerging from the now partly collapsed County Adit which drains the St. Day mining field and was mentioned earlier. In the past, copper was recovered from its emerging waters by cementation (metallic copper, commonly seen in briquetted samples of the flotation products made by the Hydraulic Tin Company, which is recovering cassiterite from tailings farther down the valley, doubtless derives from this site) and the suspended iron oxides (with their absorbed metals) were collected in settling pits (now largely obscured by vegetation) and sold as ochre. At the present time, the adit water, because of its high acidity (and possibly also because of its high metal content) is not acceptable to local cattle. Some idea of the extent to which this water contaminates the river is indicated by the marked differences (apparent in the following analyses carried out by W. Brown, Hydraulic Tin mill superintendent, in 1959) in the 'metal' content of the latter when compared with that of a neighbouring stream at points not far removed from the mill of Hydraulic Tin Limited (for further details of this area see Hosking and Obial, 1966).

Components	Parts per Thousand
A. — CARNON STREAM	
Copper sulphate	0.006027
Iron sulphate	0.007612
Aluminum sulphate	0.08041
Magnesium sulphate	0.03585
Calcium chloride	0.06073
Magnesium chloride	0.00140
Sodium and potassium chlorides	0.05462
Colloidal silica	0.004949
Stannic oxide	0.000051
pH	5.2
B. — NEIGHBOURING STREAM	
Copper sulphate	nil
Iron sulphate	nil
Aluminum sulphate	nil
Magnesium sulphate	0.00621
Calcium chloride	0.04835
Magnesium chloride	nil
Sodium and potassium chlorides	0.0042
Colloidal silica	0.0218
Stannic oxide	0.0002
pH	6.4

A further spectacular pointer to the high metal content of the Carnon stream (which is due essentially to additions from the County Adit) is the fact that some of the oysters found at the point where the stream enters the Carrick Roads are distinctly green. The high zinc and copper content of these creatures may be simply demonstrated by subjecting a portion of a gill (without ashing it) to the ammonium mercuric thiocyanate test: this results in the immediate development of purple mossy dendrites (Hosking, unpublished studies).

How far appreciable contamination persists in a stream below the point of entry of an adit will depend on a number of factors, such as the size of the stream, the rate of flow of the water in it, the heavy-metal concentration of the adit water, the quantity of adit water entering the stream in unit time, the amount of organic matter, clay and ferric oxide present — substances which tend to remove at least some of the heavy-metal ions from the water by adsorption — and the climatic factors prevailing immediately before the period of examination. Rain usually lowers the metal concentration in the river waters by dilution, but if a heavy shower falls after a long dry period it might result in the flushing out of soluble oxidation products from the superficial parts of a mine and so cause an appreciable temporary increase in the metal content of the adit water, and hence of the stream into which it flows.

Despite the apparent reasonableness of the above statement, seepages from lodes in shallow workings at the Cam-

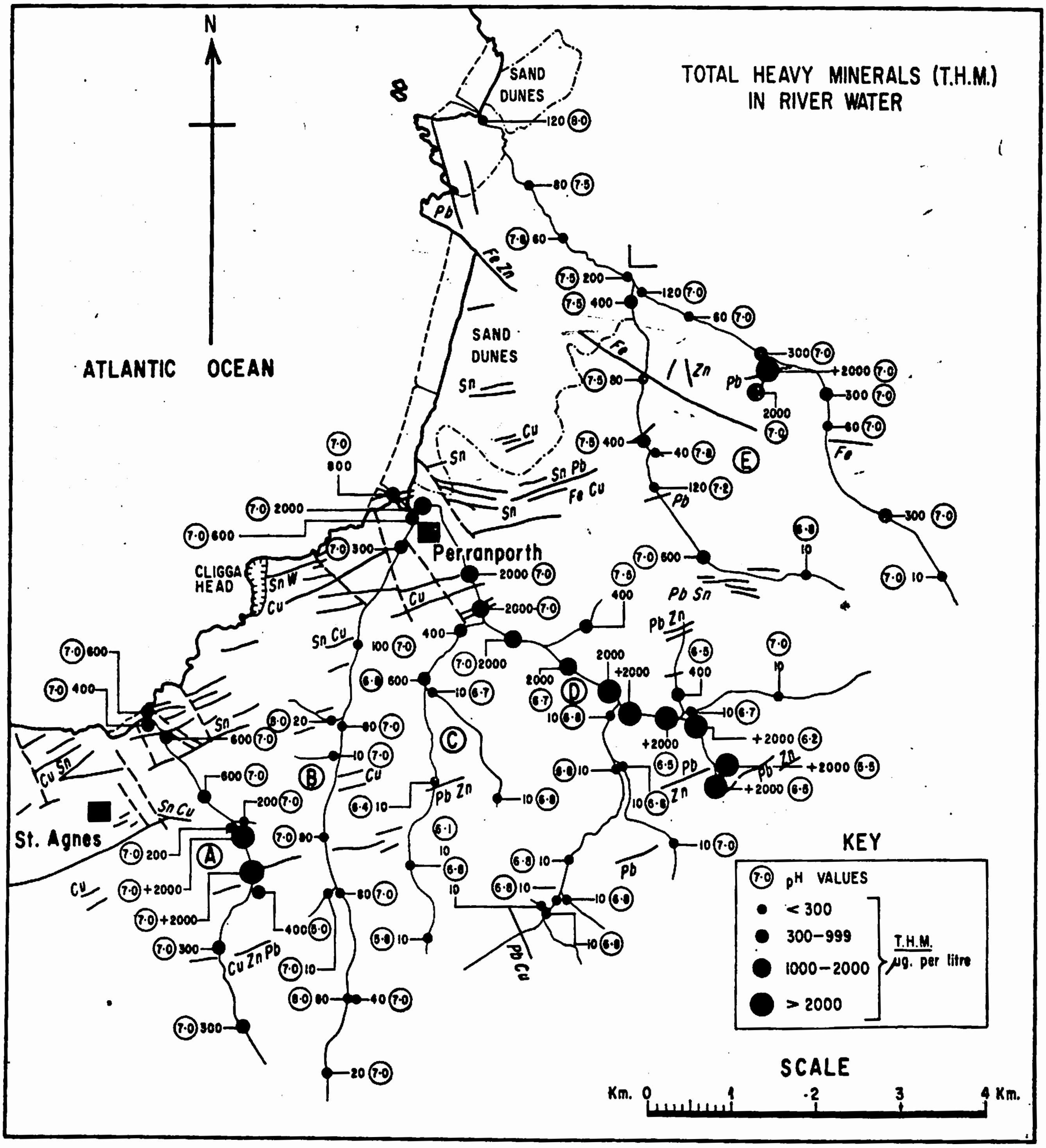

FIGURE 1 — Metal dispersion trains, due to contamination in the waters of rivers draining abandoned mines in the Perranporth district of West Cornwall (Hosking and Pisarski).

borne School of Mines experimental mine showed very little variation in their copper, zinc, iron and arsenic content throughout a period of a year. Furthermore, studies by Hosking and Pisarski (1965) demonstrated that the copper content in the minus-80-mesh (B.S.S.) fraction of sediment samples taken from streams in the St. Agnes - Perranporth area of Cornwall in the winter of 1960/61 differed but little from those collected from approximately the same spots in the summer of 1963. In the view of these workers, such a state of affairs could only be achieved by the addition of copper-charged water to the stream system followed by the removal of the copper in a constant manner, largely by absorption onto colloids. It is thought that the copper-charged water responsible for the copper in the sediments is essentially ground water which is discharged as seepages and from springs and adits into the stream systems, as additions from such sources would be made at very frequent intervals, if not continuously, throughout the year. Additions of copper made by surface run-off from dumps following periods of rain would be much more irregular, and as such water is only in contact with copper-bearing solids for a very short space of time its copper content would be relatively small. Similarly, additions of solid copper-bearing matter to the stream systems, as a result of surface run-off, wind and gravity, would also be made in a very irregular way, and, because of the heterogeneous nature of the dumps, the copper in these solids would be very variable. Furthermore, it would often not be particularly great as leaching tends to remove the copper from the fine superficial portions of the dumps preferentially, and it is these uppermost fractions which would tend to be carried into the rivers.

On occasion, the adit water flows via an ill-defined course to the main stream, and should the former become silted up, or during periods of increased flow following heavy rain, the adit water may flood the adjacent ground and deposit heavy metals there in amounts which are toxic to vegetation. Indeed, it is in the vicinity of adits particularly, although also to some lesser extent along rivers receiving mine tailings and over flattened soil-covered mine dumps, that plants are most commonly encountered which show physiological abnormalities due to excessive amounts of toxic elements in the soil. Thus, at Mr. Gray's farm, near Kehelland (Camborne area), the flooding of the meadow adjacent to the adit which drains West Violet Seton (an abandoned copper mine in which sphalerite, galena and arsenopyrite also occurred) has so charged the ground with toxic elements (see Table I) that the plants there — particularly the grasses and blackberries — show marked chlorosis (Hosking, 1955-56).

Metal dispersion trains also develop along paths taken by miners from the shaft head to the changing rooms or, before such amenities were normal units of a mine, to a warm place such as a boiler house (where they changed their clothes) or to their homes. Tributers working the dumps, etc., for tin ore after the closure of the Dolcoath mine, in the early twenties of this century, found such paths particularly remunerative. However, contamination along paths by cassiterite and other comparatively insoluble minerals is usually a superficial phenomenon. Thus, at the Castle-an-Dinas wolframite mine it was demonstrated that only the uppermost few inches of the paths used by the miners were contaminated by the tungsten mineral. It is also not inappropriate to note that at Castle-an-Dinas losses of ore from the buckets of the overhead transport system resulted in the establishment of a discontinuous superficial tungsten contamination train along which the highest values were to be found at the bases of the pylons, because it was there that the buckets received a jolt (Hosking and Curtis, 1961).

Given time, many of the mine paths become obscured by vegetation and so could provide somewhat puzzling or even misleading results during a geochemical exploration program, particularly if the samples analyzed were from the more superficial horizons, but possibly, also, if they were taken from deeper horizons. The latter possibility is, of course, most likely to be encountered when mobile elements such as copper and zinc are being determined and when the mines in these areas happened to be rich in ore containing sulphides of these elements associated with pyrite, marcasite or pyrrhotite; under such circumstances, the readily oxidizable iron sulphides would yield ferric sulphate, which is such an excellent solvent of sulphides of many of the other elements. Cell (electric) effects also permit much more rapid solution of some of the components of mixed sulphide ore than is achieved when these components occur in the same oxidizing environment but isolated from other sulphides.

Hardrock mines worked by dry open-cast methods for tin, tungsten and copper in Cornwall are surrounded by waste dumps and may be drained by adits so that they modify, by contamination, the natural metal distribution patterns in the soils and in the sediments and waters of the drainage systems in much the same way as does material derived from underground mines and so need no further comment.

Placer mines, however, pose their own particular problems to the geochemical prospector. Probably three-quarters of the Cornish rivers have contained a certain amount of stanniferous placer material and this characteristically occurs, as noted earlier, immediately above the bedrock. Most of these deposits have long since been exhausted and were mined by very primitive methods, so that by no means all the cassiterite was recovered. Areas so mined are pock-marked by small pits, some of which are now filled with water (as, for example, on the Carnmenellis granite mass) and bordered by spoil heaps. Certainly on the Carnmenellis granite, and probably elsewhere near outcropping granite, the richest placers, which were the residual ones, 'sat' virtually over the parent lodes, and in their vicinity the waste material in the dumps and rivers, where the concentrates were prepared, is richer in tin than elsewhere. Hence, geochemical analyses, particularly, of the sediments of the rivers in such areas reveal the sites of the rich residual placers and hence areas where sub-outcropping lodes are likely to occur and which might be traced by analyses of soils in the neighbourhood for tin.

TABLE I — Concentrations of Heavy Metals in Soil which is Periodically Subjected to Flooding by Adit Water from Wheal Violet Seton and on which Plants Show Marked Chlorosis

Sample No.	Soil Horizon	Parts per Million			pH
		Lead	Zinc	Copper	
1	A ('top-soil')	140	1,690	81	5.7
	B ('sub-soil')	116	1,600	72	5.9
2	A	284	760	68	5.6
	B	178	1,264	49	6.1
3	A	128	696	66	5.4
	B	140	408	44	6.0
Background values		20	50	30—40	6+

Placer mining in the lower reaches of the rivers was generally concerned with the recovery of transported cassiterite and so, because of such mining, high concentrations of tin may be found there in the superficial sediments which cannot be related to the mother lodes.

Contamination due to Mineral Beneficiation

Mills have been invariably built near rivers into which much of their tailings has been placed, and whenever this has happened the river becomes strongly contaminated down to the point were it flows into an estuary or into the sea, a feature which is, of course, due in part to the fact that most of the mines were within about 10 miles of the sea or an estuary. This feature is well demonstrated by the suspension of white clay, in this case from plants beneficiating china clay, which characterizes most of the course of the Fal and which, during periods of high tide, is deposited all over the saltings at the point where the river meets the estuary known as the Carrick Roads. It is also equally well demonstrated by the Red river, which carries a load of suspended red hematite from the Camborne-Redruth mining field to the sea, a distance of about 6 miles.

During the last century, rivers carrying tailings from important mining areas frequently became badly silted in their lower reaches, with the result that flooding was common

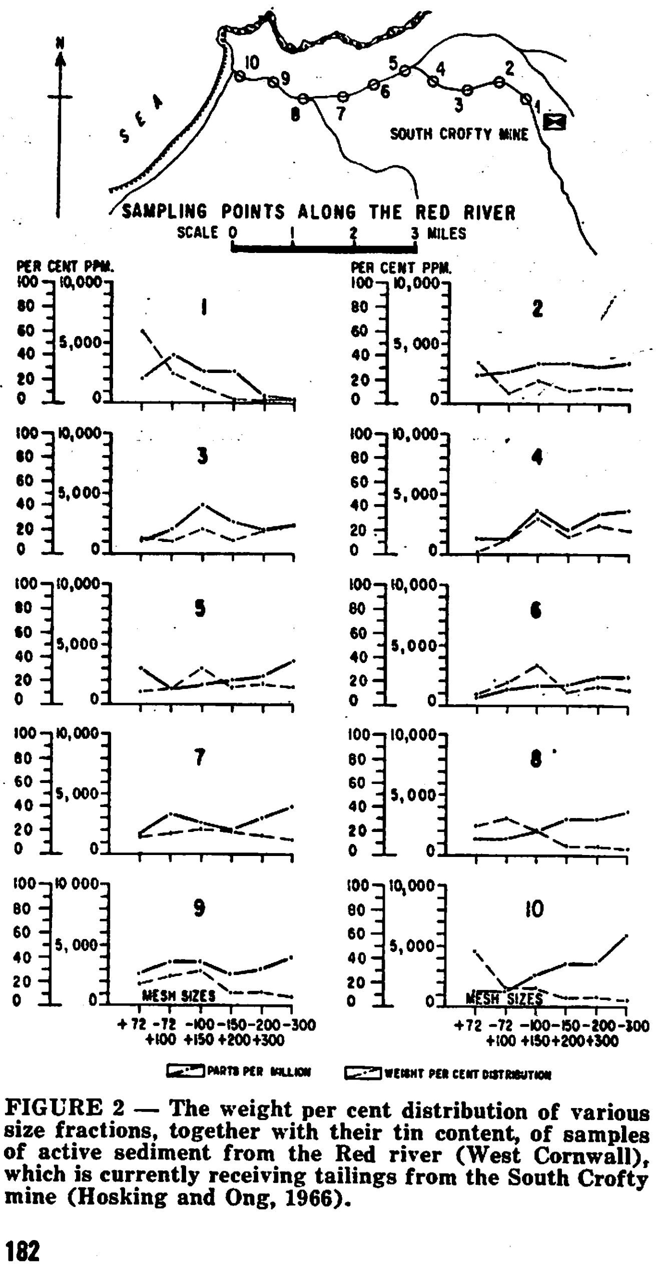

FIGURE 2 — The weight per cent distribution of various size fractions, together with their tin content, of samples of active sediment from the Red river (West Cornwall), which is currently receiving tailings from the South Crofty mine (Hosking and Ong, 1966).

there. Again, the Red river is a good example. As a consequence of the flooding, considerable quantities of copper sulphides, particularly chalcocite, were deposited over the flood plain, and as a result of repeated flooding much of the sulphide was quickly buried, thus escaping oxidation. Its presence in the alluvium of the area in question was commented upon by Stephens (1899, pp. 330-1), who noted it when he was Banka drilling in the area. Doubtless, during flooding, considerable amounts of other species, including cassiterite, were also distributed over the flood plain.

Some idea of the extent to which stream sediments were contaminated in the past by tin as a result of losses in the tailings from mills treating pimary ore is indicated by the findings of Thomas (1913, p. 57), who records that in 1890 the fifteen mines operating in the Camborne-Redruth district sold 7,131 tons of tin concentrate for £386,029, while streamers recovering cassiterite from the tailings of these mines in the Red and Portreath rivers sold, during the same period, 1,730 tons of concentrate for £69,208. The same writer (op. cit., p. 62) concluded that "if all sources of loss are taken into account and due allowance made for inaccurate weighing of the veinstuff before crushing, the average loss of tin in Cornish mines at the present time (i.e. 1913) is not less than 30 per cent". He further states that he does not know a Cornish mine where the loss is less than 30 per cent. He knows of some where it exceeds 40 per cent and in two cases which he investigated it approached 60 per cent.

The South Crofty tin mine, the tailings of which are now entering the Red river, probably does not recover more than 85 per cent of the cassiterite in its ore. At the 59th Annual General Meeting of the South Crofty shareholders, it was reported that during the working year 88,410 long tons of ore, grading 25.18 lbs of cassiterite, were treated in the mill (*Mining Journal*, May 28, 1965, p. 435). If all the tin lost during that period entered the Red river, it would represent an addition of about 104 long tons of cassiterite to that drainage system. Some idea of the distribution of the various size fractions in samples of the active sediment of the Red river, in 1960, and of their tin content is indicated in *Figure 2*. However, as stated by Hosking and Ong (1963-64, p. 365), "the results are to some extent a distortion of the truth, as the method of sampling was such that a portion of the finer fractions always escaped collection, and size analyses were affected by dry screening which permits some of the finer particles to remain attached to the coarse grains and, therefore, to report with the latter. In addition, the tin content was determined by the semiquantitative gallein/methylene blue colorimetric method".

A feature of great interest to the applied geochemist is the fact that rivers on which mills have not operated for many years are still heavily contaminated. This is so, for example, in the lead-antimony field of northeast Cornwall, where the minus-80-mesh (B.S.S.) fraction of the sediments of the River Allen shows distinctly anomalous lead values, varying from 3,000 to 150 ppm, for 5 miles below the long-abandoned mill of the Pengenna mine (Hosking, Davies and Ong, 1963). This phenomenon may be due to a number of factors, including the slow dispersion of excess tailings by the river, continual additions to the river of material from tailings dumps as a result of sheetwash, etc. and additions of material from the river bank, by slumping, etc., which had originally been removed from the river bed to prevent flooding. In addition, along those rivers draining tin fields, such as the Red river, so-called streamers operated throughout their length recovering the liberated cassiterite and generally ignoring that which occurred as components of composite grains in the sand fraction. Waste from these operations also constitutes sources from which cassiterite is liberated into the river. Each stream works contained a large number of settling pits, and even the long-abandoned ones which are now covered with vegetation commonly contain enough readily soluble zinc, etc. to cause the plants to exhibit chlorosis. In addition, they are often so rich in available arsenic that domestic animals brought in from non-mineralized areas and permitted to feed on the grass, etc., on and around such workings have been known to suffer from mild arsenic poisoning. (This, in fact, happened about 15 years ago to pedigree goats which were brought into Cornwall and grazed in the vicinity of an abandoned stream works near Reskadinnick on the Red river (D. Hunt, personal communication).

Arsenic contamination, however, was not solely due to arsenopyrite and other arsenic-bearing species that were components of the tailings, but also to the fact that beneficiation of the tin ore from the polymetallic lodes involved calcination in order to convert the sulphides and sulpharsenides into compounds which could readily be removed by gravity and/or magnetic methods from the cassiterite. Calcination also converted the arsenic present to As_2O_3 and As_2O_5 and these sublimates were in part trapped in flues from which they were periodically removed and sold. Sulphur dioxide derived from the calcination of the sulphides escaped via a stack or stacks at the end of the flues, and with it a not inappreciable quantity of the oxides of arsenic. Rain doubtless washed considerable amounts of these oxides out of the atmosphere and transported them to the neighbouring land. Indeed, in 1851, an action was brought against the owners of the Perran Smelting House (which they had converted to a calcination plant for the production of 'white arsenic') because of the deaths of cattle and other animals poisoned by grazing downwind of the stacks (Barton, 1967, p. 23). It remains to be established how long soil in the neighbourhood of arsenic stacks remains contaminated: it may well be that ultimately the oxides convert to arsenate ions which become fixed as relatively insoluble ferric arsenate.

Beneficiation has further locally increased the problems besetting those investigating the metal distribution patterns in the sediments of the Cornish streams because it was the practice to set up small custom mills on streams with an abundant water supply. Ore was transported to these mills for treatment. Consequently, in the sediments of a stream divorced from associated primary deposits, anomalous concentrations of metals, particularly tin, might be found. This was demonstrated in the Land's End area, for example, where below such a mill the minus-80-mesh stream-sediment fraction contained more than 5,000 ppm Sn (Hosking *et al.*, 1964, p. 24).

Mills established for teaching and research purposes, like customs mills, are likely to add 'foreign' elements to the local drainage systems. Such a mill is that of the Camborne School of Mines, which is situated near the village of Troon. All manner of local and foreign ore is examined there and, consequently, a most interesting metal assemblage is found in the stream receiving its tailings. In this area, a few years ago, a geochemist, unaware of the nature of the work in this mill, was elated when he found a high tantalum content in the stream sediments of the area! It is also to be remembered that on occasion soluble metallic compounds may be employed during the processing of ores and clays, and these also may report in geochemically significant concentrations in the sediments of the streams receiving the tailings.

The mill of the Hydraulic Tin Company, at Bissoe, which was referred to earlier, is also worth mentioning here, as there not only is virgin stanniferous placer material treated, but also tailings derived from now-abandoned mines farther up the river, dump material from idle mines in the area and tailings from the old neighbouring arsenic calciner which, during its operation, also imported material from many mines. Some idea of the variety of elements which might, through the normal milling losses, be incorporated into the sediments of the Carnon stream, and hence into those of the Carrick Roads estuary, is indicated by the following analysis of a sample of mill float, from Hydraulic Tin Limited, which was collected in 1958 (Hosking and Obial, 1966, p. 23).

Element (or oxide)	Per Cent
Silver	0.00935
Gold	0.00005
Tin	1.19
Lead	0.72
Copper	12.90
Bismuth	0.094
Arsenic	9.30
Antimony	0.11
Selenium	0.020
Tellurium	nil
Iron	35.66
Alumina	0.24
Titania	0.035
Manganese	0.01
Zinc	1.75
Nickel	0.02
Cobalt	0.015
Lime	0.02
Magnesia	0.08
Tungstic oxide (WO_3)	nil
Silica	0.33
Sulphur	37.20
Chlorine	tr.
Phosphorus pentoxide	tr.
Fluorine	nil
Oxygen and combined water (by difference)	0.29
	100.00

It is also probable that the overloading of a river by tailings, even if these are simply metal-free china clay, will modify and/or cover 'local' sediment, which may contain anomalous concentrations of metal due to a primary ore-body, to such a degree that geochemical methods involving stream-sediment analysis will fail to establish the presence of an anomalous zone. However, on occasion, the presence of a lode in a valley through which flows a stream contaminated by tailings from mines nearer its headwaters may be established by the analysis of the stream sediments; of course, in such a circumstance the threshold value is usually very high. Years ago, this fact was established by the writer (unpublished studies) during studies of a river, flowing through Chacewater, which had received tailings rich in tin, copper and arsenic from Wheal Busy.

Contamination due to Smelting

Barton (1967, p. 289) lists twenty-eight Cornish tin smelting houses but notes that there were others scattered throughout the country. The last of these, which was sited near Redruth, closed in 1931. In addition, copper was smelted in a few localities (e.g., Hayle and the St. Austell district) and so also was lead (e.g., Penpol and Charlestown). The sites of some of the smelters are unknown (Barton, *op. cit.*, p. 44) as, indeed, are the sites of the 'blowing houses', which were quite numerous, and which were the forerunners of the tin smelting houses.

When the smelters and blowing houses were operating, the ground in the neighbourhood of each must have been contamined by metal lost as 'fume'. In addition, piles of slag were accumulated around most of these places, and although much of this was not readily decomposed by agents of weathering, any copper, tin, etc., that occurred in the metallic state, and was in contact with the atmosphere, was likely to become mobilized. The fine components of slag heaps near rivers would also be particularly prone to transport by run-off, etc., and so were incorporated into the active sediments of the drainage system.

Locally, it was customary to cast the slag into rectangular blocks and to use them for building walls. Thus, in the Copper House area of Hayle, the retaining walls of the Hayle tidal pool, together with walls bordering certain business premises, and also even those of dwelling houses, have been constructed largely of such blocks of copper slag. Some of these show the blue-green stains of mobilized copper. Elsewhere, blocks of tin and copper slag have been built into hedges surrounding fields. During the 1939-45 war, several of the heaps of tin slag were removed and retreated by smelters outside the county. It seems likely that superficial soil samples, at least, from these sites may contain distinctly anomalous concentrations of tin.

Although no studies have been made in Cornwall aimed at determining if those areas once occupied by smelters are still contaminated and, if so, whether the extent and degree of the contamination decreases with time, it is thought by Hosking and Obial (1966, p. 35) that the high concentration of tin (locally more than 2,500 ppm) in the minus-80-mesh (B.S.S.) fraction of the active sediments in the Truro river may be due, in part, to the fact that there were a number of tin smelters in that area.

Contamination due to Agricultural Activities

Contamination due to agricultural activities stems essentially from the farmer's desire to reclaim land, to improve the quality of his land, to prevent his crops from suffering from disease and to ensure that his animals have adequate water.

Particularly in the past he reclaimed moorland by moving boulders and outcropping rocks (including gozzan) to the perimeter of his plot, where he piled them up to form hedges. Any prospect pits and trenches were filled in with the piles of spoil bordering each excavation. Both in the past and in the present, land occupied by shafts and dumps of waste rock was reclaimed by using the rocks to build hedges and form roads. Today, in addition, some or all of the dump may be bull-dozed down the shaft. Having flattened the area, soil was brought in from elsewhere to cover the site of the dump. Farmers lacking rock on their properties commonly acquired some for hedges from the nearest mine dump. Such operations, of course, tended to obscure obvious signs of mineralization and establish conditions for the development of numerous linear zones of contamination. Wherever a hedge exists which contains an abundance of mixed sulphide mine waste, the soil, for several feet on either side of the feature, tends to be contaminated, most commonly by zinc and/or copper, and often the contamination is very marked. For this reason, it is usual practice to refrain from taking soil samples within about 10 feet of such a hedge. Similar contamination zones fringe roads that have been constructed by the farmer from 'mine stone'.

Sites of dumps covered by a comparatively thin layer of soil brought in by the farmer are also areas which may yield distinctly misleading results to the unwary geochemist. Samples taken from such areas, particularly near the base of the soil, usually contain very variable concentrations of metal, and such results should, of course, be immediately suspect. Of course, examination of old maps, discussion with local farmers, etc., may reveal the former presence of mine dumps and, in any case, the unnatural character of the soil profile, together with the presence of blocks of fresh rock at shallow depths, provide certain evidence of what has occurred.

For reasons of economy of effort, should there be any prospect pits or trenches on the area being reclaimed, each was infilled, by the farmer, with its own spoil. Thus, there was very little dispersion of mineralized material from these excavations, and for this reason lodes can be traced quite effectively in such an area by geochemical methods involving soil analyses. This has been demonstrated very nicely in the Nangiles Mine area (Hosking and Radull, unpublished studies, 1968). There, the numerous pits and trenches which were excavated in the late 18th and early 19th centuries (and which were recorded on a map drawn in about 1810) but which were later filled in, and are no longer visible, have, clearly, not prevented the Sn-Cu-As-Zn-bearing lodes from being traced by geochemical means involving soil analyses (*Figures 3A* and *3B*). It is also interesting to note that although the early prospectors needed to pit and trench each lode before they could decide whether it consisted simply of useless quartz and pyrite or whether it contained elements of interest, namely tin, copper and zinc, geochemical methods enabled this to be done without such work.

The farmer improves the tilth of his land essentially by ploughing and the addition of fertilizers. Neither of these operations presents the applied geochemist with problems. It was demonstrated years ago, for example, that the position of the wolframite-bearing lode of Castle-an-Dinas could be clearly defined by the determination of tungsten in samples of soil taken from the B horizon about 15 inches below the general surface of a ploughed field (Hosking and Montambeault, 1956). Clearly, ploughing only disturbs the more superficial parts of a soil horizon, and such disturbance only involves a very limited lateral displacement.

There is no reason for thinking that in Cornwall the use of fertilizers introduces, on occasion, metal contamination, and in this respect it differs from areas elsewhere in England where the use of lime from lead-mineralized districts has caused the ground to become lead-contaminated. It may be, however, that the addition of phosphates may serve to fix elements such as copper and zinc, but a consideration of this is outside the scope of this paper.

Finally, the farmer employs fungicides, and some of these can, doubtless, effect a marked metal contamination of the ground. From this point of view, the two most important are Bordeaux Mixture, a copper-bearing solution which is used as a spray against potato blight, and a solution of calomel (mercurous chloride) into which the roots of young brassica plants are dipped, to prevent club root, before being transplanted in the fields. The dangers inherent in such practices to the unsuspecting geochemist need no further comment.

In the past, before farmers were very critical of the possible toxic effects of some mine waters, they sometimes piped such waters to various parts of their farms for consumption by their animals, sometimes with disastrous results. Thus, years ago, water from the abandoned shaft of the Trevinnick mine (in the antimony field of northeast Cornwall), which has a high antimony-lead-arsenic content, was piped by the local farmer to the drinking troughs in his farm. Use of this particular source was discontinued when it was found to have resulted in the death of some of his poultry! Metal-rich waste water from such a source might, over a prolonged period, result in the distinct contamination of those patches of soil into which it sank.

Finally, if one is prepared to regard the replacement of indigenous plants by imported ones of economic value as a particular sort of contamination, then it is reasonable to include in this paper the fact that such activities have militated against the search for mineral deposits in that they have tended to remove any indigenous plant species which by their presence indicate the disposition of sub-outcropping orebodies. Furthermore, in part by contaminating the soil with fertilizers, etc., the farmer has decreased the chances of a sub-outcropping mineral deposit being indicated by the fact that plants growing over it show physiological abnormalities. To date, Cornwall can boast only one indicator plant, *Erica vagans*, which is confined to magnesium-rich areas.

Contamination due to Industries Other Than Those Covered in the Previous Sections

Cornwall's other long-established industries, namely fishing, boat-building (on a small scale) and the manufacture, in the Camborne area, of mining and allied machinery and fuse, have caused no contamination of great importance to the applied geochemist. Even if the covering of mineralized areas by factory sites is placed in the category of contamination, the areas so covered were either so disturbed and contaminated by mining, as in the Camborne district, that the geochemist could do little of use there, except, possibly, investigate the dump material, or they are in barren areas, or they are so small that they could not seriously affect mineral exploration work. On the other hand, towns in the mining fields owe their growth largely to mining and allied industries, and this results in considerable areas of interest to the mining industry being inaccessible to the applied geochemist.

It is common practice to paint the bottoms of boats with a copper-bearing anti-fouling paint, but as the copper from this is only released at a very slow rate, and taking account of the density of boats in the creeks and estuaries, it can be safely concluded that copper contamination of the sediments because of this is infinitesimal. It is, of course, not likely that the Cornish estuarine deposits will ever be studied with a view to finding hardrock deposits, although it is just possible that some may be reinvestigated with a view to assessing their tin potential.

Contamination due to Domestic and Allied Activities

It is well known that effluents from domestic sources may effect marked pollution of rivers. Such effluents in any given region are unlikely to vary markedly, from a qualitative point of view, from one area to another. In Britain they may contain considerable concentrations of ionic copper and zinc (derived from taps and other domestic appliances composed of these elements) which are in part in solution and in part adsorbed on colloids. In addition, considerable amounts of copper and other metals occur in raw sewage as organo-metallic complexes which have been eliminated by men (and animals) in excreta and urine. Some idea of the concentrations of certain metals which may occur in urine and tapwater (in part derived from abandoned mines) may be obtained from Table II. (It is of interest to note that subject A was suffering from multiple scleroris.) (See Hosking *et al.*, 1965, pp. 34-35.)

The distribution pattern of domestic-derived 'effluent metals' in a natural drainage system is likely to be quite complex and to depend on many factors such as sewage outlets, the nature and extent of sewage treatment before it is released into the river systems, etc. Clearly, however, metals from such sources are likely to provide distinctly anomalous concentrations in river waters and/or sediments below settlements of appreciable size. In this respect, it is of interest to note that locally the minus-80-mesh (B.S.S.) fraction of stream sediments below Truro contains 400 ppm copper and 600 ppm zinc, and Truro is in an unmineralized area! (Hosking and Obial, 1966).

In the country districts, the water of wells in villages, farms, etc., is often anomalously high in zinc, due to the loss of galvanized buckets down the wells, and in the Castle-an-Dinas area of mid-Cornwall this was found to be so common that only water from flowing springs could be used with confidence during studies involving the natural heavy-metal content in the ground water (Hosking, Derici and Lwin, 1962).

In streams in the vicinity of settlements in Cornwall it is common to find metallic odds-and-ends which have been discarded; there is, however, no evidence that their presence has a significant effect on the metal content of the stream sediments. However, a locally high lead content in the sediments of one of the creeks of the Helford river was shown to be due to the presence of a high concentration of lead-glazed pieces of Medieaval pottery (Hosking, unpublished studies).

THE CIRCUMSTANCES UNDER WHICH GEOCHEMICAL METHODS HAVE BEEN, OR MAY BE, USED TO FACILITATE THE SEARCH FOR OREBODIES IN CORNWALL

In view of what has been written above, it might appear that there is little point in considering the use of geochemical methods when searching for ore deposits in Cornwall, and, indeed, there are those that hold this view. However, in fact, the situation is by no means as bleak as such people imagine. It is, of course, true that a very large number of the rivers are so contaminated that it is unlikely that analysis of their waters or sediments will generally facilitate the search for ore in a small area. However, it has earlier been noted that the presence of mother lodes has been indicated by the analysis of the sediments of streams of the Carnmenellis area that had been seriously contaminated locally by placer miners. Also, it has been shown, as a result of studies in the Carnmenellis area (Hosking, 1967, p. 289), the Land's End area (Hosking, *et al.*, 1964) and the antimony field of northeast Cornwall (Hosking *et al.*, 1963) and elsewhere, that if sediment samples from *all* the streams in an area of about 100 square miles are analyzed for appropriate elements, then consideration of the results in the light of the knowledge of the activities of the past and present industries, etc., which might cause contamination makes it possible to delineate those sub-areas in which any anomalous concentrations of metal in the

TABLE II — The Zinc-Copper-Lead Content of the First Tap Water Drawn in the Morning from a House in Camborne (Cornwall) and of the first Voided Urine of Two of its Occupants

	Zn		Cu		Pb	
	Concentration in µg/litre	Absolute amount voided (in µg)	Concentration in µg/litre	Absolute amount voided (in µg)	Concentration in µg/litre	Absolute amount voided (in µg)
Subject A.........	1,500.0	234.0	1.5	0.2	54.0	8.4
Subject B.........	266.0	133.0	10.0	5.0	9.0	4.5
Tap water........	86.9	—	12.5	—	10.0	—

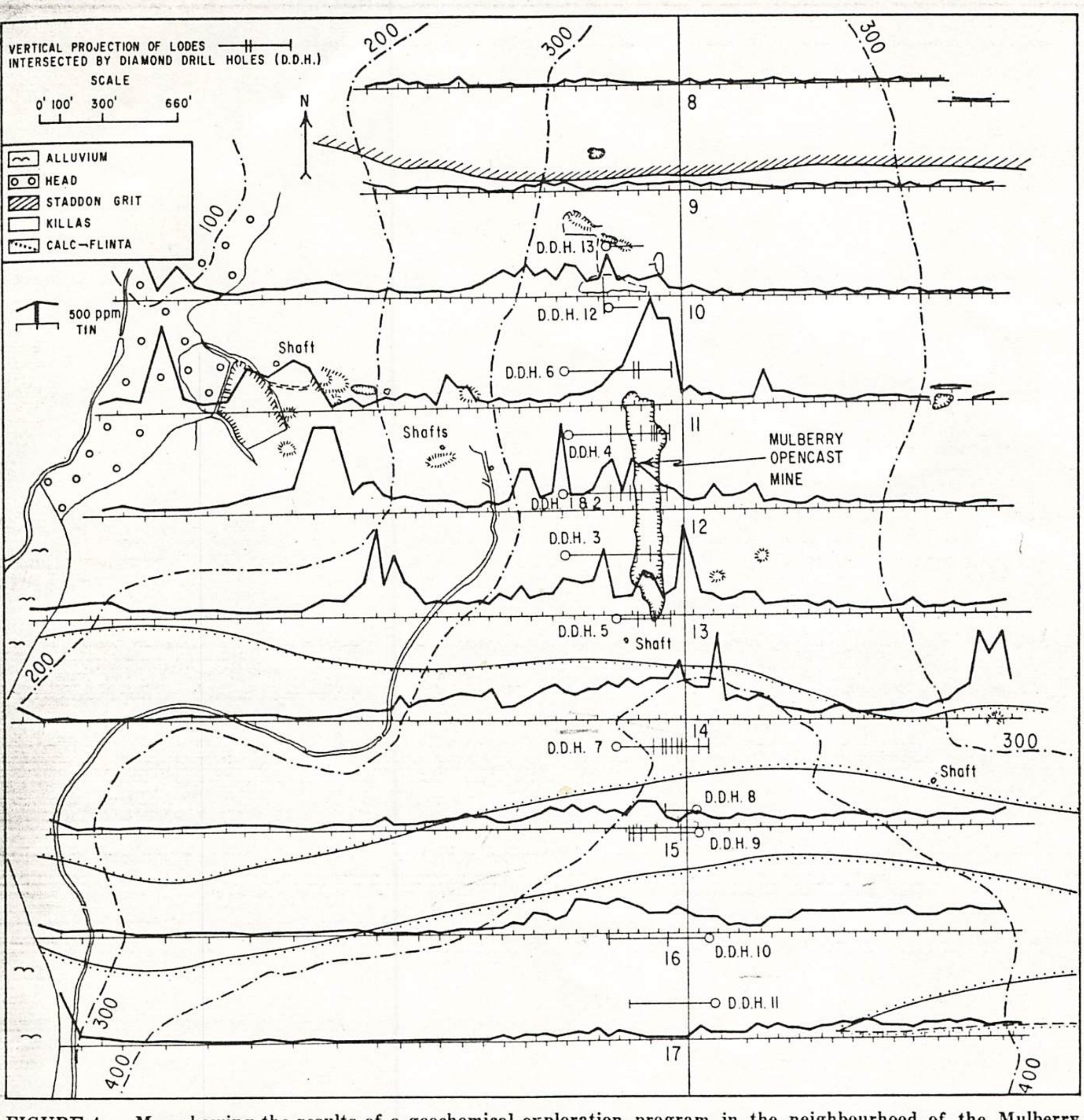

FIGURE 4 — Map showing the results of a geochemical exploration program in the neighbourhood of the Mulberry open-cast mine (Central Cornwall) in which the minus-80-mesh (B.S.S.) fractions of samples of soil were analyzed for tin (Hosking and Watters).

drainage systems are probably due to natural causes. In this way, certain areas of interest *were* established in the Land's End area (Hosking *et al.*, 1964) and in the antimony field noted above (Hosking *et al.*, 1963). Somewhat similarly, having established that the sediments of the Carnmenellis streams generally showed an antipathetic tin-lithium relationship, further search in an uncontaminated low-lithium area, in which both further stream-sediment and soil samples were analyzed for tin, established the presence of a hitherto unknown cassiterite-bearing lode, albeit poorly mineralized (Hosking, K. H. G., Hosking, J. A., and Thomas, G. B., unpublished studies, 1964).

It has also been demonstrated that the prudent application of geochemical methods of prospecting involving the analysis of soil samples is not without merit. Earlier, for example, it has been noted that sub-outcropping lodes were located successfully in the Nangiles area by such a method even though the area had been previously considerably disturbed. On occasion, also, as noted earlier, contamination due to mine dumps is so limited that uncontaminated B-horizon soil samples can be taken within 20 or 30 feet of them. This fact enabled certain copper lodes to be traced in the Wheal Alfred area even though one of them was only about 40 or 50 feet away from a heavily mineralized but small dump (Hosking, 1955-56, p. 61). In some areas, also, the mine dumps are so disposed that they pose no problems when sub-outcropping extensions of known lodes and/or parallel lodes are being sought by studies of the metal content in soils. At the Mulberry mine, Lanivet, where a stanniferous stockwork had been worked by opencast methods, the extension of the mineralized vein swarm was traced by geochemical methods, which involved the analysis of the minus-80-mesh (B.S.S.) fraction of soil samples for Sn, As, Cu, W, Zn, etc., for a considerable distance beyond the limits of the pit. Subsequent drilling demonstrated that the distribution of tin in the soil reflected very closely the distribution of the underlying tin-bearing veins (*Figure 4*) (Hosking and Watters, unpublished studies). In this area, as *Figure 4* shows, the tin content in the soil to the west of the pit is locally much greater than that over the orebody itself. These high tin values are due to contamination produced by gross disturbance of the ground during mining and mineral dressing activities. At Castle-an-Dinas, analysis of soil samples for tungsten enabled the sub-outcropping Main Lode to be located beyond the limits of the underground workings and, in addition, revealed the presence of an anomalously high tungsten zone to the west of the Main Lode which was subsequently intersected by a cross-cut and shown to be a weak system of wolframite-bearing veins (Hosking and Montambeault, 1956). Other examples of the successful application, in Cornwall, of geochemical exploration methods involving the analysis of soil samples are known to the writer, but the results of these are the property of mining companies and hence details cannot be divulged.

Naturally, the application, in Cornwall, of geochemical aids to mineral exploration involving the analysis of hard-rock samples is not complicated by any contamination problems other than those with which one has to contend elsewhere. In this field, the most rewarding work has involved the analysis of diamond drill core and sludges from diamond drilling and longhole drilling, underground samples, particularly vein material, and samples from mine dumps. Although several studies have been carried out in order to establish 'ore-metal' distribution patterns in surface granitic and other exposures, the results have given little reason for believing that such investigations are generally likely to facilitate the search for ore deposits in the South-west. Perhaps the most interesting of the results stemmed from the analysis of several hundreds of samples of granitic dikes (the 'elvans'). This work demonstrated that if the material contained more than about 10 ppm tin, tin-bearing veins occurred in the vicinity; however, should the sample contain only a few parts per million of the element in question, it might equally well have been collected literally a few inches away from an economically important tin lode or miles away from one! (Hosking and Lee, unpublished studies) (*Figure 5*).

A few years ago, during the early phases of the resurgence of interest in the tin potential of Cornwall, the sludges from diamond drilling operations were routinely analyzed for tin by the gallein-methylene blue method. This proved to be of great value in locating zones of interest cheaply and rapidly, something which could not always be done visually, even by those with much experience of the Cornish deposits, because of the small quantity of cassiterite (about 1 per cent) needed to make a lode a few feet wide of economic importance and because, at best, only some of a number of superficially similar lode intersections might be portions of tin-bearing bodies. One drawback to the method lay in the all-too-common failure to recover the sludge. For this and other reasons, it is now usual to scan the core with a P.I.F. Analyzer in order to locate stanniferous intersections.

A few years ago, through a study of diamond drill core from the South Crofty mine, it was established that, at least on occasion, there is a tendency for the density of early-developed mineralized fractures to increase toward a lode and for their tin content, also, to increase, albeit somewhat erratically (Hosking and Burn, unpublished studies). This interesting finding does not appear, however, to have been followed up by exploration companies to the extent which it merits. At the South Crofty mine, also, the analysis of sludge for tin, tungsten and arsenic by rapid colorimetric methods, from a series of longholes drilled in the 3A, B and C plexus of veins, which contain cassiterite,

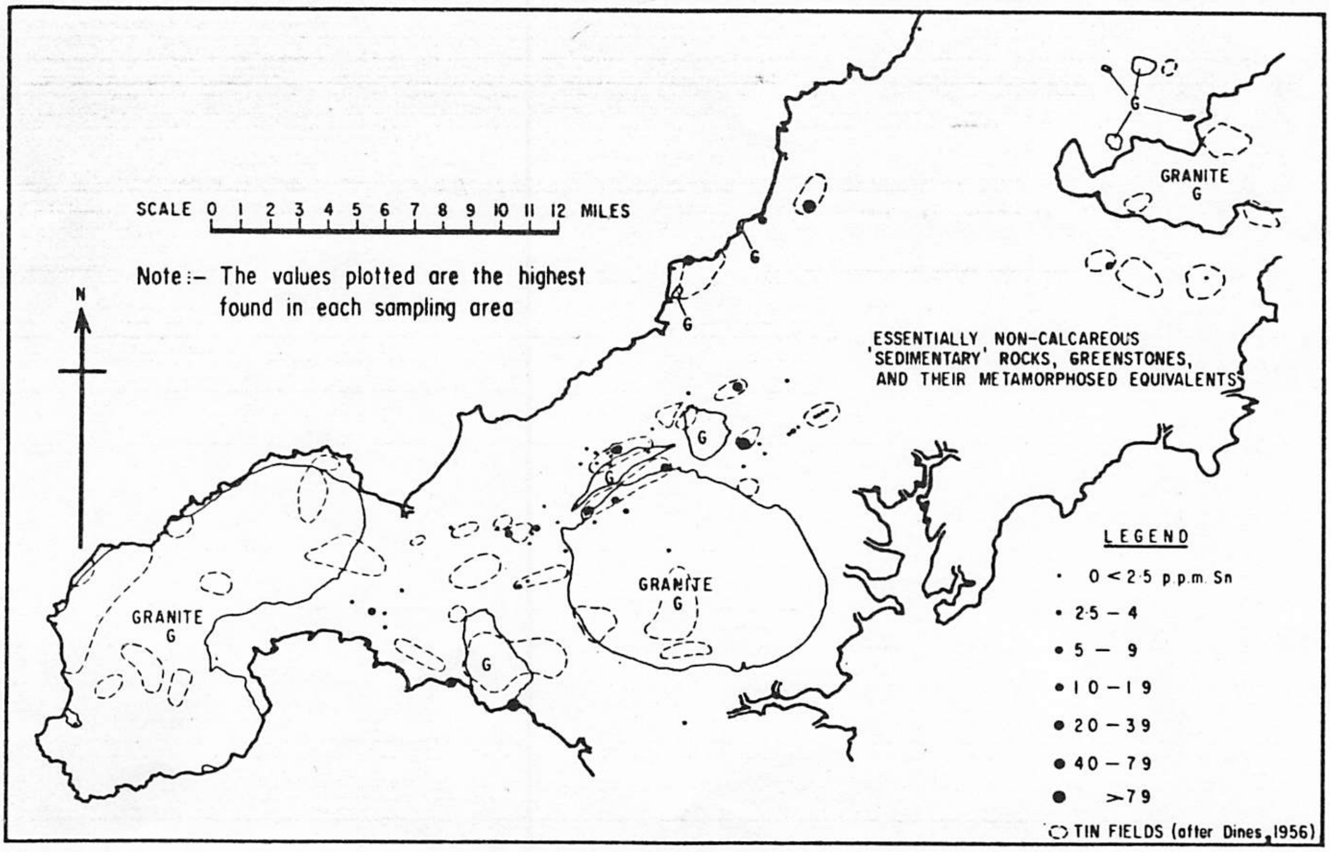

FIGURE 5 — Tin content of the porphyry dikes of West Cornwall (Hosking and Lee Moreno).

wolframite, arsenopyrite, etc., enabled metal distribution 'maps' of these elements to be constructed easily and quickly (Hosking and Burn, unpublished studies).

Based on the fact that preliminary studies by the writer at the Beralt Tin and Wolfram mine (Portugal) had indicated that the tungsten content of 'pure' quartz samples from productive bodies was significantly greater than that from barren ones, a somewhat similar study was carried out at the Geevor mine. This involved the sampling of about fifty veins from a cross-cut and subsequently analyzing the samples, by rapid colorimetric methods, for tin, copper, zinc and arsenic. The results were both unexpected and spectacular. Briefly, they indicated that only those veins which elsewhere in the mine developed into important tin lodes were characterized by distinctly anomalous concentrations of copper! (Garnett, 1967, pp. 158-9). That further work along these lines might facilitate the underground search for lodes in Cornwall is self-evident.

Finally, it has been demonstrated that geochemical studies involving the analysis by rapid semi-quantitative methods of samples from dumps of abandoned and perhaps little-documented mines might, on occasion, provide data of value to the prospector. During such studies, and particularly when the dump consists of material from a small mine, perhaps little more than a 'prospect', it is useful to regard the dump as equivalent to drill core which, instead of being preserved in labelled boxes, has been dumped in such a way that the core from the shallowest horizons constitutes the basal 'heart' of the heap and that from the deepest horizons constitutes its 'skin'. Rapid analysis of lode material from dumps of mines about which little was known, from a mineralogical point of view, in the Nangiles - Wheal Jane area, indicated that some contained lodes that were distinctly stanniferous, and hence might be of importance to those searching for tin deposits. In a number of cases, this fact would not have been appreciated had the study been confined to the examination of thin and polished sections. In addition, as the material examined during this investigation, which was not taken beyond the orientation stage, was collected from the dumps' surfaces, some idea of the depth from which it probably came could be estimated (Hosking, unpublished studies).

At the Ding Dong mine (Land's End area), cassiterite was recovered, by underground methods, from a plexus of narrow veins in granite. It was considered by some that in all probability the wall rock, for a considerable distance beyond the walls of the veins, contained appreciable cassiterite and that the grade might be such that the deposit might sustain an open-cast mine. Determination of the tin content, by the rapid gallein-methylene blue colorimetric method, of samples of wall rock collected from the dumps indicated that the tin content was extremely low, often less than 20 ppm, and that which was left in the mine was, therefore, unlikely to have any real value. This conclusion was subsequently confirmed by diamond drilling.

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