A Study of the Distribution of Tin, Tungsten, Arsenic and Copper in the Sediments, and of the Total - Heavy - Metals in the Water, of the Menalhyl River, Mid-Cornwall

K. F. G. Hosking, S. M. Naik, R. G. Burn and P. Ong.

SYNOPSIS

A STUDY of the distribution of certain metals in the sediments and water of the Menalhyl River, which drains the northern portions of the Castle-an-Dinas/Belowda Beacon mineralised belt, failed to reveal (with one, probably unimportant, exception) the presence of hitherto unknown lodes. It demonstrated, however, that whereas tungsten (as wolframite) tends to concentrate in progressively finer fractions as the distance from the source increases, tin (as cassiterite) does not. Unlike wolframite, cassiterite is neither readily abraded nor disintegrated, and so both coarse and fine fragments can be found far from the source, and at any given point the manner in which the mineral is distributed amongst the various size fractions must depend on many factors such as the velocity of the river water, the nature of the channel, and the proximity of tributaries.

Finally, the work established that no marked concentration of the elements studied has taken place on the beach through which the river flows to the sea, although some of the sand samples which were collected contained quite high concentrations of tin and tungsten which indicated the nature of the mineralisation of the hinterland.

Recently, third year students of the Camborne School of Mines studied the distribution of certain metals in the sediments and water of the Menalhyl River, primarily with a view to obtaining further experience in certain geochemical prospecting techniques, but also in order to learn something more of the mineral potential of the area and of the dispersion characteristics of tungsten, tin, arsenic and copper — particularly the first two elements.

General geology of the study area. (See Map 1.)

The area transected by the river consists essentially of a portion of the northern limb of the E.-W.-trending Watergate Bay anticline. The oldest rocks — the red and purple Lower Devonian Dartmouth Slates — form a tongue which extends eastwards from the coast almost to St. Columb Major. These are bordered to the north and the south by the Lower Devonian Meadfoot Beds which, in this area, consist of pale slates and interbedded rocks which were originally impure limestones. The northern edge of the area is

ATE Map -Geological sketch map MEADFOOT STADDON of GRITS by Menalhyl River

fringed by the Middle Devonian Staddon Grits. In Permo-Carboniferous times a granite batholith was emplaced in the South-West of England and two small cusps of this mass — Castle-an-Dinas and Belowda Beacon — are important geological units of the area under consideration. These cusps are surrounded by a halo of thermally metamorphosed and hydrothermally or pneumatolytically altered Meadfoot slates, whilst outside this aureole, and to the north, the originally impure limestones have been converted by underlying granite to calc-flintas. During, and after, the final phases of granite emplacement, porphyry dykes were emplaced just to the south of the cusps and also near Withiel, and hypothermal lodes containing cassiterite, wolframite, loellingite, etc., were developed in the vicinity of Castle-an-Dinas and Belowda Beacon. Subsequently, iron lodes were formed near Withiel and at Trewolvas. (The mineralogical character of the various lodes is discussed further in a later section.)

During Mesozoic times sub-aerial erosion exposed the granite and the lodes, but after the Alpine disturbances the South-West was almost totally submerged and was represented solely by an archipelago of granite islands. This submergence was followed by emergence in stages during Pliocene times, and this resulted in the formation of usually well-defined marine platforms, of which the one now standing at about the 400-foot contour is the most extensive. The Menalhyl River rises on a portion of this platform.

Elevation continued into Pleistocene times, with the further development of three more platforms of which the most marked is the one at the 14-foot contour, and upon which a well-preserved raised beach is often found. At Mawgan Porth, where the Menalhyl River reaches the sea, the 14-foot platform can be seen.

At this time an ice sheet extended over the land as far south as a line joining Bristol with London, and possibly an "offshore" tongue reached the Scilly Isles: Cornwall, therefore, was subjected to permafrost conditions. At the end of Pleistocene times the climate became more temperate and the accompanying thaw caused much of the surface debris to move to lower levels. The result of this was that masses of angular rock, in a matrix of sand and clay, were deposited in small valleys and on the various marine platforms. This periglacial solifluction product is termed "head-of rubble".

Elevation continued into Recent times, probably raising the land some 30 feet above its height in the Pleistocene. During this period the climate was very wet, and consequently the rivers were swollen and hence able to deepen their channels rapidly and to effect the concentration of dense resistates — particularly cassiterite. At the same time, torrents flowing from the higher ground on to the 400-foot platform built up local concentrations of cassiterite there. [In the study area "head" containing cassiterite and wolframite accumulated in the basin (in which the Menalhyl River rises)

Study of the Distribution of Tin, Tungsten, Arsenic etc.

between the mineralised hills of Castle-an-Dinas and Belowda Beacon, and also in that part of the valley which lies just to the north of the former hill. During the subsequent uplift the heavy rains not only caused additional amounts of heavy minerals to be washed into these "collecting grounds", but, by increasing the flow of the river, they indirectly caused the cassiterite to be concentrated, as a rule immediately above the bed-rock, and primarily in the basin and upper reaches of the river (judging by the distribution of the alluvial workings). Apparently local concentrations also occurred at points further down the river where conditions happened to be particularly favourable, as report has it that the valley deposits have been "worked" for alluvial cassiterite at many points between Belowda Beacon and the sea.

During this phase any liberated wolframite which was subject to the violent action of the turbulent river was probably rapidly disintegrated, and much of it was, doubtless, transported to the sea.]

Following this period was one in which peat beds developed on the low-level alluvials, and during which the lower reaches of the rivers were drowned and the peat was covered by estuarine sands and muds. Finally, sand-dunes developed along certain stretches of the coast (The lower reaches of the Menahyl River have not been bored, but it is probable that were this done a sequence of deposition of the type noted above would be revealed. Certainly the lower part of the valley appears to be a silted-up creek, in part covered by dunes.).

Further data concerning the sources, etc., of the tin, and other elements studied, in the uppermost horizons of the river sediments.

At the commencement of the study (and since its completion) the only known primary sources from which the river system could obtain comparatively large quantities of minerals containing the elements investigated are the lodes and stringers in and about Castle-an-Dinas and Belowda Beacon. At Castle-an-Dinas a N.-S.striking lode — which was worked intensively until a few years ago - consists essentially of wolframite and loellingite in a quartz matrix. Some arsenopyrite is associated with the loellingite and cassiterite occurs sporadically and in small amount, in stringers adjacent to the main lode. The major wolframite shoot outcrops near the crest of the hill and from this point the tungsten content of the lode decreases markedly northwards — so much so, that before the river is reached geochemical analysis of the soil for tungsten fails to reveal the presence of an underlying lode. Although loellingite is not absent from the northern part of the lode it is much more prevalent in its southern portions. The orebody has been but slightly oxidised, although a number of rare supergene species, notably russellite and rashleighite, are found there. The presence of the latter mineral, together with the occasional occurrence of cuprite and native copper, indicate that the area was subject to incipient copper mineralisation.

In addition to the major lode there is some geochemical, and other, evidence that a tin lode exists to the N.N.W. of the Main Shaft and between it and the river, and that it has been worked in a small way.

Castle-an-Dinas mill is situated near the Main Shaft, at some considerable distance from the river, and its tailings were piled on the site. The tailings water, however, flowed via a small stream to the river, and this, which was sampled at point 14, naturally contains sediments high in tungsten and arsenic. The high tin content of these sediments may be due largely, or entirely, to losses from the mill, but as the old tin mine was near this stream earlier local mining operations may also have contributed significant amounts of this element.

For a limited period of time, when Castle-an-Dinas mine was active, tailings were transported to a site near the Menalhyl River (in the vicinity of sampling point 12) and retreated there. It is likely that much, perhaps virtually all, of the tungsten, tin, arsenic and copper occurring in the superficial layers of the sediments were introduced during this operation. However, unknown, though perhaps significant, quantities of minerals containing these elements may have been washed in, at about the same point, by water emerging from the No. 4 adit level of the mine. There is also the possibility that an appreciable proportion of the tin, and conceivably of the tungsten and arsenic, in the uppermost layers of the sediments are there because of the losses incurred by the alluvial miners when they were working the "pay-dirt" lying immediately above the bed-rock.

No lodes are known at Belowda Beacon which are so situated that they could have contributed to the sediments of the Menalhyl River. However, favourably placed stringers containing wolframite, cassiterite, tourmaline and topaz are known to occur there and it is generally thought that much of the cassiterite in the alluvials must have been derived from such sources. Certainly the basin to the west of Belowda is pock-marked as a result of the activities of alluvial miners, but nothing is known of the amount of cassiterite they recovered. The present studies suggest that in the upper reaches of the Menalhyl the tin content of the superficial sediments decreases to the east of the Castle-an-Dinas tailings retreatment site. This could be interpreted in a number of ways: it might be taken to indicate that the major sources of the superficial cassiterite were the tailings together with the sediments from the adit: it could be used in support of the contention that the alluvial miners found the richest deposits and sustained the greatest losses there, and that this alluvial cassiterite was derived largely from Castle-an-Dinas: finally, it might be interpreted as a recent concentration of cassiterite which had, to a large extent, been washed down from the workings at the foot of Belowda Beacon. Although it is clear that a certain answer cannot be given concerning the source of the tin which is concentrated in the uppermost horizons of the sediments here, the writers are of the opinion that the evidence gives most support to the hypothesis that it, and the spatially associated tungsten, arsenic and copper, have been derived primarily from the tailings retreatment plant. So far as the last three elements are concerned it is pertinent to state that copper minerals have only been recorded from Castle-an-Dinas, and the tailings are comparatively high in arsenic. not only because of its presence in the ore treated, but also because loellingite was used as the jig ragging in the mill; and although wolframite veins occur at Belowda, the alluvial miners did not find any in their cassiterite concentrates to the east of Castle-an-Dinas.

Little is known of the nature of the Trewolvas iron deposit between Castle-an-Dinas and St. Columb Major, except that near surface it consists of hematite and limonite, and is, therefore, of little interest in the present study.

Field procedures and analytical methods used.

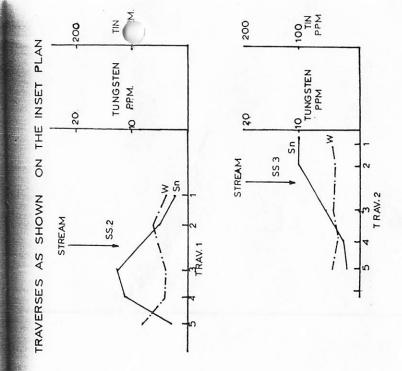
At each sampling point the approximate pH of the water was determined by B.D.H. papers, and determinations, in duplicate, of the "heavy-metal" content of the water were carried out by Huff's dithizone method. (Huff, 1948.) (These determinations were made primarily to give the students practice in the method: it was appreciated, at the outset, that the area as a whole is deficient in lead, copper and zinc, and so a study of their distribution in the river water was unlikely to contribute much to an evaluation of the mineral potential of the area. The results, however, are not without interest)

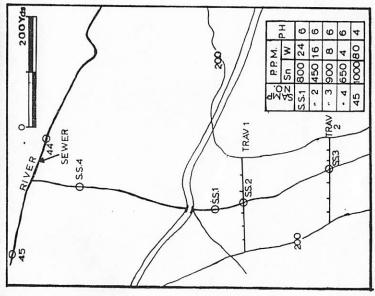
In addition, at each sampling point, two samples of sediments were analyzed for cold-extractable copper, and a composite sediment sample was collected in a resin-impregnated envelope and brought to the field laboratory where tin, arsenic, tungsten and "total" copper were determined in the minus-80-mesh (B.S.S.) fraction. Four samples of sediments, collected at widely separated points along the river, were subjected to size analysis, and each fraction was analyzed for tin and tungsten. Finally, sand samples, each from one foot below the surface, were taken at points along a number of traverse lines at Mawgan Porth beach: the minus-80-mesh fractions of these were analyzed for the four elements noted above.

The analyses used were as follows:—

Tin:—Stanton and McDonald's modified gallein method. (Stanton and McDonald, 1961-62.)

Tungsten: - The D.S.I.R. dithiol method. (North, 1956.)





Columb Major which of St. deposits of the valley to the west fig. 1a.

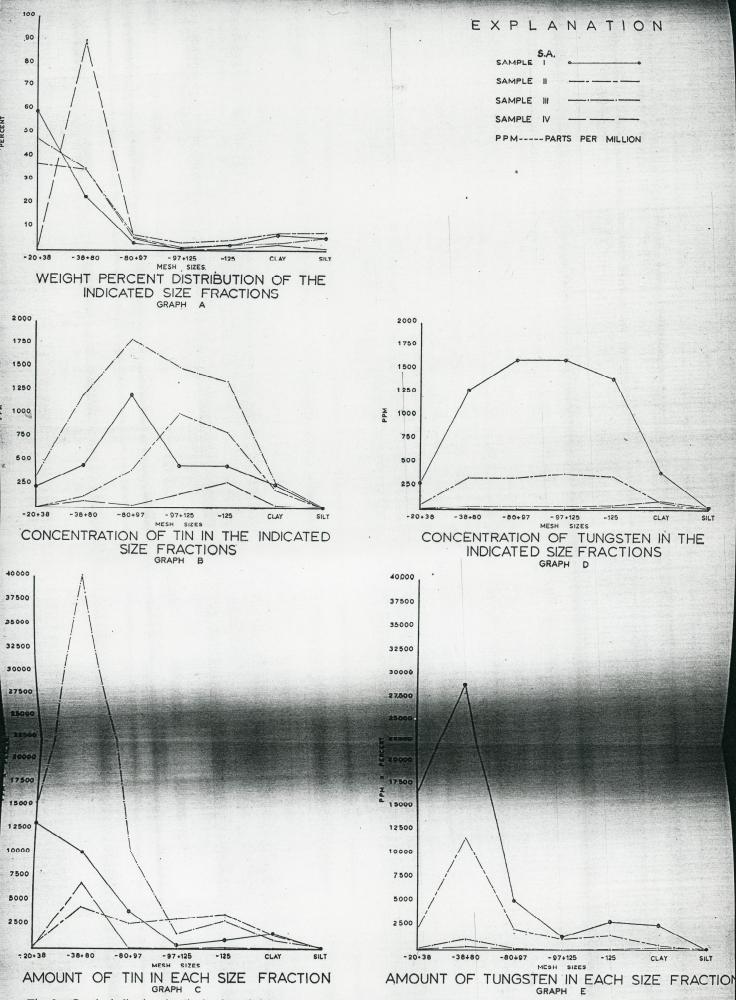


Fig. 2. Graphs indicating the distribution of tin and tungsten in various size-fractions of the four samples S.A.1,2,3, and 4 obtained from points indicated on the map of figure 1.

Arsenic:—The modified Gutzeit method. (Almond, 1953.)

Total copper:—A modified dithizone method. (Stanton and Gilbert, 1956.)

Size analysis:—A wet dispersion method [described by Piper (1950)] was used to effect the separation of the sample into clay, silt and sand fractions.

Discussion of the results.

The sampling points and results are recorded in figs. 1A, 1B, 2 and 3, and the following observations, etc., emerge from a consideration of these:—

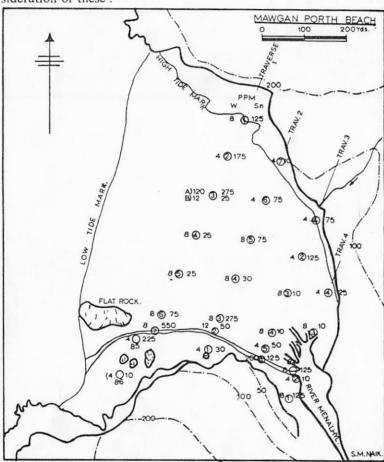


Fig. 3. Map of Mawgan Porth indicating sampling points and the tin and tungsten content of the minus-80-mesh fractions (B.S.S.). The tungsten content (in p.p.m.) is shown on the left of each sampling point, and the tin content (in p.p.m.) appears on the right.

If certain comparatively minor irregularities in the graphs are ignored the concentrations of arsenic and tungsten in the minus-80mesh fraction show a reasonably regular decrease from the "point" of introduction of the loellingite and wolframite to the sea. In addition, as the distance from the point of introduction to the sampling point increases, so the tendency for the tungsten to report in progressively finer fractions increases. (This is probably equally true of arsenic although the work necessary to confirm this was not undertaken.) On the other hand the concentration in the minus-80mesh fractions varies in a most erratic way down the stream, and the size fraction in which the tin is most prone to concentrate is not primarily related to the distance of the sampling point from the source. The distribution patterns exhibited by tungsten and arsenic are doubtless due primarily to the ease with which loellingite and wolframite are disintegrated, whilst that shown by tin is due fundamentally to the fact that cassiterite, besides being dense and chemically inert, is also comparatively tough. Hence a grain of cassiterite liberated into the drainage system is capable of being transported considerable distances without marked loss of size.

Obviously, at those points where the flow of the stream is decreased heavy minerals generally will tend to concentrate. It is therefore, not difficult to understand why, for example, the concentration of tin, tungsten and arsenic increases somewhat in the comparatively flat reaches of the river immediately behind Mawgan Porth. On the other hand, it is not possible to give a really satisfactory explanation of the manner of distribution of tin in the various size fractions of those samples which were subject to this form of examination. Clearly, the factors determining the size distribution pattern of cassiterite must be due to many interacting factors, such as the rate of flow of the river at the sampling point, the degree of turbulence, the nature of the bed, the form of the river channel there, the degree of fall-in from the banks, the nature of the sediments introduced by adjacent tributaries, etc.

Just to the seaward side of St. Columb Major there is a local concentration of tin, tungsten and arsenic in the sediments, and, in addition, the waters there possess a local anomalous concentration of heavy metals. As this interesting state of affairs could be due to the introduction of the elements in question by the northward-flowing tributary that enters the Menalhyl there, further samples were taken from the valley of the feeder stream and analyzed. The results indicate that the small stream is contributing some tin, together with comparatively minor amounts of tungsten and arsenic and so is, probably, to some degree responsible for the local anomalies in the main river valley. However, it is thought that these anomalies may be due, to some considerable extent to other causes. At this point effluent from the St. Columb Major sewage farm enters the river, and this is undoubtedly the cause of the local increase in

the heavy metal content of the water. Furthermore, the addition of these metallic ions, plus a wide variety of soluble and insoluble organic material, could induce a local concentration of tungsten, arsenic and tin by flocculating colloidal particles of the appropriate minerals from up-river sources, and by entanglement. Finally, here the river is comparatively slow-flowing, and this alone could be the main reason for the anomalous concentration of tungsten, tin and arsenic in the sediments. The sediments of other tributaries of the Menalhyl are not devoid of the elements under examination, but the concentrations are not great and the tributaries are small, so it is probable that additions from these lateral sources have not contributed significantly to the metal-content of the main stream. On the other hand, the flow characteristics of the water of the main river must be altered at points where a tributary enters, and this must affect the behaviour of the sediments: furthermore, although the tributaries may not have made significant contributions of heavy minerals some of them probably contributed considerable quantities of rock-forming species and so locally "diluted" sediments of the main river. In general, however, it is believed that the distribution patterns of the elements investigated in the sediments of the Menalhyl have been determined primarily by the physical properties of the minerals in which they occur, and the variations, from point to point, in the relative efficiency of the various natural concentrating operations. If this is accepted, it follows that as tin, unlike tungsten and arsenic, is capable of concentrating, in a most marked manner, at numerous points down-stream from the source, a search for tin-lodes based on an investigation of stream sediments is likely to be more time-consuming than a similar one aimed at locating arsenic- or tungsten-bearing bodies, as the ground adjacent to each anomally may well have to be investigated. It is also pertinent to emphasise the fact that when investigating stream sediments with a view to discovering primary deposits of wolframite a comparison of the distribution of tungsten in the various size fractions of appropriate samples can greatly facilitate the search.

Only a few further remarks need be made concerning the heavy metal content of the water and the copper content of the sediments. Variations in the concentration of heavy metals in the water, and of cold extractable ("on-the-spot") copper in the sediments of the drainage system, suggest that the headwaters are emerging from a mineralised area — albeit, one, in which base metal sulphides are not abundant. The comparatively high "on-the-spot" copper content of the sediments in the vicinity of St. Columb Major is probably due to contamination caused by material being deposited in the river by the inhabitants. Neither the total copper content of the sediments, nor the pH of the water, vary in such a way that they facilitate, to any marked degree, the search for ore, or add materially to an understanding of the dispersion of metals in the water and sediments of the drainage system. The results of analyz-

ing Mawgan Porth beach sands for tin and tungsten indicate that there is no widespread concentration of these elements there as is found on several of the Cornish beaches. Only in the vicinity of the river are the sands comparatively high in tin, and it was from here that the single tungsten-high sample was collected. These "river" samples clearly indicate that the hinterland has a tin and tungsten potential, and such samples from unprospected areas might be equally revealing. However, because of the fundamental differences in the physical properties of cassiterite and wolframite, the chances of finding a high concentration of tin in such a sample taken at random are considerably greater than the chances of picking one high in tungsten. From the point of view of the prospector this is an important fact which he should take into account when determining the number of samples to be taken, and assessing the analytical results.

Perhaps the most important general conclusion which can be drawn from the work as a whole is that the distribution "pattern" of an element in the sediments of a river is determined primarily by the physical properties of the minerals containing the element in question, which are liberated into the drainage system.

REFERENCES

- ALMOND, Hy. A field method for the determination of traces of arsenic in soils. A confined spot procedure using a modified Gutzeit apparatus. Additional field methods used in geochemical prospecting by the U.S. Geological Survey. Open-file report, 8-11, Sept. 1953.
- HUFF, I. C. A sensitive field test for heavy metals in water. Econ. Geol., 43, 675-684, 1948.
- NORTH, A. A. Geochemical field methods for the determination of tungsten and molybdenum in soils. Analyst, 81, 660-668, 1956.
- PIPER, C. S. Soil and plant analysis. White Inst. Monograph.
- STANTON, R. E. and GILBERT, M. A. Copper, etc., in soils, sediments, and rocks by dithizone in carbon tetrachloride. Technical Communication No. 2. Geochemical prospecting research centre of the Imperial College of Science and Technology. 1956.
- STANTON, R. E. and McDONALD, A. J. Field determination of tin in soil and stream sediment surveys. Trans. Inst. Min. Metall. (Lond.). 71, 27-29, 1961-62.

