APPLIED GEOCHEMISTRY: STUDIES IN CORNWALL

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ABSTRACT

A suitable background against which to review the main theme is provided by brief accounts of the fundamentals of geochemical prospecting, together with a broad survey of the basic geology of Cornwall and of the major soil types encountered there.

The contamination problem is discussed in considerable detail, and it is established that of the several surface geochemical methods of prospecting that are available, only the one which depends on the analysis of soil-samples is likely to be of general use to the mining community. In addition, however, it is claimed that the investigation of drill-cores and wall-rock samples by geochemical methods might facilitate underground exploration.

Finally, the results of a number of geochemical studies are given which serve to indicate that, on occasion, in Cornwall, geochemical prospecting may be usefully applied to trace lode extensions, to search for parallel lodes, to examine virgin areas, to amplify existing knowledge of the composition of lodes, and to establish the nature of geophysical anomalies.

Geochemical prospecting, as defined by Hawkes (1957, p.226) "... includes any method of mineral exploration based on systematic measurement of one or more chemical properties of a naturally occurring material. The chemical property measured is most commonly the trace content of some element or group of elements; the naturally occurring material may be rock, soil, gossan, glacial debris, vegetation, stream sediment or water. The purpose of the measurements is the discovery of a geochemical "anomaly" or area where the chemical pattern indicates the presence of ore in the vicinity".

That geochemical surveys can facilitate the search for ore is due to the manner in which 'ore-forming' elements are distributed in the country-rock during, and possibly immediately before, the phase of ore-development, together with their mode of dispersion, during erosion of the ore-body, into the overlying soil and adjacent drainage systems.

Jedwab (1956) and others, have demonstrated that in some metallogenetic provinces the granitic masses with which lodes are intimately related are frequently characterised by considerably higher background concentrations of 'lode-forming' elements than their barren neighbours. Factors governing the entry, and manner of distribution, of these elements in the country-rock need not be discussed, but it is clear that if Jedwab's findings are generally true the analysis of granite samples taken over a widely-spaced grid might considerably expedite regional surveys which are carried out with a view to discovering those areas most likely to be ore-bearing, and, therefore, most worthy of detailed investigation.

During the formation of ore-bodies generally, the ore-forming elements tend to migrate into the country-rock beyond the obvious limits of the ore-body and even beyond the zone of wall-rock alteration. Thus, around an ore-body there is usually an envelope of rock containing higher than background concentrations of the ore-body elements. The width of the envelope around any given ore-body depends on many factors, such as the nature of the mineralising agents, the composition and physical characteristics of the wall-rock, etc. However, because such envelopes exist, and because they can be detected by geochemical methods of analysis, it is possible, on occasion, to establish the presence of a lode just beyond the end of a cross-cut or just outside the limit to which a core-drill has penetrated.

Often associated with ore-bodies are fissures which are barren. Ore-forming agents moved through some of these to the centre of deposition, and leaked away from this centre via others. Despite the fact that optical methods may not reveal the presence of ore-minerals in them, they may, nevertheless, contain much higher concentrations of the ore-forming elements than either the wall-rock or fissures which are not related to ore-bodies, and these phenomena can be revealed by geochemical studies. It follows, therefore, that examination of barren fissures which are encountered underground, by geochemical methods, may point the way to ore. Furthermore, should ' leak-away ' fissures intersect the surface, the analysis of samples taken from them, or from the soil overlying them, may reveal that they contain anomalous concentrations of metals when compared with those of the background, and so indicate the presence of ore-bodies which may, in fact, be at very considerable depths below the surface.

When ore-bodies are subjected to erosion their components are dispersed in the soil, ground and stream water and stream sediments. Many factors determine to what extent a given ' ore-element ' will be dispersed in residual soil overlying an ore-body, but for reasons of space only a few of the more important will be discussed, and for the same reason, and also because it is of minor importance to geochemical investigations in Cornwall, the question of metal dispersion in a non-residual cover will be omitted.

If the element is part of an insoluble ' ore-body ' mineral then its degree of movement in residual soil will be governed largely by the slope of the land. If, on the other hand, the element is liberated in a soluble form its movements away from the source will be largely dependent on the ability of the soil to immobilise it by processes of adsorption or precipitation. However, in this case also, a slope facilitates movement.

In acid soils, into which zinc and copper are normally liberated from the ore-body in soluble forms, the zinc migrates much more readily than the copper. It follows, then, that other things being equal, a sub-outcropping lode which contains both these elements can be located more readily by analysing the soil for zinc than for copper, as in the case of the former element a larger sampling interval can be employed. It also follows that in planning a soil survey the degree of mobility of the elements of interest must never be forgotten.

Anomalous concentrations of ore-body elements are encountered both in the water and the sediments of a stream below the point at which it intersects a lode.

Anomalous concentrations of those elements which are liberated in soluble form are frequently found not only in the stream water, but also in the sediments, because metallic ions tend to be adsorbed very readily by colloidal clay and organic material. As the concentrations of ore-derived elements in sediments are much less prone to change in response to varying climatic conditions than are those of stream water, there is a growing tendency amongst geochemists to confine their attention largely to sediments when conducting regional surveys. Naturally, insoluble minerals liberated from the ore-body will be found in anomalous concentrations below the point at which the body is intersected by the stream, and for oenturies lodes have been found by examining concentrates panned from rivers. The advantage of examining sediments by geochemical methods lies in the fact that anomalous metal concentrations can often be established at far greater distances below the source than is possible by simple physical and/or classical chemical methods of investigation.

Some species of plant accumulate certain metals from the soil in amounts which are roughly proportional to the concentrations of these metals in the soil. A given element may be preferentially stored in the stem, leaf, bark, root, etc. It follows, then, that in some instances plant analysis may be used to locate sub-outcropping ore-bodies. However, before this method of prospecting can be used in a given area a great deal of preliminary work has to be carried out in order to establish not only the most suitable species with which to work, but also to determine which part of the plant should be analysed. As the preliminary work, routine sampling and even the analyses, are somewhat prolonged, and it is likely that if anomalous metal concentrations occur in the plants of an area similar anomalies will also occur in the superficial horizons of the soil (due to the accumulation of dead plant material there), surveys depending on plant analyses are rarely justified.

The presence of high concentrations of heavy metals in the soil overlying an ore-body may be reflected in the composition of the plant community there, and, on occasion, this may differ so markedly from that of the community living over barren ground that the position of the ore-body is clear. Sometimes a given species is only found growing over the ore-body and such a one is termed an indicator plant. On the other hand, the presence of an ore-body may be indicated, not by changes in the numbers or kinds of species growing over it, but by reason of the plants there displaying physiological abnormalities, due principally to the toxic effect of the heavy metals derived from the ore-body. Obviously, careful search for botanical indications of hidden ore is well worth-while, and they are probably considerably commoner than has been generally realised. The fact remains, however, that often there are no obvious botanical indications, even when the soil over the ore is heavily charged with potentially toxic elements.

For a number of years the author has carried out researches aimed at arriving at a better understanding of the factors involved in the use of geochemical prospecting in non-glaciated temperate regions of the Cornish type. During these studies the ways in which geochemistry oan best be applied to facilitate the search for ore in Cornwall have been broadly established and in this paper it is the writer's major aim to record these. However, a real appreciation of the geochemical data can only be made against a background composed of, at least, a broad knowledge of the present climatic and soil characteristics, and of the general geological history of the county. For reasons of economy of space a disoussion of field procedures and analytic techniques are omitted, but these aspects of the work can be obtained by reading the works of Hawkes (1957) and of Lakin, et. al. (1952).

CLIMATE

The climate is of the temperate type with an average annual rainfall of c. 48 ins. Within the County, however, the annual rainfall often shows considerable variation from one area to another.

Although during the winter months, and particularly in January, the temperature frequently falls below zero, heavy falls of snow are not common, and except on the comparatively high moors in the east of the County, the snow rarely persists for more than a few days on the ground. During some winters in West Cornwall there are no falls of snow or only very slight ones.

GEOLOGY

For the purpose of this paper the Lizard Peninsula can be neglected, and so Cornwall can be regarded as consisting essentially of intensely folded Palaeozoic sediments which are, for the most part, non-calcareous, and with which are intercalated many comparatively small basic and ultrabasic intrusives and extrusives. These are penetrated by a granite batholith of Permo-Carboniferous age — the highest parts of which are now uncovered and form the dominant high areas of the County — which has thermally and pneumatolytically (or hydrothermally) altered the adjacent rocks that it penetrated. Genetically related to, and assooiated with, the granite are numerous minor intrusives — particularly porphyry dykes — and swarms of hypothermal Sn/W/Cu lodes which, in any given area, tend to strike parallel to the dykes there. Locally, both early lodes and dykes are faulted by mesothermal veins which strike approximately at right-angles to the tin-lodes and which may contain economically interesting amounts of such elements as zinc, lead, iron, silver, uranium, nickel, cobalt and antimony.

Primary zoning is often prominent in the mineralised areas.

Oxidation of the lode components is sometimes very pronounced and has, on occasion, led to the development of an embarrassing assemblage of supergene species. Furthermore, there is some evidence for believing that locally oxidation persists to depths below the surface of the order of a thousand feet (Hosking, 1950): on the other hand, certain ore-bodies — for instance, the wolframite/loellingite lode of Castle-an-Dinas — are only mildly oxidised, even near the surface.

Following the Alpine disturbances the Cornish area, which had been land during Mesozoic times, was almost totally submerged, and was represented solely by an archipelago consisting, for the most part, of granite islands. In the subsequent Pliocene, Pleistocene and Recent times the area was elevated in stages and this resulted in the development of a well-defined series of marine platforms of which the 400 ft. member is the most prominent.

Although Cornwall was not covered by an ice-sheet during the glacial phase it was, doubtless, subjected to permafrost conditions and when, towards the end of the Ice Age, the climate became more temperate and a thaw set in, masses of clay and rock slid into the valleys thus forming the so-called head-of-rubble — a typical periglacial solifluction product.

During the initial phases of the Recent times very rainy conditions prevailed and, consequently, rivers carried large volumes of water which enabled them to deepen their channels rapidly and at the same time to concentrate the heavy minerals (particularly cassiterite) in their sediments immediately above bed-rock. At the same time, torrents flowing from the higher regions on to the 400 ft. platform locally deposited considerable quantities of cassiterite there.

Following this period forests flourished, and the organic debris from these was deposited on the 'low-level' gravels. This was succeeded by a period of depression which lowered the river-beds by as much as 40 ft. below low-water level, thereby bringing about the development of rias. At the same time the low-level gravels (which were already covered with sand) and certain of the forests occupying low-lying areas, were invaded by the sea.

Finally, at the end of this stage, sand dunes were developed, usually on coastal areas which faced west, and where the cliffs were low and an abundance of sand was available.

SOIL CHARACTERISTICS

Although there are many different types of soil in Cornwall discussion will be limited to the two most commonly met with during geochemical investigations.

On those parts of the granite which are reasonably well-drained the soil is often only a foot-or-so thick and is made up of an A horizon consisting largely of raw humus derived from the partial breakdown of bracken, ericas and other calciphobes, and an underlying B horizon in which the clay often shows little variation in character from the top to the bottom.

Due to the frequent burning of the vegetation on some of the granite areas appreciable amounts of charcoal may accompany the humus, whilst the upper part of the clay horizon is terra-cotta in colour, due to incipient baking. Soil showing these characteristics near a copper lode on Carn Brea was interesting in that the copper content of the material near the top of the B horizon was almost double that of the clay near the base. This may be due to the conversion, as a result of the fires, of the soluble, and therefore readily leached copper compounds, to comparatively insoluble ones.

It is also of importance to note that where the granite slopes are thickly strewn with boulders the latter markedly restrict soil-creep — a fact which was very apparent when the spatial relationship between the House of Water lode, on the northern slopes of Carn Brea, and the heavy metal content of the soil in its vicinity was investigated (see Fig. 3.).

Where slate and greenstone areas are freely drained the soils usually show the characteristics of the Brown Earth group. When well-developed these soils are often about 36 ins. deep, and typical profiles just to the north of Camborne are composed of a surface layer — about 10 ins. thick — of dark-brown stony loam with a fairly high organic content, whilst below this is a brown stony clay loam which passes through yellowish loam clay to clay at depths ranging from 14 to 26 ins. In the same area immature soils are also encountered which consist of 6 to 12 ins. of dark-brown stony loam resting directly on weathered rock.

The work which has been carried out in West Cornwall shows that in well-drained soils, whilst the heavy metal content of the A and B horizons at a given sampling point may, or may not differ appreciably, samples from different points vertically below each other in the B horizon rarely show significant variations These findings agree with those of Millman who worked on the soils of the Gunnislake area (1957). It follows, therefore, that samples should normally be taken from the B horizon, and where the soil is shallow it is the writer's practice to take samples from the base of this horizon.

It might be thought that areas which have been ploughed repeatedly would not be particularly good geochemical prospecting sites, but it has been demonstrated over and over again that provided the samples are taken from well below the top of the B horizon the fact that the land has been ploughed is of no importance.

Soil overlying slate or greenstone adjacent to mine dumps containing actively oxidising sulphides is subjected to the leaching action of strongly acid solutions and then it loses its Brown Earth character to varying degrees and becomes somewhat podsolic. This has been noted, for example, in the vicinity of Wheal Alfred dumps, near Hayle, where pyrite, chalcopyrite, etc., are undergoing degradation. It is also of interest to note that there, despite the fact that the dump is steep-sided and reasonably rich in sulphides, the soil is not contaminated beyond about 20 ft. (Fig. 1A.) (See footnote.) Whilst this aspect of soil contamination requires much more study it is likely that in many cases it will prove much less serious to the geochemical prospector than has hitherto been assumed.

Footnote :—Furthermore, it is distinctly possible that this contamination at Wheal Alfred was effected — not by solutions leaching from the present dump — but by those derived from material that once covered the zone of contamination but which has since been removed.

THE CONTAMINATION PROBLEM

If Cornwall were a newly-discovered country it would be a paradise for the geochemical prospector, but now general surface prospecting is limited to those areas which have not been built over, or otherwise covered, and only some of these are sufficiently free from contamination, caused largely by the products of mining and allied activities, to be prospected by geochemical means. As an appreciation of possible sources of contamination is of fundamental importance to every geochemical survey, those sources which are most likely to be encountered in Cornwall are now discussed.

Adit water. Wherever there has been mining in Cornwall the river water is likely to be seriously contaminated by mine water — often heavily charge with copper, etc. — which emanates from a multitude of adits. How far appreciable contamination persists in a stream below the point of entry of adit water 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 the heavy metal ions from the water by adsorption — and the climatic conditions prevailing immediately before the period of examination. Rain usually lowers the metal concentration 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.

On occasion, the adit water flows via an ill-defined course to the main stream, and should the former become silted up, or during a period of 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, though to some lesser extent along rivers receiving mill tailings, 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, the flooding of the soil adjacent to the adit which drains Wheal Violet Seton (a disused copper mine in which sphalerite, galena and arsenopyrite also occurred) has so charged the ground with toxic elements (see Table 1) that the

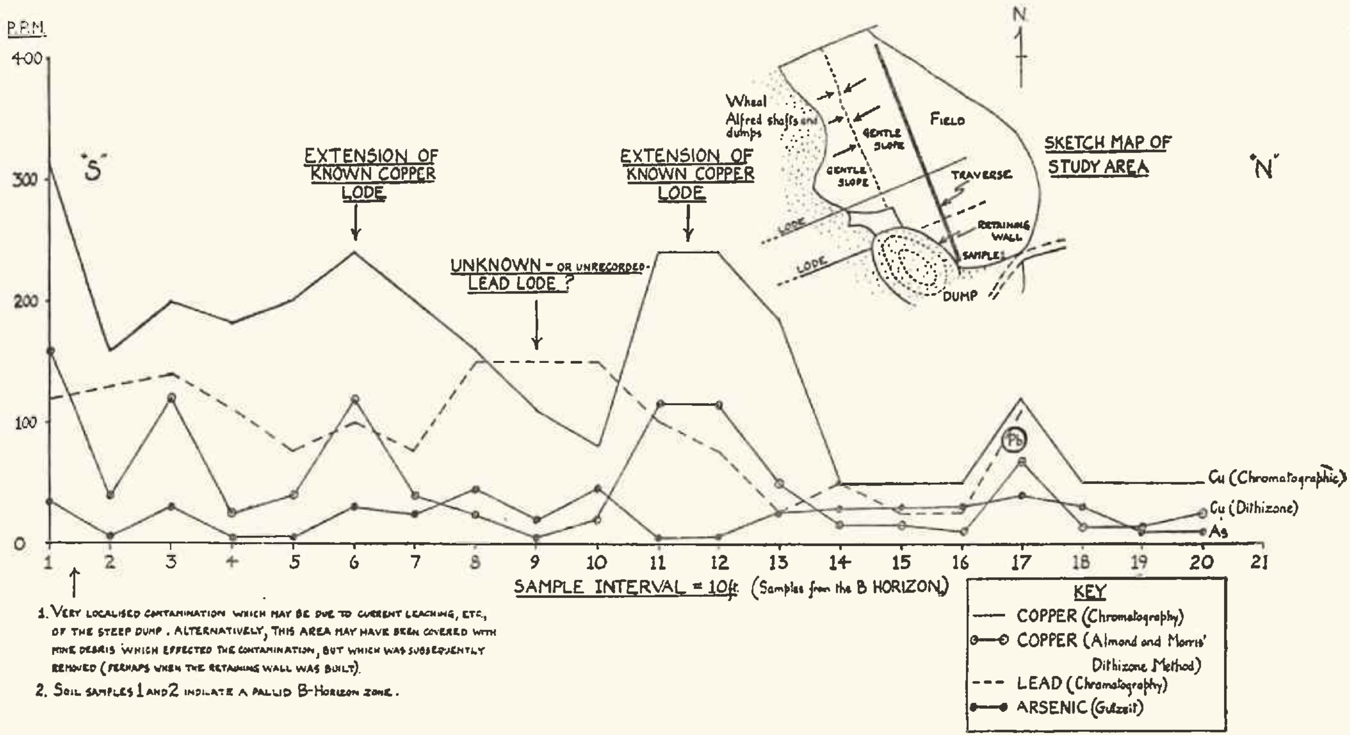

FIG. 1A. Distribution of copper, lead and arsenic, in the soil near Wheal Alfred, Hayle.

plants there — particularly the grasses and blackberries — are markedly chlorotic. (The grass leaves are 'tram-lined' — a phenomenon also noted near the Red River where tin-streamers have locally contaminated the soil by discharging the metal-rich waters and sediments of the river over it.)

TABLE 1.

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.	Horizon	Parts per million Lead	Zinc	Copper	pH
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+

Mill tailings. As the milling of ore in Cornwall has always involved the use of considerable quantities of water, mills were erected, whenever possible, at points on the drainage from where this water could be obtained, and, more particularly, into which 'used' water and tailings could be discharged. However, despite the dampness of the Cornish climate water had to be carefully conserved in the more intensely-mined areas (such as those near Camborne and Redruth) during the hey-day of the industry in order to meet the requirements of the mills. Indeed, water was, on occasion, 'carried' from one mill to another by a system of leats, and in the Carn Brea area traces of one still exist. When carrying out geochemical soil studies in such areas, infilled plant-covered leats might yield disturbing linear anomalies.

During the period of intensive tin-mining a number of small mills were almost invariably set up at points along those rivers which were receiving tailings from the mines, in order to recover cassiterite from them. It is probable that the mills of the older mines only recovered about half of the cassiterite in the feed, and of that which was lost, some was, doubtless, extremely fine — probably colloidal — and capable, therefore, of being transported considerable distances. Though each mill along a river collected a fraction of the cassiterite by ingeneous methods, considerable quantities continued down to the sea. (From the geochemical point of view it is important to realise that wherever tin-streamers have operated the soil adjacent to the rivers is likely to be heavily contaminated.)

One might cite the Red River as an excellent example of the type under review. This river, which rises in the Carn Menellis mass, has received tailings from a number of large mines. Half-a-dozen, or more, mills were scattered along its course, yet despite this, a sample of sand taken from it near the Godrevy bridge (i.e., at a point 5-6 miles from the nearest mine-mill which tailed into it) contained c. 10 lb. of tin per ton. Even though only one mine is now tailing into this river, its waters are heavily charged throughout its course with clay and finely-divided hematite, and as much of this material is colloidal it is likely that it is charged with adsorbed heavy metals. Furthermore, examination of sediments from near the mouth of the river has shown that sulphides — derived from the mines — are reasonably common constituents, and it is probable that those sulphides, which are 'jigged' down to the lower horizons of the stream sediment, where there is commonly a deficiency of oxygen, will survive indefinitely.

It is also pertinent to state that a recent examination of the sediments in the river which runs approximately north to south through Chacewater to Bissoe, and which received the tailings from Wheal Busy, established that they contain very high concentrations of tin (locally of the order of 1 per cent.) and also of copper.

Many streams are also being constantly contaminated by solutions containing heavy metals which are derived from the natural leaching of dumps situated in, or on the sides of the valleys. Furthermore, it is likely that, on occasion, appreciable amounts of finely-divided insoluble heavy minerals, notably cassiterite, are also transported by surface run-off from mine dumps into the permanent streams.

To summarise, then, the contamination of stream water and sediment by past and present mining and streaming activities may often make the systematic examination of drainage systems of little practical value in those very areas where ore is most likely to occur. It must be conceded, however, that on occasion it may be possible to establish bona fide anomalies even when the drainage contamination level is high. This method of prospecting may also facilitate the search for ore in areas which are known to be lode-bearing but which have, for one reason or another, been largely neglected by those interested in mining.

Mine dumps. That contamination of the drainage can arise from the leaching of mine dumps has been noted above, but the widespread occurrence of these potential centres of contamination demands that they should be considered in some detail.

Obviously, the nature and amount of contamination due to these dumps is dependent on many factors. The metals liberated from the dumps by leaching, etc., will clearly depend on the composition of the latter. Many of the small dumps are memorials to ancient, abortive prospects which failed to find ore, 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, not only on the amount of that metal in the dump, but also on its manner of occurrence therein. Thus, for example, chalcopyrite disseminated in a quartz matrix is largely protected from attack, whereas isolated fragments of the sulphide are not. Supergene minerals, developed in the zone of oxidation, are considerably more stable than the sulphides, so the lode-horizon from which the dump material was derived is important. The mineral association, and the relative amounts of the various species present, are also not without effect because it is probable that when, for example, sulphides are being attacked on the dump in the presence of abundant arsenopyrite, the heavy metals liberated from the sulphides are likely to be fixed as fairly insoluble arsenates. 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 shape of the dump. Thus, if the dump is composed largely of large lumps of rock, water can penetrate readily through it : if, on the other hand, the dump contains a high percentage of fine 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 fragments 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, the leaching is likely to be inversely proportional to the slope of the dump. It is probable, also, that assuming constant climatic conditions, the amount of heavy metals removed from the dump in unit time 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 oxidised coatings and the dump will be in its most permeable state. Later, many of the unstable species will be protected from further sub-aerial attack by coatings of relatively impermeable secondary minerals, whilst the compaction of the dump by gravity, and the blocking of channels by the washing in of fine 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.

Though the degree of contamination due to a mine dump depends, to a large extent, on the character of the dump, it is also partly governed by the nature of the terrain. It is obvious, for example, that whereas the zone of contaminated soil may be quite small on flat ground, an extensive contamination train might well be found below a dump on a steep hill- or valley-side.

Whenever a dump is encountered during a geochemical survey, steps are taken to determine its effects on the natural distribution patterns of 'ore-elements' in the vicinity. However, on many occasions, dumps have been flattened by farmers and then covered

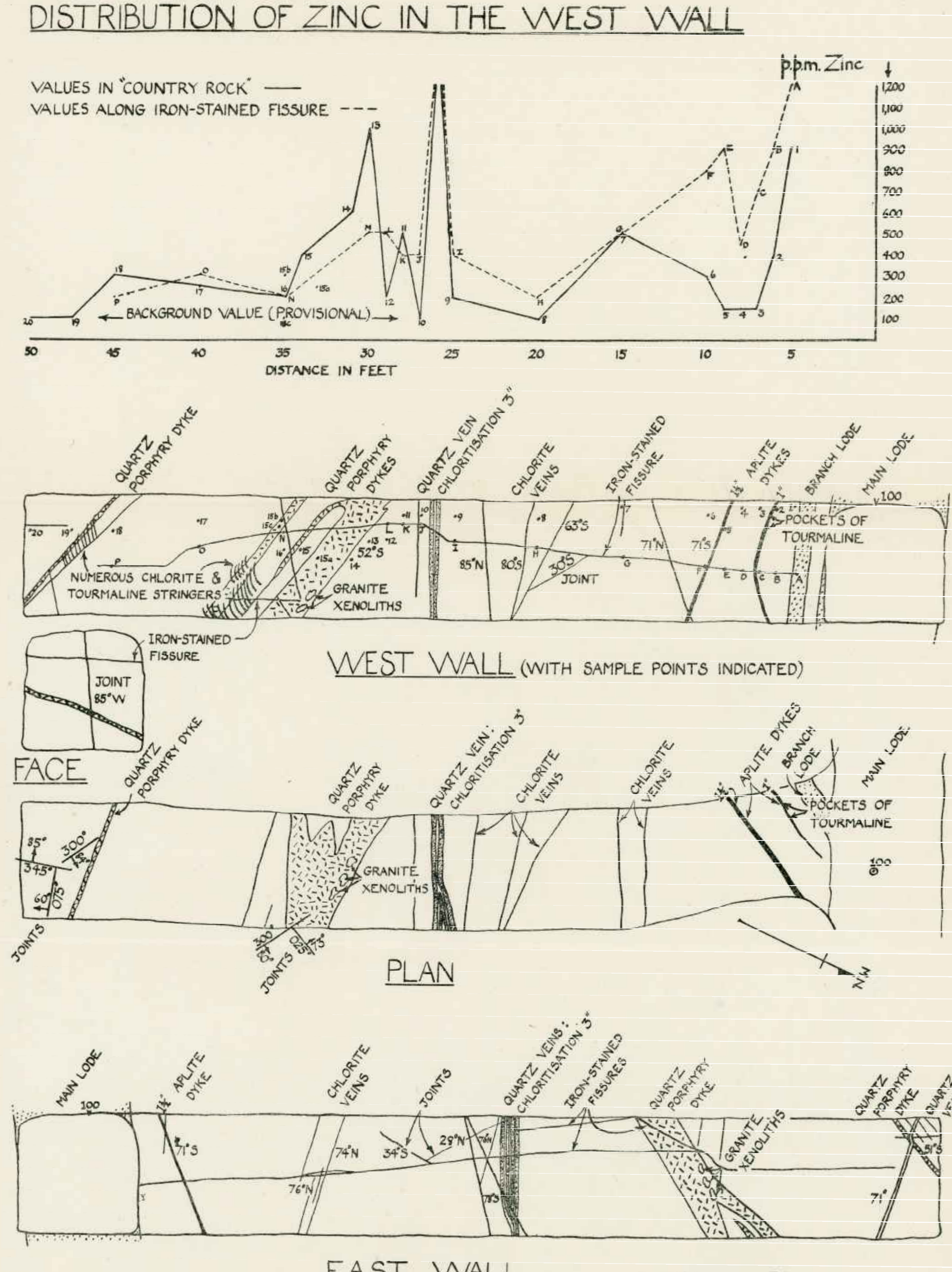

FIG. 1. Plan and section of cross-cut at King Edward Mine, Camborne, and graph indicating distribution of zinc. (Reproduced by permission of the Editor, School of Mines Magazine.)

with soil and grass. These may cause major difficulties, particularly as they may not be recorded on existing maps. (It is also to be noted that spoil from quarries and slag from tin and copper smelters have been similarly treated.)

Hedges, roads, miners' paths, etc. On the granite masses of Cornwall many of the hedges are of considerable antiquity and pre-date the era of active mining by many centuries. They, and indeed many of those that are of more recent origin, are composed of boulders taken from the ground when the neighbouring ground was cleared for farming. They are rarely active seats of contamination.

The hedges on the slate 'low-lands' are, on the whole, much younger than most on the granite, and whilst some are made up of rock from local quarries, many in the mining districts have been built of mine rock, and these are often highly mineralised. The latter are sources of contamination and high metal concentrations do occur in the soil near them, but usually the band of contamination is narrow. Furthermore, in certain areas it was the practice to use blocks of copper slag for building walls, so here is yet another source of contaminating substances.

Mine waste was often used in the construction of roads but it is only when these are on steep hill-sides that they are likely to cause serious contamination. However, 'short-cut' paths over fields and moors which were used by the miners, and have since become obliterated, may give rise to linear anomalies during geochemical surveys, particularly if the samples are taken from shallow horizons. However, whilst it is certain that these paths are often heavily charged with minerals that have dropped from the miners' boots, the writer has established at Castle-an-Dinas that samples taken from points 6 to 9 ins. below the surfaces of such paths are uncontaminated so far as tungsten and arsenic are concerned. Despite this, contamination might be found at considerably greater depths elsewhere, as it must depend on such factors as the solubility of the minerals deposited on the path, the slope of the path, etc.

Paths along which ore was carried are likely to be heavily contaminated — at least superficially — and the line over which aerial ore-transporting buckets operated is likely to be characterised by patches — rather than a continuous ribbon — of contamination.

Slender linear anomalies might also exist under copper electric-cables.

Smelters and arsenic calciners. From the point of view of contamination, what has been noted about mine-dumps is broadly applicable to tin and copper smelters, but, in addition, there is likely to be a fan-shaped zone of contamination to the leeward side of both smelter and arsenic calciner stacks due to the washing out of copper, arsenic, etc., from the fumes by rain. That this is so in the vicinity of arsenic calciners is indicated by the fact that 'foreign' cattle were poisoned when allowed to graze there.

Excavations. There are many Iron Age hut-circles, ditches, etc., scattered over the granite masses, and their construction often involved considerable soil disturbances which may result there in a somewhat diffuse heavy metal anomaly over a lode which is elsewhere characterised by a clear-cut anomaly. This state of affairs was encountered during an investigation of certain sub-outcropping lodes at the top of Carn Brea (which is discussed later), but here the issue was further complicated by trenches dug during the war-years.

THE CHOICE OF GEOCHEMICAL METHOD

So far as the application of geochemical methods to the search for ore in Cornwall is concerned it should be clear from the foregoing discussion that the systematic examination of stream waters and sediments is likely to be of little use. The remaining methods depend on the examination of hard-rock, or soil, or vegetation. The writer knows of no Cornish area where the systematic geochemical examination of outcropping rocks is likely to yield results of use to the mining industry in the near future. There is, of course, much information of fundamental importance to be obtained by examining the distribution of trace-elements in the various rock-types, and as such work has already demonstrated that the Cornish granites are unusually rich in caesium, lithium and rubidium (see Bowler, 1958, and footnote) it may ultimately be shown to be of considerable

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Footnote :—Bowler (p.21) notes that " the average (alkali content) of four main granites which have been analysed quantitatively is : Na 2.26%, K 4.29%, Li 635 p.p.m., Rb 420 p.p.m., Cs 47 p.p.m., K/Rb 102, and further data show that the granites of S.W. England are characteristically enriched in rare alkalis when compared with values for granites in other parts of the world."

economic value. However, geochemical examination of drill-cores and rock samples from cross-cuts may facilitate the search for ore underground. It may also assist in the correllation of lodes in a mine and in determining if a lode which is barren where it has been intersected is likely to be ore-bearing elsewhere.

Generally speaking, the extent to which geochemical prospect- can be usefully employed underground in Cornwall has not yet been adequately investigated. However, a small survey made at the mine of the Camborne School of Metalliferous Mining demonstrated that anomalous concentrations of acid-soluble zinc occurred in the granite for several feet from a sphalerite-rich lode, and well-beyond the zone of obvious wall-rock alteration. Although this work also revealed that the interpretation of the results of surveys of this type might be rendered somewhat difficult because of the fact that barren fissures and veins often contain markedly anomalous 'trace' concentrations of heavy metals, it established, nevertheless, that under such circumstances, geochemical studies may indicate that a zinc lode is being approached before there is any obvious indication of it. (See Hosking, et al. 1956, and Fig. 1.)

Geochemical soil surveys, despite the contamination problem, are, from fundamental considerations, those most likely to be of value in the search for ore in Cornwall. Because the soil is, for the most part, residual and shallow, the chances of finding sub-outcropping lodes are very high, and because of the general lack of dense vegetation the rate at which samples can be taken is also very high. In addition, permission to carry out such surveys over farming land is rarely refused as the auger method used to take up the necessary small amount of soil from each sampling point causes no damage to the fields.

Although study of the relationships between the heavy metal concentrations in plants and those in the soils in which they grow is likely to yield significant contributions to the corpus of geochemical knowledge, and although it has been established by Millman (1957) and the writer, that such work can lead to the discovery of ore, the fact remains that in Cornwall geochemical soil studies are much more easy and reliable than those based on plant analysis, and so no case can be made for the latter when the discovery of ore is the main object. In support of this contention it can be stated that the collection of plant samples, and their subsequent analysis, are much more time-consuming than the collection and analysis of samples of soil. Furthermore, as species often differ markedly in their response to variation in the heavy metal content of the soil in which they are growing, it follows that it is usually necessary to confine one's attention to a particular species when attempting to discover hidden ore, and frequently the most suitable species is distributed so erratically that a wholly satisfactory sampling pattern cannot be achieved. Obviously, a considerable amount of research is necessary to establish the most suitable species, and further investigations must be carried out in order to determine which part of the plant is the most reliable accumulator of the metal whose distribution is to be studied. In East Cornwall, Millman (op. cit.) established that " for lead, Betula sp. appears to be favourable ; for copper Quercus sp. ; and for zinc, Salix sp. and Betula sp. Fagus sp. was found to be inferior to the other species examined in its capacity to accumulate lead and zinc. No common species was found to show preferential concentration of tin ". He also notes that in the West of England, lead is concentrated preferentially in the twigs of several species as compared with their leaves, and that copper, tin, zinc and silver are concentrated in the leaves. The present writer has shown that on the granite mass of Carn Brea variations in the copper, arsenic, tungsten and manganese content of the soil are broadly reflected by the concentrations of these elements in the stems and leaves of Erica tetralix, and that this can be established by submitting the plant ash to the same colorimetric methods which are used to analyse soil. (Millman, it is to be noted, used semi-quantitative spectrographic methods.)

Further difficulties arise when employing bio-geochemical methods in Cornwall because the profiles are often much less smooth than those obtained by analysis of the soil, and because the anomalous areas — which are often narrow — are frequently the adequately covered by the accumulator selected for study. Both Millman and the writer have experienced these difficulties, and the erratic copper profile obtained by analysing the leaves and stems of Erica tetralix near a copper-bearing lode at Carn Brea (Fig. 3) is particularly relevant. (It is, however, worth noting that certain of the low copper values recorded near the lode are, doubtless, due to the fact that the plants in question were growing on a thin immature soil which lay on partly-covered boulders.)

Finally, Millman has proved that the problem is still further complicated, and he states that "replicate analyses of several samples of leaves and twigs of the same tree show deviations of up to 50% from the average content of leaves or twigs from the particular tree". (Op. cit., p.92.)

Because the Cornish soil is usually thin and residual it might be expected that sub-outcropping lodes would commonly liberate such quantities of metal-ions into the overlying soil that the presence of the hidden ore-bodies would be indicated by bands on which distinctive floral communities lived, or where the plants displayed distinct physiological abnormalities. Strangely, this is not the case. It is well known, however, that Erica vagans is an indicator of magnesium and that it grows in profusion on the Lizard serpentine and also in certain areas — such as Wheal Trevascus, near Gwinear Road Station, where the lodes contain ankerite or dolomite. No other Cornish indicator plant is known to the writer, nor has he seen a single example of a significant compositional change in the floral community near a sub-outcropping lode. To some extent this may be due to the fact that in many areas farming activities, etc., have, by destroying the native vegetation, destroyed the evidence.

That plants growing over lodes in Cornwall rarely show physiological abnormalities, is truly amazing, and in this connection Millman (op. cit., p.89) notes that in Nigeria plants may concentrate large amounts of heavy metals without displaying abnormalities. He also points out that the accumulation of metals by plants in Cornwall is much less spectacular and states that "a maximum of 1 p.p.m. Sn was found in Quercus sp. growing on soil containing 250 p.p.m. Sn, up to 360 p.p.m. Zn in Salix sp. on soil containing 300 p.p.m. Zn, and 12 p.p.m. Cu in Quercus sp. on soil containing 200 p.p.m. Cu". The present writer has, however, noted that Erica tetralix growing over, and near, the cassiterite/wolframite/arsenopyrite veins at the top of Carn Brea are distinctly stunted where the available evidence suggests the veins are most heavily mineralised. (See Fig. 2.) Whilst future investigations may demonstrate that subtle physiological abnormalities — such as peculiarities in the amino acid content, or in the root development — commonly characterise plants growing over lodes, it is clear that geobotanical studies will not help the searcher for ore in Cornwall. (See footnote.)

SPECIFIC WAYS IN WHICH APPLIED GEOCHEMISTRY MIGHT ASSIST THE CORNISH MINING INDUSTRY

Some might argue that as mining has been carried on in Cornwall for many centuries the distribution and nature of the lodes are so well known that even if difficulties due to contamination, and such-like, were overcome, the applied geochemist could do little or nothing to assist the mining industry. The writer, however, believes that not only can geochemistry facilitate the search for ore underground (as has already been noted), but, in addition, it can sometimes be profitably employed at the surface, as the following brief accounts of certain geochemical studies will show :—

It is well known that many of the older Cornish mines were opened on a 'shoe-string' and many of them were abandoned as soon as the lodes became sub-economic, despite the fact that many of the best Cornish lodes showed marked, and often quite unpredictable, variations in width and value along the strikes. It follows, therefore, that there must still be lodes in the County which have only been examined over very limited distances, and if it could be shown that these do, in fact, extend for considerable distances beyond the points at which they have been worked, they might, in

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Footnote :—Even on the mine dumps the flora usually does not display marked physiological abnormalities. However, it is clear that the nature and distribution of the floral population of the dumps is determined by many factors, and though this subject is to be treated in a separate paper, it can be stated here that in many cases the dominant factors are the degree to which leaching processes have removed toxic substances and the extent to which a substrate of clay particles, etc., suitable for plant growth, has accumulated as a result of the action of run-off. Thus, at Wheal Alfred, near Hayle, a small, lead-rich 'stepped' dump is characterised by the fact that the plant species decline in number and vigour from the top, most-leached platform to the base where there is standing metal-rich water. Furthermore, on many Cornish dumps the maximum vegetation occurs in the shallow — often somewhat sheltered run-off gulleys in which 'fines' have collected and where surface leaching is readily effected. Here, too, it is noticeable that plants tend to avoid the deeper metal-laden horizons by confining themselves largely to lateral — rather than vertical — root extension.

due course, be worthy of further development. If such lodes are sub-outcropping they could, in many cases at least, be traced by geochemical means, and it is the writer's opinion that such lodes might exist, for example, in the Godolphin-Tregonning areas and along the eastern part of the Land's End mass.

That such exploration offers no great difficulty is indicated by some work carried out by the writer at Carn Brea, near Camborne. On the fairly flat top of the Carn there are a few small greisen-bordered veins which strike parallel to the long axis of the granite mass. These veins — which do not exceed 2 to 3 ins. in width — consist of irregularly distributed masses of wolframite, cassiterite and arsenopyrite set in a quartz matrix. The wolframite is incipiently oxidised and some of the arsenopyrite has been converted to scorodite. The soil is never more than c. 18 ins. thick, and consists of a typical thin raw-humus-rich A horizon underlain by a B horizon — usually of brown clay. A limited amount of pitting exposed the lodes near the monument but they were only traced for a short distance. Analysis of B horizon soil samples taken at 10 ft. intervals along a number of traverses, which were very approximately at right-angles to the strike of the veins, established that the veins did extend for a considerable distance beyond the area which had been pitted. Furthermore, the distribution and magnitude of the various tin, tungsten and arsenic anomalies suggested that the economic minerals were erratically distributed and that — at least near the surface — mineralisation was strongest in the area which had been most intensively pitted. This work also established that it is necessary to employ a sample interval of not more than 10 ft. in order to pin-point such veins regardless of whether tin, tungsten or arsenic is used as the indicator element. It was also shown that whilst a slight manganese anomaly occurred over the lode — due presumably to manganese liberated from, or possibly in, wolframite — the element was not a particularly useful indicator of wolframite-bearing lodes (a fact which was also confirmed by other work which was carried out over the Castle-an-Dinas wolframite lode). It is of interest that colorimetric analyses of the ash of stems and leaves combined of Erica tetralix showed that anomalous arsenic and tungsten values occurred in the plants growing over the lode, but that the manganese content was somewhat erratic, and in air-dried plants approximated to that of the soil in which they had grown. (Fig. 2.)

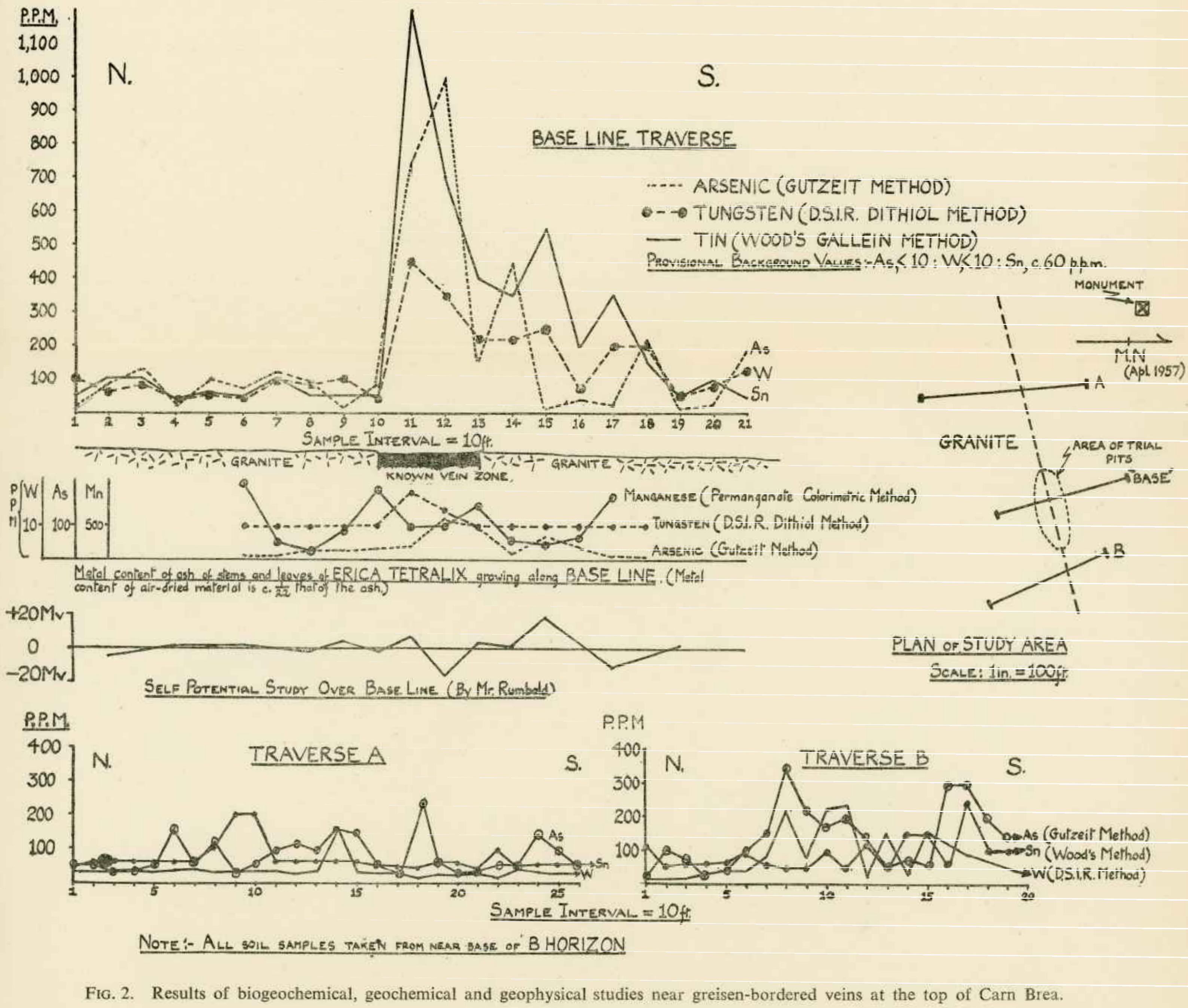

FIG. 2. Results of biogeochemical, geochemical and geophysical studies near greisen-bordered veins at the top of Carn Brea.

On the steep, boulder-strewn, north slope of Carn Brea a limited amount of trenching has been carried out on a lode which is closely associated with the roughly N.E.-S.W.-trending House of Water porphyry dyke. That this lode — which is not now exposed — developed along the granite/dyke junction is indicated by specimens in the pile of rock excavated by the early prospectors. The lode material consists essentially of arsenopyrite, together with minor amounts of chalcopyrite and pyrite, set in a chlorite and quartz matrix. Cassiterite has only been seen in thin section whilst wolframite has never been recorded. Samples were taken from the B horizon at 20 ft. intervals along approximately N.-S. traverse lines and these were analysed for tin, copper, arsenic and tungsten. Anomalous concentrations of each of the four elements were shown to exist in the vicinity of the lode, and, in addition, another lode, which was quite unknown to the writer, was established at c. 180 ft. north of the one which was the major subject of the study. Subsequently some preliminary work, which was carried out by Mr. Rumbold, indicated that these lodes, and also the greisen-bordered veins on the top of the Carn, could be revealed by self-potential methods, whilst the fact that anomalous copper values characterised the ash of Erica tetralix growing in the vicinity of the House of Water lode has been commented on earlier. (The results of analysing soil and plant samples from one of the traverse lines appear in Fig. 3.)

The results of this study indicate that geochemical prospecting can be carried out over rough, boulder-strewn granite terrain. They also establish the interesting fact — which is noted earlier — that the boulders retard soil creep and so tend to prevent a marked displacement of the anomaly down the slope. Furthermore, they have shown that geochemical methods may reveal the presence of hitherto unsuspected elements in lodes (in this case tungsten) and so might be used to differentiate between those lodes which contain a given element and those which do not, when other means fail. Finally, they have shown that geochemical studies might be employed to reveal the cause of a geophysical anomaly, and in this last connection it is worth noting a further example of the value of combined geophysical and geochemical investigations. Brokenshire (1948) recorded that he had, in a somewhat unsatisfactory manner, traced the Bolenowe Lode, near Troon, by carrying out a self-potential survey. Recently the author collected soil samples along

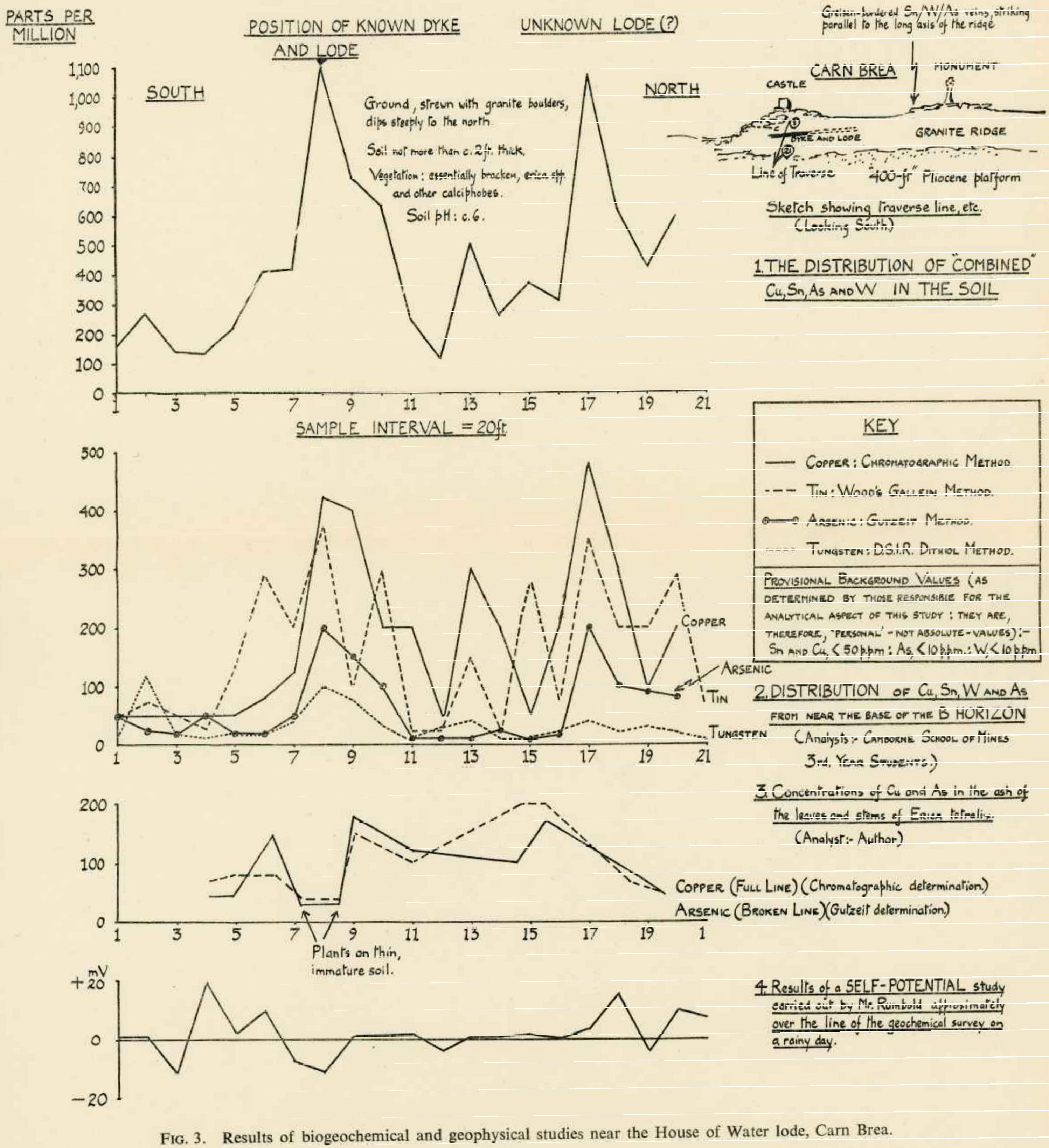

FIG. 3. Results of biogeochemical and geophysical studies near the House of Water lode, Carn Brea.

Brokenshire's traverse lines at 10 ft. intervals and determined their tin, copper and arsenic contents. No anomalous values were found and so it was concluded that the lode was probably barren. This is

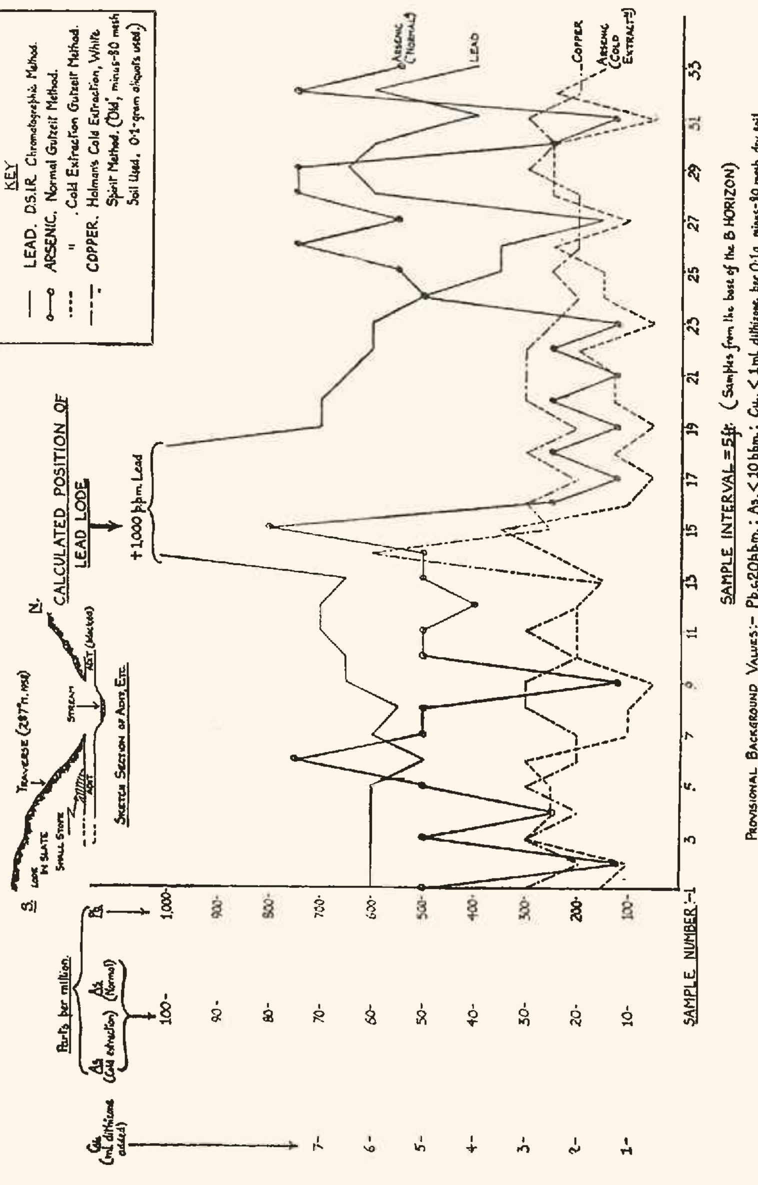

FIG. 4. Distribution of lead, arsenic and copper across a N.—S. Lead lode at Butterdon Mill, Liskeard. The lead-arsenic patterns suggests incipent mineralisation in fissures east and west of the main lode.

substantiated by the limited amount of attention the lode has received in the past. As a few specimens of lode material consisting of quartz and minor amounts of chlorite and pyrite, were collected from the dump of a prospect shaft on the body, it is thought that Brokenshire's anomalies could have been due to the oxidation of pyrite.

At Butterdon Mill, near Liskeard, a foot-wide, near-vertical lead-lode was exposed for a short distance along its strike by means of an adit, and subsequently a small amount of stoping was carried out. The lode, which occurs in pale-grey slate, consists of large randomly-distributed crystals of galena (containing 35 ozs. of silver to the ton), together with minor amounts of pyrite, siderite and chalcopyrite. Oxidation appears to be confined to that part of the lode which is immediately below the soil and there cerussite and pyromorphite/mimetite occurs in an ochreous-coloured gossan.

To test the possibility of tracing this lode by geochemical means, a series of B horizon samples were taken at 10 ft. intervals along the steep valley side and approximately at right-angles to the lode, and these were subsequently analysed for lead, copper and arsenic. The lode position was revealed by a very marked lead anomaly. Results of the copper and arsenic analyses established a number of anomalies which suggest that other — possibly minor — mineralised veins exist in the vicinity. (Fig. 4.)

This study indicates that lead lodes occurring in this rolling slate country, which has received but scant attention in the past, but which borders an area noted for the richness of its lead lodes, could be easily and quickly located and traced by geochemical methods. (See footnotes.)

Footnotes :—(i) During this work it was shown that variations in the arsenic content of the soil could be established rapidly by employing a cold-extraction technique. 0.1 g. of minus 80-mesh soil was placed in the Gutzeit tube, then 3 ml. conc. HCl and 2 ml. of 10 per cent. $SnCl_2$ (in conc. HCl) were added. Finally, 5 g. of arsenic-free granulated zinc were inserted and the tube was immediately corked with the normal Gutzeit head. After an hour the stain on the mercuric chloride paper was compared with artificial standards which were prepared in the usual way.

The arsenic extracted by this method was considerably less than that liberated by the usual method which involves a preliminary fusion.

(ii) The Butterdon soil samples have not yet been analysed for silver, but it seems very likely that when this is done distinctly anomalous values will be revealed in the vicinity of the explored lode.

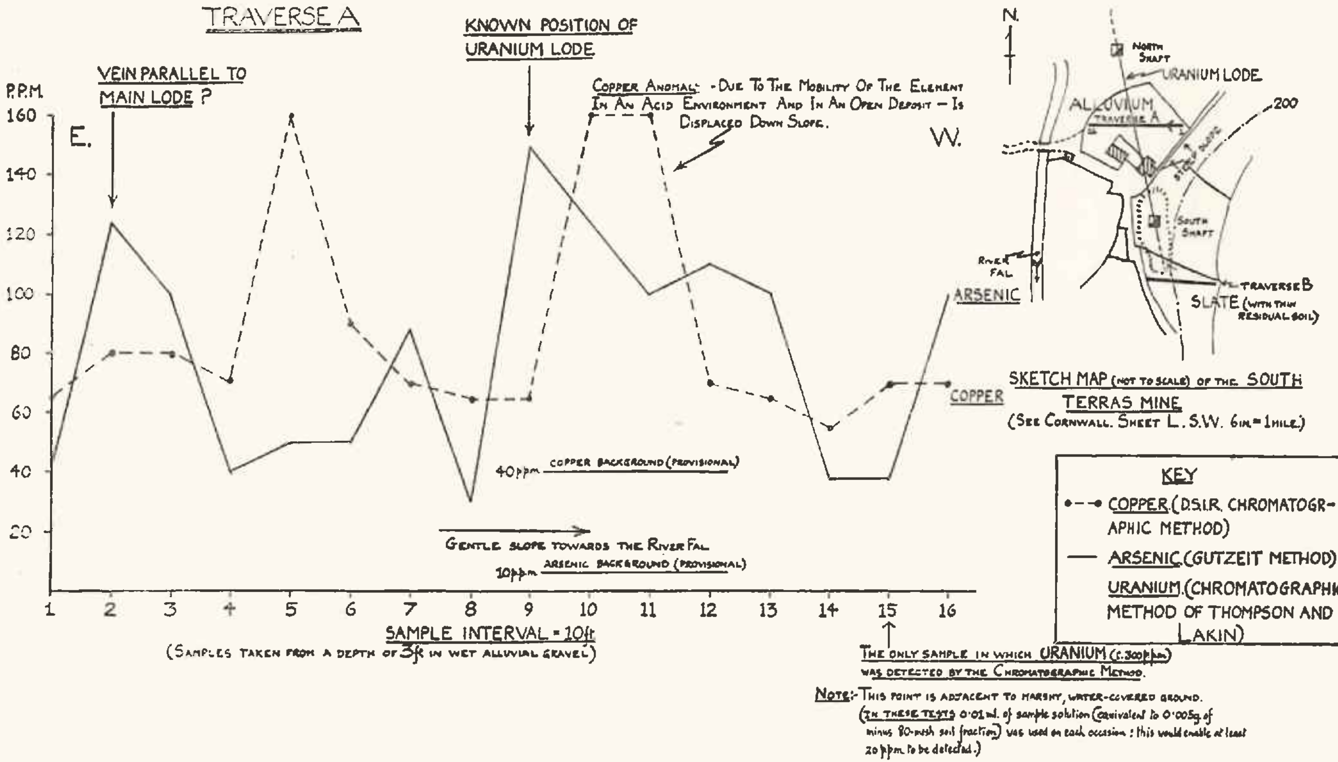

FIG. 5. Distribution of copper, arsenic and uranium in the alluvium over the South Terras uranium lode. (Soil samples from Traverse B failed to reveal anomalous concentrations of heavy metals over the projected line of the lode.)

At South Terras Uranium Mine, near Grampound Road, the rich lode is composed of primary ore, which contains pitchblende, together with a number of sulphides, sulpharsenides, etc., of copper, cobalt, nickel, lead and iron, overlain by oxidation products, amongst which torbernite is prominent. This lode has not been traced beyond the porphyry dyke which is situated just to the south of the South Shaft. (See Fig. 5.)

A series of soil samples were taken at 10 ft. intervals along a traverse just to the south of the dyke and approximately at right-angles to the strike of the lode. Subsequent analyses of these samples failed to reveal anomalous copper, nickel, cobalt and uranium anomalies and so confirmed the opinion that the lode did not persist beyond the dyke.

A further series of samples were taken across the lode, between the two shafts, where the ground consists of coarse, wet river-gravel which is covered with grass. Analyses of these samples — which were taken at depths of c. 3 ft. — established that whilst anomalous copper and arsenic concentrations existed over the lode, the amount of uranium present was below the limit detectable by the chromatographic method that was used. In fact, uranium was only detected in one sample and that was taken near standing water and adjacent to the River Fal. The lack of readily-detectable uranium over the lode is probably due to the fact that as this element is very mobile in an acid environment, as soon as it is liberated from the lode it migrates rapidly over the bed-rock, down the slope, and into the river. Judgement must be reserved as to the cause of the copper and arsenic anomalies just to the east of those over the known lode; possibly they are due to a parallel lode. (Fig. 5.)

Geochemical methods have already been employed successfully in Cornwall to determine if lodes exist near the wolframite-producing mines at Castle-an-Dinas and at Hawkswood which could be worked by these mines. Only the work carried out at Castle-an-Dinas will be discussed. There, until recently, ore was obtained from a single, roughly N.-S. striking, near-vertical lode, which consisted essentially of wolframite and loellingite in a quartz matrix, and which had developed in slate. A series of B horizon samples were taken at 20 ft. intervals along a number of traverse lines at approximately right-angles to the strike of the Main Lode. Analysis of these for tungsten enabled the lode to be traced to the south considerably beyond the point at which it had become too poor to work. Lines of small anomalies were also established to the east and west of the Main Lode, but these were considered to be of no economic importance by the writer. Subsequently, however, a crosscut, which was driven west through completely barren slate, intersected some small quartz stringers which contained traces of wolframite immediately below the anomalous band which had been revealed by soil analysis. Further work indicated that distinctly anomalous concentrations of arsenic also existed in the soil over the Main Lode but that there was no significant variation in the manganese content. (Figs. 6a, 6b and 6c.) For further details of this work see Hosking and Montambeault, 1956.

In view of the ever-increasing demand for metals it may well be that renewed interest will be taken in certain areas of Cornwall which are known to be lode-bearing, but which are still essentially virgin. Such areas are ideal subjects for investigation by geochemical methods, and although the Butterdon Mill district is a fairly typical member, work carried out in another — near the North Cliffs (Camborne) — will be described, as there opportunity to test such methods is unique.

At the North Cliffs a number of lodes, which strike roughly parallel to the coast, were intersected by a tunnel, which was driven to convey sewage to the sea. These lodes were subsequently mapped, and their mineralogic — and other — characteristics — were recorded in some detail ; they vary considerably in dip, strike and mineral content. A few contain considerable quantities of chalcopyrite, and a few others are essentially galena-bearing. Many contain sphalerite, whilst pyrite and arsenopyrite are also recorded. One lode is radioactive, though the cause of this is not recorded. Of the slate country-rock passed through by the tunnel, about a third was spotted — a fact suggesting that the granite is at no great depth below the surface. Mining activity was very slight and confined to limited parts of one or two lead-bearing lodes near the coast, and the ground over the tunnel is, for the most part, uncontaminated and readily accessible. The soil is everywhere thin — rarely more than a foot deep.

A series of B horizon samples were taken at 10 ft. intervals over the line of the tunnel and along certain other parallel lines

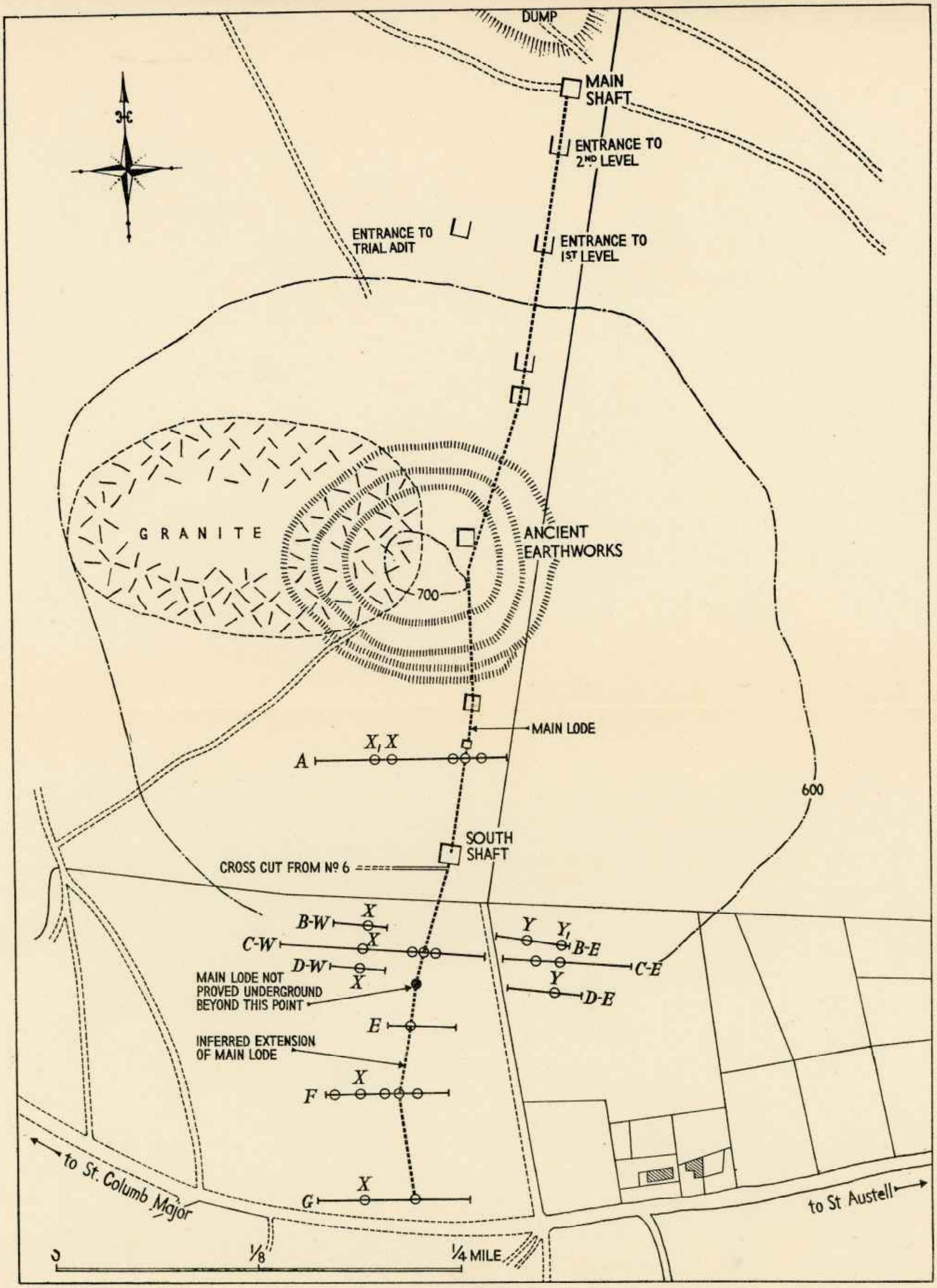

FIG. 6a. Map of Castle-an-Dinas Wolfram Mine showing the geochemical traverse lines and the positions of the anomalies.

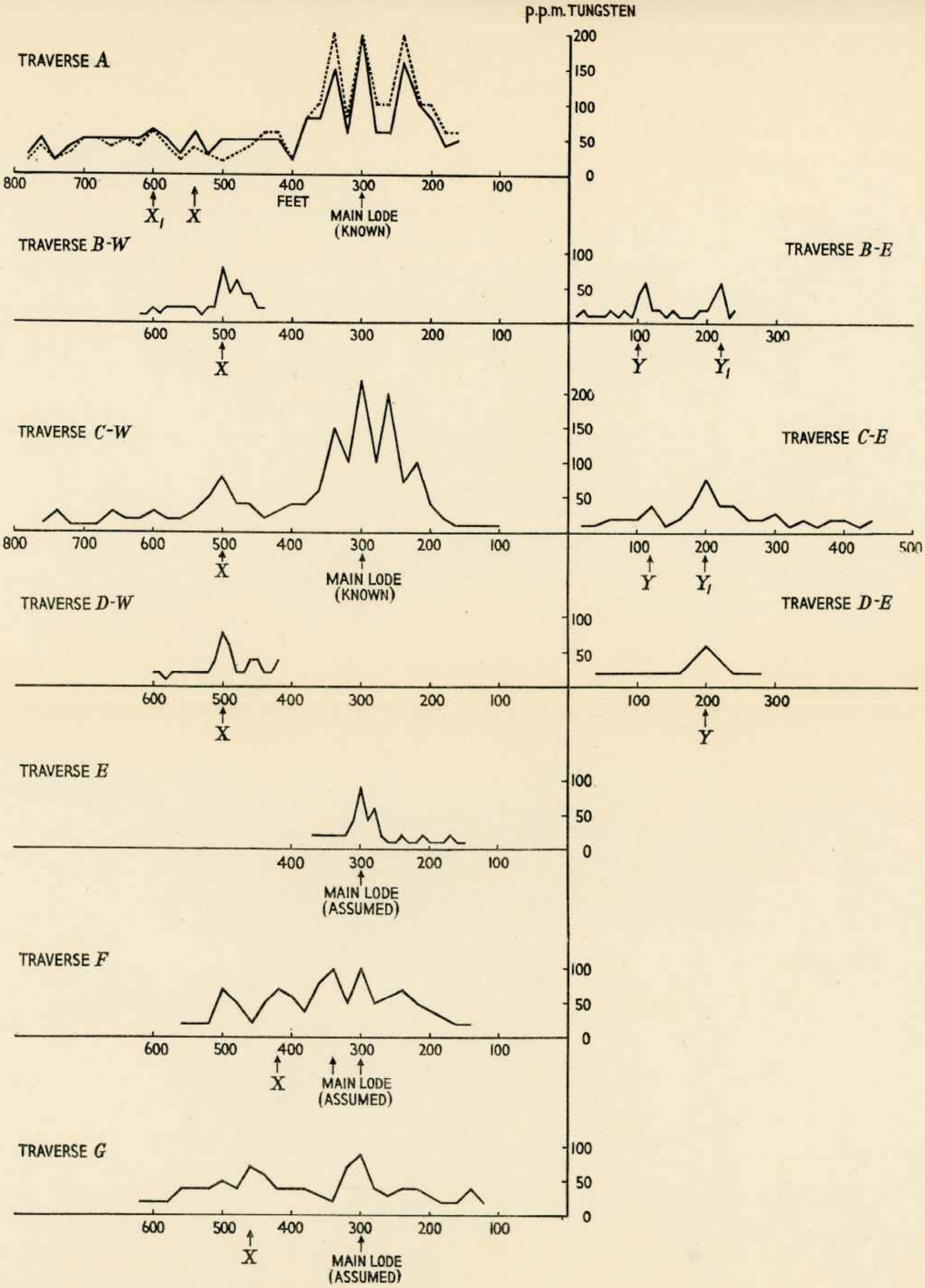

FIG. 6b. Graphs showing the results obtained by analysing Horizon B soil samples for tungsten in the vicinity of Castle-an-Dinas Mine.

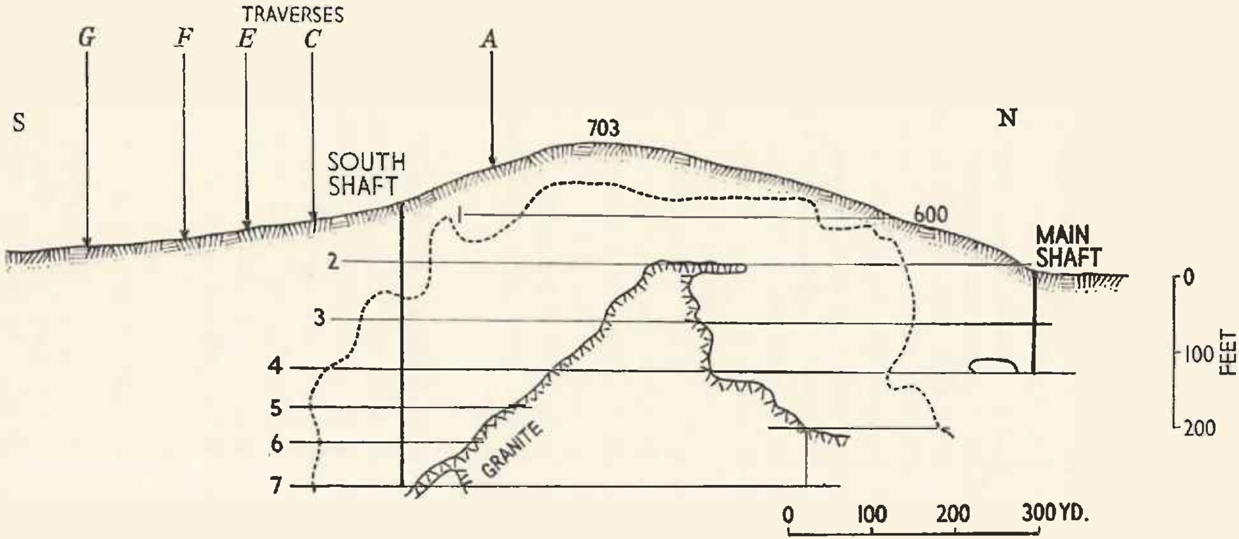

FIG. 6c. Longitudinal section of the Main Lode, Castle-an-Dinas Mine, showing the relation of the soil traverse lines to the ore-shoot.

(see footnote*). Subsequent analysis revealed copper and lead anomalies which could be correlated — with reasonable certainty — with underlying lodes. However, because of the marked mobility of zinc, and because zinc mineralisation is widespread in the area, an anomaly from one lode overlapped those due to adjacent lodes and so the results were not particularly useful in pin-pointing individual ore-bodies. The work also established the necessity of using a very close sampling interval if lead or arsenic anomalies were not to be missed, and it revealed two small cobalt anomalies in the vicinity of the radioactive lode. This last fact is of interest as cobalt had not been identified in the tunnel. The radioactive lode, on the other hand, could not be located on the surface either by means of a Geiger Counter or by analysing the soil for uranium. Analysis of samples along lines parallel to the base line for copper enabled the general strike of the ore-bodies to be determined whilst subsequent work showed that the copper-bearing lodes could be located very rapidly in the field, either by using Holman's cold-extraction technique (1956-57. Also see Webb & Tooms, 1958-59, and footnote†) or by the rubeanic acid method recently developed by Warren and Delavault. (See Renshaw and Price, 1958.) Further studies are being carried out, and in due course it is hoped to devote a paper to the results obtained in this area. In the meantime, however, the above brief account, plus those of the results which are recorded in Fig. 7, will serve to show how useful geochemistry can be in an essentially unmined area.

ANALYTICAL METHODS

Whilst the writer does not intend to describe or discuss the analytical methods used in the particular studies which form the basis of this paper, he regards it essential for the reader to know, in every case, which method was used, and where a description of it can be found. Therefore, the methods are declared in the various figures accompanying the text, and the sources of these are noted below.

Footnotes:—*Each sample was analysed for lead and every fifth for copper and zinc.

†As an interesting aside it may be mentioned that it seems that when a given soil sample is dried in the laboratory its readily-soluble copper content — as determined by Holman's method — is markedly decreased. This phenomenon is now being further investigated.

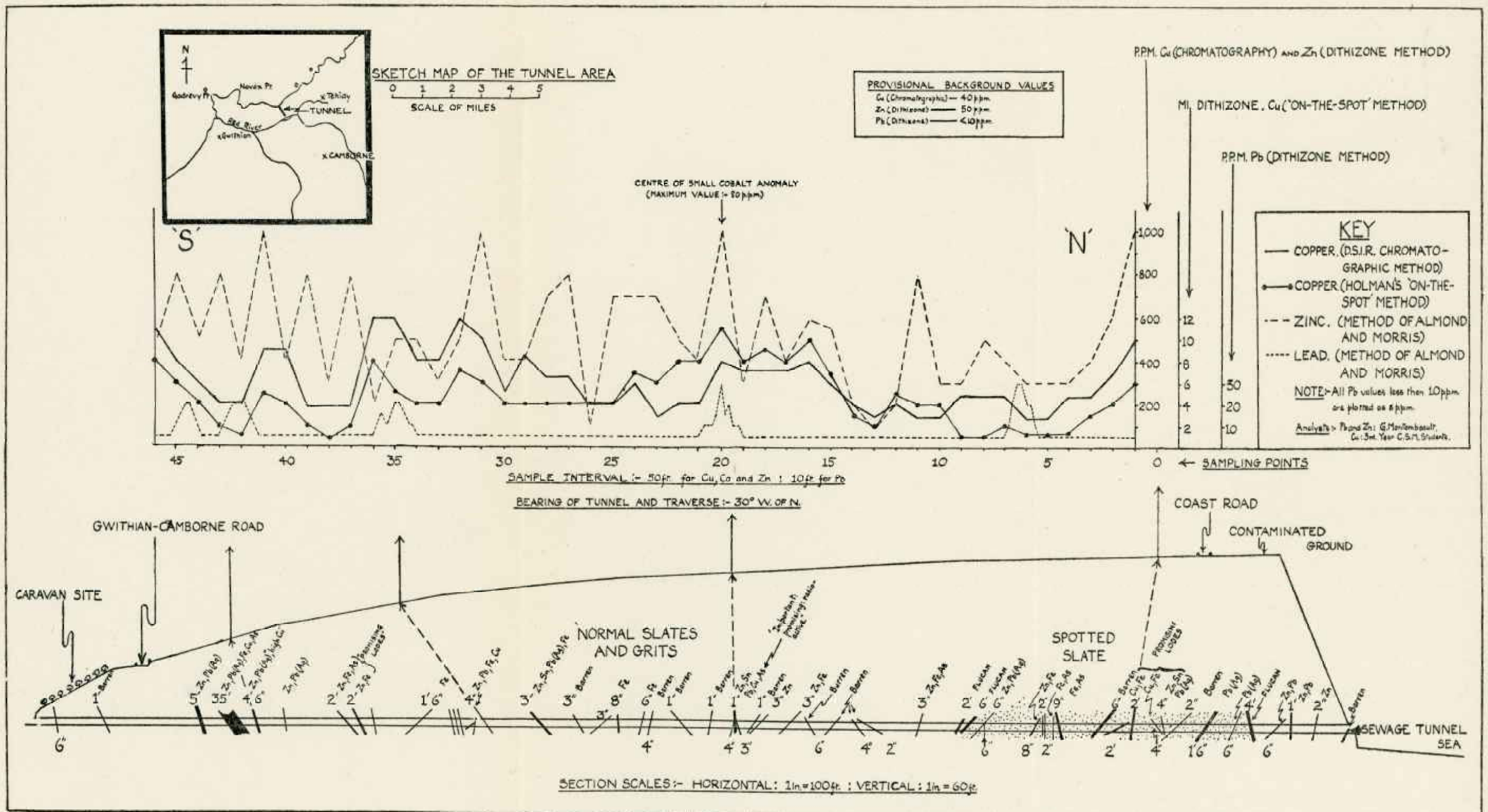

FIG. 7. Distribution of copper, lead, zinc and cobalt in the soil over the North Cliffs tunnel, Camborne. (Soil samples were taken from near the base of B-horizon.)

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BACKGROUND VALUES

In order to obtain the maximum information from the analytical results of a geochemical survey it is always desirable, and for the most part necessary, to determine the background value of the element under examination. That is to say, the amount of the element in soil overlying non-mineralised country-rock must be found. Thus, if the lodes being surveyed occur in, say, blue slate, soil samples must be analysed from areas over the same blue slate which are free from mineralisation. Furthermore, if the lodes pass through a number of different types of rock, the background value of the soil over each of these should be determined. This may sound a simple thing to do, but, in point of fact, in an intensely mineralised region such as Cornwall, it is often exceedingly difficult to obtain really reliable background values. In addition, it must be stressed, that in any given study it is not the absolute background value which is needed, but that which is established by means of the particular analytical method used in the survey, and, ideally, by the same person who is carrying out the analytical work of the survey. The reasons for this will be clear when it is appreciated that the chemical methods employed are semi-quantitative, and not only is there often only a partial extraction of the element from the soil sample, but considerable variations in the results of two reliable analysts can accrue from personal analytical idiosyncrasies.

Because of the above facts, the provisional background value for a given element recorded in the various studies described in this paper varies from area to area.

ACKNOWLEDGMENTS

The writer wishes to acknowledge the great assistance given to him during these studies, both in the field and in the laboratory, by Mr J.. P. R. Polkinghorne and 3rd year students of the Camborne School of Metalliferous Mining. To Dr. J. S. Webb, and his colleagues, of the Geochemical Prospecting Research Centre of the Imperial College (London), he owes a debt of gratitude for numerous discussions he has had with them on geological topics. He also wishes to extend his thanks to Mr. Rumbold for carrying out some preliminary geophysical studies over certain geochemical traverse lines at Carn Brea. He is grateful to the Directors of Tehidy

Minerals, Ltd., for making geological data of the North Cliffs Sewage Tunnel available to him, and to Mr. Patey, Editor of Mine and Quarry Engineering, for permission to reproduce the Castle-an-Dinas illustrations. Finally, he wishes to express this thanks to those land-owners of Cornwall — too numerous to mention individually — who have allowed him unrestricted access to their fields, and so have rendered this work possible.

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