CHEMICAL CHARACTERISTICS OF THE CEMENTS OF THE GODREVY 10-FT. RAISED BEACH AND OF CERTAIN DEPOSITION PIPES IN THE ST. AGNES PLIOCENE DEPOSITS, CORNWALL

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SYNOPSIS

A study of the major—and trace-element content of the ferruginous and manganiferous cements of the Godrevy raised beach and of certain 'deposition pipes' in the St. Agnes Pliocene sands indicates that in both cases Fe and Mn are related antipathetically whilst there is a sympathetic relation between Fe, As and Mo, and between Mn, Co, and Ni. Cu, Zn and Pb may show sympathetic relationships with either Fe or Mn, though they generally 'follow' the former.

At Godrevy, in the vicinity of a much oxidised, originally sulphidic, lode, the raised beach cement is anomalously high in Cu, Pb, Zn, Ni, Co and As, but generally the components of the cements at Godrevy and St. Agnes have been leached primarily from the killas (non-calcareous sedimentary rocks) occurring as fragments in the Head (which were derived by frost shattering of local rocks in glacial and immediate post-glacial times) which, when fresh, vary but little compositionally within the study areas.

The element relationships of the cements agree broadly with those of desert varnish which were established by Lakin and others (1963).

Finally, although the genesis of the cemented bodies is discussed, many questions concerning it still remain unanswered.

INTRODUCTION

During 1964 a study was made of some of the chemical characteristics of the cements of certain curious ' deposition pipes ' in the Pliocene beach deposits surrounding the St. Agnes beacon at *ca,* the 400 ft O.D. line and of the cements of the so-called 10-ft raised beach of Godrevy. Both sites are in West Cornwall.

The main object of the study was an applied geochemical one. It was to determine to what extent analysis of cements and similar chemical deposits might be used to locate the presence of mineral deposits of economic interest in the underlying and neighbouring earlier rocks.

Clearly the material for the development of cements is often derived, in part at least, from the components leached from surrounding rocks, and hence, during a preliminary consideration of the subject it would not be unreasonable to anticipate that variations in the chemical composition of the source rock might be reflected, without undue distortion, by variations in the composition of the cement. Therefore the presence of chemically unusual units, e.g., ore bodies, in the parent rock might be broadly revealed by a study of the chemical composition of derived cements.

There are, of course, likely to be complicating factors. In the case of hard-pan developed in sand dunes (which the writers have recently studied in some detail) it is certain that the cementing material may be derived in part from the sand itself and in part from the underlying and neighbouring rock: the cements of fossil beaches could be similarly derived. However, should chemical deposits reflect, in the manner indicated above, the chemical nature of earlier neighbouring lithologic units, then a study of the former could be of considerable value in the search for ore deposits. Not only might such work reveal the presence of primary deposits beneath comparatively young raised beaches, but it might also reveal them below ' old ' cemented sedimentary rocks. In the latter case material for analysis might be outcrop material, samples from underground workings, or diamond drill core. In arid regions the analysis of desert varnish might be rewarding and in coastal, or other, areas where caves are frequent, analyses of efflorescences from their walls might point to hitherto unknown mineral deposits of economic interest. In point of fact some work has already been done in some of these fields and some of it will be referred to later.

As a prelude to the application of these possible exploration techniques it is necessary to assess the significance of variations in the concentration of a given element from one sampling point to another. It is of paramount importance to know the answer to the questions to what extent is the concentration of an element in a given chemical deposit—say a sample of cement—dependent on the concentration of other elements in the sample and to what extent is it dependent on chemical and mineralogical variations of the source rock. Work by others, which is discussed below, indicates that a great deal of inter-dependence may exist between certain elements, and the major object of the present study was to investigate this particular phenomenon further. In addition it was hoped that the work might increase the knowledge of some of the factors which control the metal distribution patterns in soils, which are much more complex systems than the predominantly inorganic ones studied by the writers. It was also anticipated that some further light might be thrown on the developmental history of the particular deposits investigated and on the genesis of certain types of sedimentary iron-manganese deposits.

PREVIOUS WORK. Previous work relating to the nature of chemical deposits in an arenaceous environment is very limited, but details of studies relating to chemical deposits in other superficial deposits, which are relevant to the work under review, are rather more plentiful.

Engel and Sharp (1958) studied the trace element content of desert varnish and the results of their work led Lakin, Hunt, Davidson and Uteana Oda (1963) to consider the possibility of using desert varnish as a geochemical regional prospecting tool. Their work demonstrated that in the desert varnish of Death Valley and S.E. Nevada there was a close correlation between the cobalt and manganese content, and that there was a general correlation between the content of barium, lanthanum, molybdenum, nickel, lead and yttrium and that of manganese. They concluded, therefore, that ' the content of these elements in desert varnish may not be meaningful as an indicator of mineralised zones '. However, they state that " correlation with ore provinces may be represented by the high B content of varnish from Death Valley, Calif., by the high As and Sb content of that from the Edna Mountains, Nev., and by the high Cu content of that from the Antler Peak—Copper Basin Area, Nev."

Hawkes and Webb (1962, p. 167) record the following details re metal inter-relationships:—

White (1957) carried out experiments on Tennessee soils which indicated that about 50 per cent. of the Zn in the residuum derived from the weathering of a limestone under a humid sub-tropical climate occurs in the hydrous iron fraction.

Tooms and Webb (1961) noted that there was a strong enrichment of firmly bonded anomalous Cu in ferruginous concretions of the B horizon of Rhodesian latosols and that Cu and Co were enriched in manganese wad. Previously Jay (1959) had demonstrated a similar correlation in the same soils between Co and Mn.

In 1959 Mather, working in Sierra Leone, recorded concretions of both As and Mo in iron-rich soils.

In tropical soils both Webb (1958) and Ledward (1960) have shown that Pb tends to concentrate with either Fe or Mn.

PRACTICAL DETAILS OF THE STUDY. The study under review involved the following work:—

(i) Field study, including ' sketch ' mapping and photography.

(ii) Collection of samples for analysis, etc.

(iii) Analysis of appropriate samples for iron and manganese by classical wet methods, and for Cu, Co, Ni, As, Pb, Zn and Cr by rapid semi-quantitative colorimetric currently used by applied geochemists.

(iv) A few preliminary studies of the sand fractions of the deposits and particularly of the ' heavy minerals '.

(v) Graphing and assessment of the results.

GENERAL GEOLOGY OF THE STUDY AREAS

ST. AGNES. The St. Agnes area consists essentially of Devonian non-calcareous sediments which were locally thermally metamorphosed and otherwise altered during their invasion, in Permo-Carboniferous times, by granitic magma which consolidated as a granite cusp under what is now the Beacon. Following the consolidation of the granite a series of rich copper and tin lodes developed largely in the killas flanking the granite (of which only two small outcrops can be seen). In Pliocene times all but the granite-cored Beacon was submerged, but subsequently uplift occurred in stages and now the Pliocene platform is *ca.* 400 O.D., whilst the Beacon is surrounded, almost completely, by beach sands and clays, and possibly locally by 'fossil' dune-sands in addition. In glacial and/or immediate post-glacial times a comparatively thin covering of 'Head-of-Rubble', a periglacial solifluction product, was deposited over the sands, and it in turn is now mantled by a thin soil.

The Pliocene deposits occur between the 320 ft and 420 ft contours, and the total thickness of soil, Head, and underlying Pliocene sands and clays, though variable, is locally of the order of 30 ft.

From place to place the Pliocene profiles show considerable variation (see Ussher 1879, pp. 12-5; Robson 1943-44, p. 141) but commonly the sequence from top to bottom, beneath the Head, is bluish-grey clay, sand, red poorly-cemented sandstone and pebbles. For the greater part the platform on which these rest is Killas, but locally it is granite.

Macro-fossils are absent from these deposits and the possibility of micro-fossils occurring in them has not yet been examined.

The deposition pipes, which are discussed in some detail below, were found by the writers in the waste dumps bordering the pits from which sand is presently being extracted: these are a few hundreds of yards to the N.N.E. of the disused Cameron granite quarry and are near the site where Kitto and Davies first noted them (see later note). However, despite numerous visits to these pits the writers were never successful in finding any pipes in situ, but they probably occur in the red sand horizon, probably near its base.

The actual lengths of individual pipes is unknown as only portions, up to *ca.* 6 in long, have been recovered. These fragments vary considerably in complexity, but all so far found are composite in character and consist of a series of minor pipes, whose long axes are approximately parallel, cemented together so that their walls touch. Each member of a series consists of a wall of heavily cemented sand which encloses a soft core containing only a comparatively small quantity of cement. The cement, which is largely ferruginous, varies in colour from one specimen to another, and, in the more complex bodies, from one part to another (Pl. 1). The common colours are ochre, various shades of red, and dark brown. Judging by the way in which the pattern of the transverse section of a given complex pipe changes it seems likely that each of the pipe-like components may well be very elongate, irregular ellipsoids. (Fig. 1). A complex pipe system, because of the way in which it is constructed, has a fluted exterior, so that the body, which may vary in width from *ca.* 1.5 in

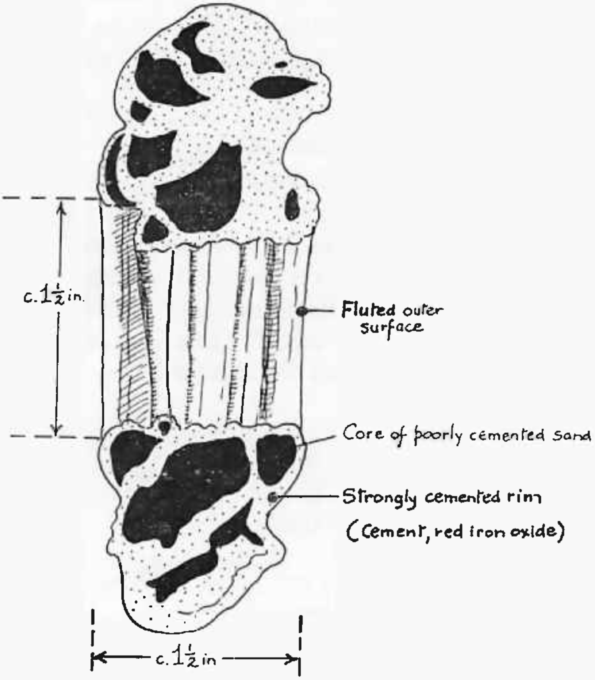

FIG. 1. Sketch of a comparatively simply constructed pipe from St. Agnes.

to 7-8 in, is reminiscent of portions of trunks of small fossilized trees.

In addition to the pipes, *ca.* 1 in thick slabs of sand, strongly cemented by oxides of iron, have also been found by the writers, whilst on the sand belt, near Wheal Coates, and *ca.* 0.5 mile from the Cameron Pit, whitish sand, cemented to varying degrees by black manganese dioxide, has been discovered. Some specimens consist of densely cemented slabs from which black globular bodies, about the size of large black currants, hang into uncemented sand. Each globule consists of a hard, intensely cemented rim enclosing a core of comparatively poorly cemented sand grains (Pl. 2). It is significant that the Great Lode of Wheal Coates, which sub-outcrops, contains some manganese (Tweedy 1845, p. 20) so possibly this accounts for the chemical nature of the cement noted above which is not at all characteristic of the St. Agnes Pliocene belt. If this is so, it follows that the cement reflects the presence of the orebody.

The occurrence of cemented sands, etc., in the St. Agnes beds have been noted briefly before by several workers.

Davies and Kitto (1878 pp. 200-1) when describing a Pliocene profile near the present Cameron pits state that " at or near the bottom we meet with sand, hardened and cemented together by oxide of iron, and taking a remarkable form, being not unlike the roots of trees, or rather the thick bark of trees squeezed flat. They are cores of sandstone with a centre of free sand, and were probably formed by water percolating through, having oxide of iron in solution, as they run in an easterly direction, and eastward we find a stratum of hardened sand for a great distance, at one place no less than 6 feet thick ".

Ussher (1879, p. 13) notes that " the sandstone is produced by cementing oxide of iron, and occurs sometimes in cores with a sand centre, sometimes in flat uneven layers ".

Reid and Scrivenor (1906, pp. 63-4) mention the presence of blocks of conglomerate between Wheal Coates and Higher Bal consisting of pebbles of quartz and of slate, identical with that on which the Pliocene beds rest, in a ferruginous matrix. They state that " owing to the mask of head this bed cannot be seen anywhere in situ, but there can be no doubt of its existence, and that it is the bed of pebbles mentioned by De la Beche as the base of the Tertiary deposits, and the hardened and iron cemented sand mentioned by Davies and Kitto as occupying a similar position ".

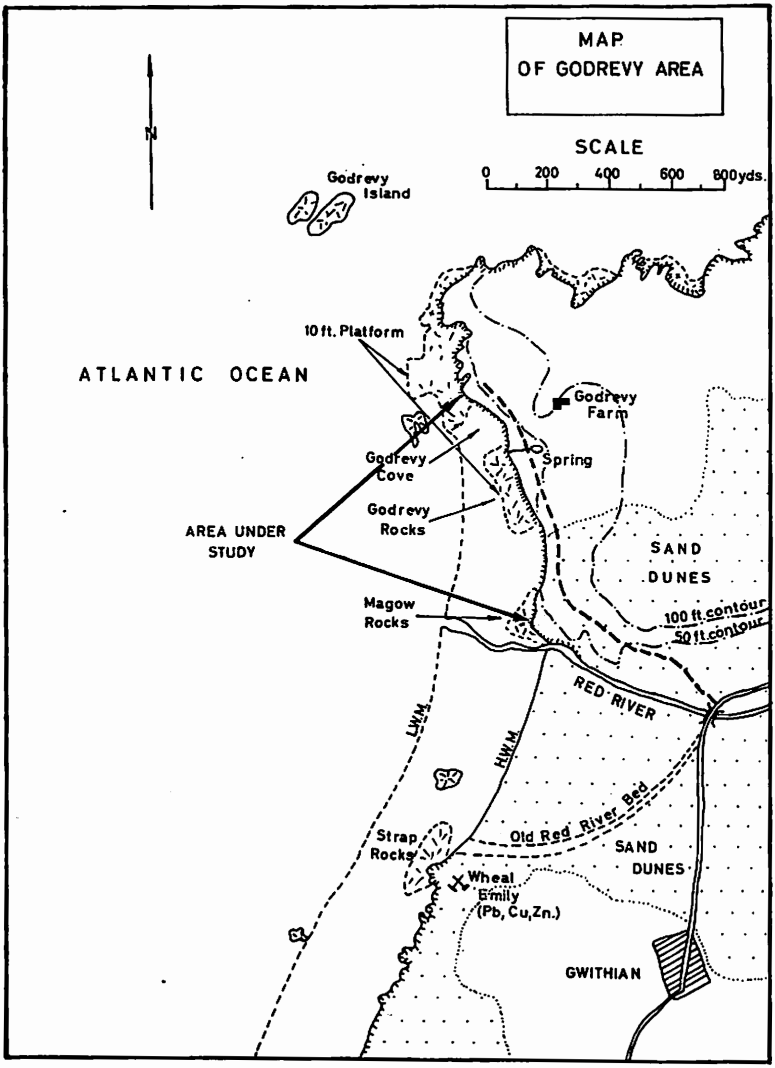

FIG. 2.

GODREVY (see Figs. 2 and 3). The Godrevy coastal section consists essentially of Mylor (Lower Devonian) slates and grits which are highly contorted, intersected by quartz veins of several generations together with some feldspar/quartz veins and at least one lode. This lode is steeply dipping and consists of quartz in which are voids, once occupied by galena, arsenopyrite, pyrite and chalcopyrite, but which are now filled to varying degrees with limonite, or simply stained by it. The slate cliffs are interrupted by a valley, which predates the so-called 10-ft raised beach, which is now infilled with beach material and more particularly by Head.

At the northern end of the section the slates are pale grey, but elsewhere, apart from that portion immediately to the south of the valley, they are bluish-grey, light- and dark-striped, and are associated with a few sandstone bands. The slates immediately to the south of the valley are soft, yellow, markedly jointed and locally sphaeroidally weathered. They have obviously been leached, but when traced away from the valley they become distinctly harder and 'finger out' into the blue grey variety: perhaps they are simply slates which were originally blue-grey but which have been highly altered by ground water action which was facilitated by the local topography and by the fact that they were intensely jointed.

The raised beach, which rests on a well preserved slate platform is *ca.* 5 ft above high-water mark, but from notch to notch it is 14 ft above the present beach. This raised beach consists, near the bottom of the valley in particular, of a pebble horizon which is cemented by oxides of iron and manganese, but on the valley slopes the pebble bed is locally poorly developed or absent and the basal sand which takes its place may not be cemented. Overlying the pebbles are littoral sands of variable thickness, and towards the northern end these reach the top of the slate cliff, having been banked up against a minor promontory and subsequently cemented by calcium carbonate. This grit is penetrated by vertical, hollow pipes, of varying diameter, but which is commonly about 6 in, and by possessing these curious features, of uncertain origin, resemble the 10-ft raised beach grit of Fistral Bay, near Newquay (Reid and Scrivenor 1906, p. 67). Near the base of the Godrevy Grits, are pebble horizons, and some of the components of these, and of the basal pebble horizon of the beach elsewhere, are exotic. These, which include major and minor granitic rocks, spilites, dolerites, white and red sandstones, etc., together with a large dolerite block resting directly on a beach-stripped portion of the platform, were transported to the site on icebergs which became stranded there.

Overlying the raised beach sand, and completely filling in the valley in the centre of the section, is Head of Rubble. The Head can be divided into a 'lower' which consists of coarse quartz fragments embedded in a clayey matrix and an 'upper' in which the quartz fragments, embedded in the clay are distinctly finer.

The Head is covered by a thin layer of blown sand and this, in turn, is mantled by a thin soil layer.

The spatial distribution characteristics of the iron oxide and manganese dioxide cemented deposits merit further description. As stated earlier, the most markedly cemented beach deposits occur near the base of the valley and the cement is confined to the basal pebbles and immediately overlying sands. Generally the lowest horizon is cemented by brown iron oxide and this is overlain by a horizon cemented by black manganese dioxide which is sharply demarked from the former. On rare occasions this sequence may be repeated two or three times, and masses of iron oxide-cemented sand, elliptical in section occur sporadically within the manganiferous deposit. Oxides of iron and manganese have also been locally deposited along joints in the slate platform immediately below the basal conglomerate.

Iron and manganese oxide deposits also occur just below the Head/beach sand junction, particularly near the centre of the valley. There the deposits are convoluted and locally they assume the form of an inverted capital omega, and one such portion which had become detached has been chemically investigated by the writers (see Fig. 4).

Unlike the basal cemented deposits of the beach, in the above mentioned deposits the manganese-rich band lies *beneath* the iron-rich one.

Occasionally the undersurface of the manganese horizon has, like the Wheal Coates material, black globular bodies attached to it which hang into uncemented sand.

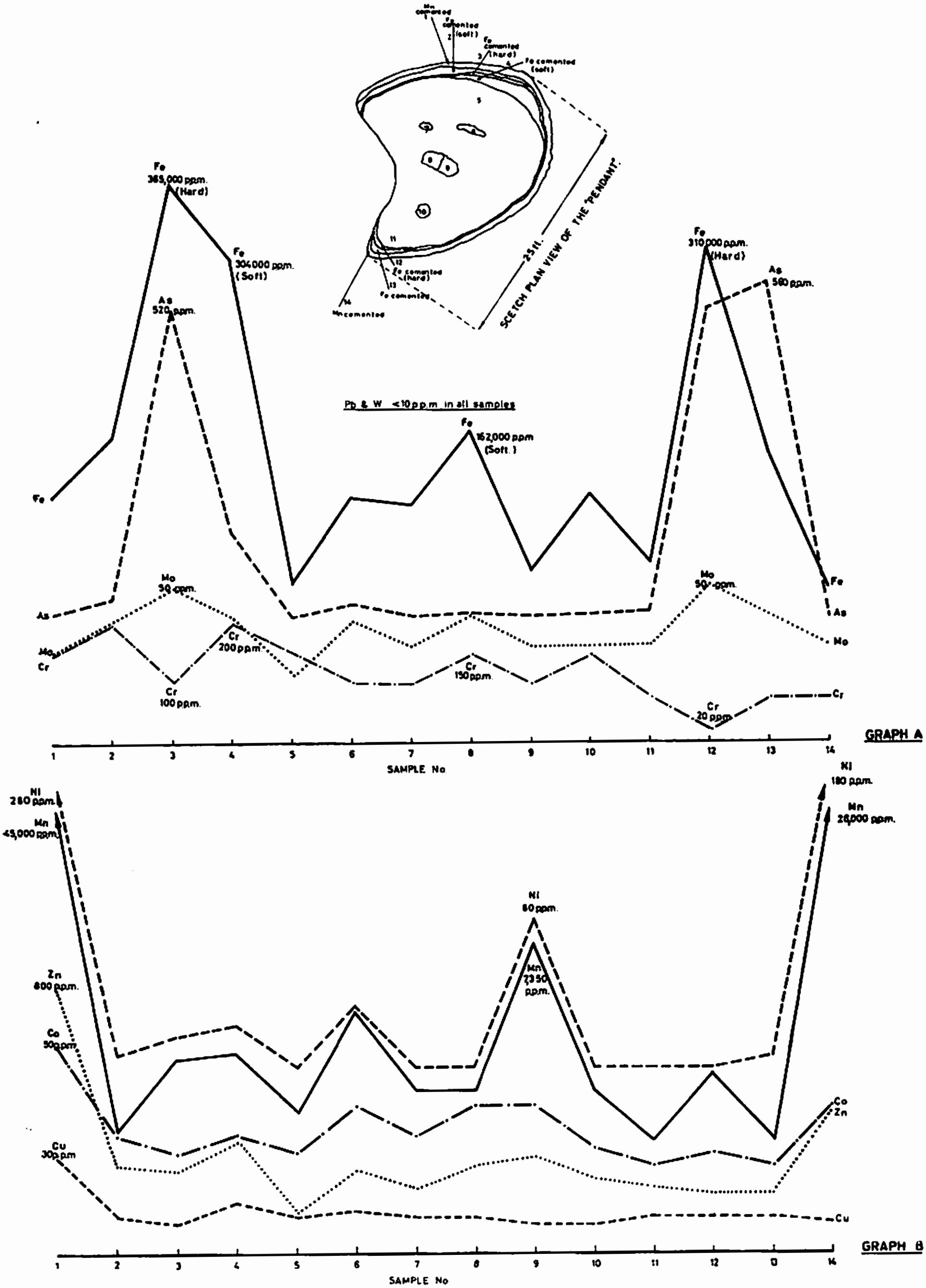

FIG. 4. Distribution of certain elements in the cement of a Deposition "Pendant" from the raised beach at Godrevy.

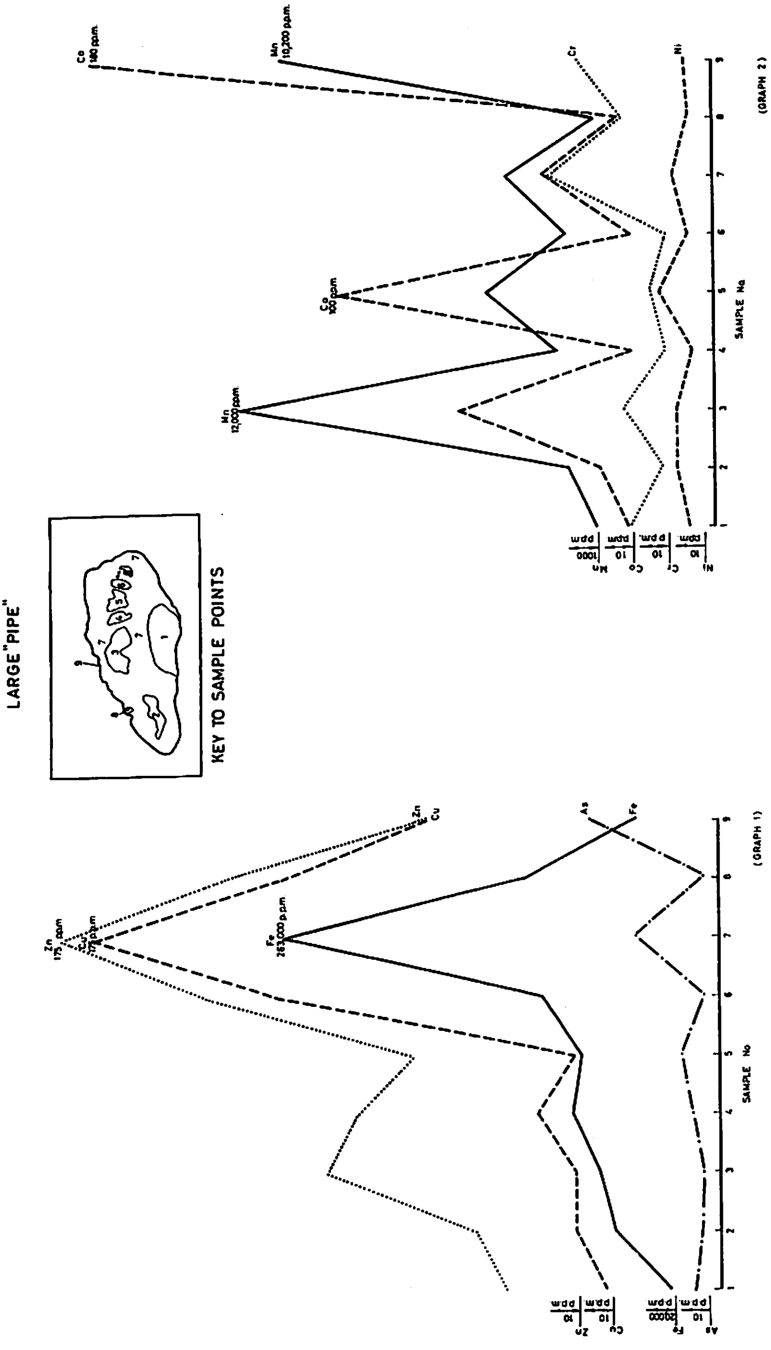

FIG. 5. Distribution of metals in the large "Pipe" from the St. Agnes Pliocene Beds.

The significance of these various characteristics will be discussed later.

RESULTS OF ANALYSIS OF THE CEMENTS, ETC.

(Figs. 3-6)

(i) So far as the cements of the Godrevy raised beach and of the large complex pipe of St. Agnes are concerned, iron and manganese show an antipathetic relationship, whilst arsenic, molybdenum are sympathetically related to iron. Cobalt and nickel, on the other hand, are sympathetically related to manganese.

(ii) When all the analyses are considered it is clear that copper, zinc and chromium fluctuate in their behaviour, tending to vary sympathetically with iron in some cements and with manganese in others.

(iii) The small ferruginous pipes (Fig. 6, nos. 1-11) do not display such clearly defined relationships between the concentrations of the various elements as do the bodies noted in (i) above.

(iv) The manganese-cemented sands from Wheal Coates (Fig. 6, no. 12) do, however, contain, in addition to a high concentration of manganese in their cements, comparatively high concentrations of cobalt, nickel, and zinc.

(v) At Godrevy, cements of the raised beach, in the vicinity of the lode, noted earlier, are characterised by very marked concentrations of lead, zinc, copper, cobalt, nickel and arsenic.

(vi) The unconsolidated sands and clay of the St. Agnes Pliocene deposits are, as indicated in Table 1, very low in the elements which are markedly concentrated in the cements of the pipes there.

TABLE 1:

Concentration of Certain Elements in Unconsolidated Pliocene Sands, etc., of St. Agnes

	P.P.M.							
	Fe	Mn	Cu	Zn	Pb	As	Ni	Co
Soil	9,000	Tr	25	75	Tr	25	25	Tr
Yellow sand	500	Tr	<12.5	35	Tr	Tr	2	Tr
Red sand	4,000	Tr	12.5	35	Tr	Tr	7	Tr
Grey clay	500	Tr	12.5	50	Tr	Tr	7	Tr
White sand	500	Tr	12.5	25	Tr	Tr	2	Tr

(vii) At Godrevy the slates, as indicated in Table 2, contain appreciable concentrations of all the elements revelant to the present study, but the soft yellow leached member contains, not unexpectedly, the lowest concentrations.

TABLE 2:

Concentration of Certain Elements in Various Godrevy Slate Samples

	P.P.M.								
	Fe	Mn	Cu	Zn	Pb	As	Ni	Co	Cr
Bluish slate	40,000	1,000	30	150	40	10	50	10	140
Bluish slate	40,000	1,000	40	300	25	6	60	20	125
Grey slate	36,000	800	30	120	10	2	40	6	N.D.
Soft grey slate	32,000	400	25	150	10	2	30	10	125
Yellow slate	32,000	200	25	250	10	2	30	4	100
Soft, leached, yellow slate	20,000	200	8	50	12.5	2	10	2	100

THE SIGNIFICANCE OF THE ANALYTICAL RESULTS

(a) EXPLORATION. The analytical results broadly parallel those obtained by Lakin *et al.* (1963) during their studies of desert varnish and serve to confirm that in chemical deposits of the type under review the concentrations of many elements when occurring in trace-amounts in a given sample tend to vary with the concentration of iron or manganese present. That is to say a given rock unit of constant composition may supply the components of a cement whose composition, due to local variations in the physiochemical environment of the zone of precipitation, may vary markedly from sampling point to sampling point. However, should a lithologic unit be present which is capable of supplying abnormally high concentrations of metals to the ground water, for example, an oxidising sulphidic orebody, then its presence may be revealed by the abnormally high 'ore-metal' content of cements, or other chemical deposits, in the near vicinity, at least. It follows, then, that the analysis of cements, and other broadly similar deposits, may, if prudently applied, play a useful role in the search for ore deposits.

The results also counsel that during geochemical exploration surveys in which the analyses of latosols and other superficial deposits in which chemical deposition with the development of concretions, etc., figures prominently, considerable variations in the concentration of a given element may occur from sampling point to sampling point which may not be related to variations in the nature of the suboutcropping deposits.

(b) THE GENESIS OF THE CEMENTED BODIES OF GODREVY AND ST. AGNES. When considering the cemented bodies of Godrevy and St. Agnes, several questions present themselves which, unless they can be answered, prevent the genesis of these bodies from being determined. At the outset, however, it may be stated that the present study has, from the point of view of the genesis of such deposits, and perhaps from that of sedimentary iron and manganese oxide deposits generally, raised more problems that it has solved, and to the writers, at any event, it has served to demonstrate that though a vast literature relevant to the subject exists, little is, in fact, known with certainty about the way in which such deposits have been formed.

If the Godrevy deposits are considered then, as a prelude to interpreting their genesis the following questions must be answered:—

(i) What is the source of the cement components?
(ii) In what form were the cement components transported to the site of precipitation?
(iii) How was the precipitation effected?
(iv) What caused the development of iron-rich and manganese-rich deposits?
(v) What caused the sympathetic relationships between certain elements, noted earlier, to develop?

Comparison of the analysis of the various slate members of the cliff section indicates that the yellow, much jointed variety which occupies the southern wall of the infilled valley, has been subjected to severe leaching, and the components which were so removed, probably contributed significantly to the development of the raised beach cements. It is also probable that material leached from the Head also made an important contribution, probably the major one, to those chemical deposits; this possibility will be returned to later.

The nature of the leaching solution presents problems. It is unlikely, for example, that ground water charged with carbon dioxide would effect the marked removal of iron from the slates which is required, as much of the element is in the ferric state: it is also doubtful if such a solution would mobilise, to the required degree, the other slate components reporting in the cement. However, leaching experiments are clearly necessary before dogmatic statements can be made.

Sea-water cannot be reasonably invoked as the leaching agent as it is probable that cementation took place after a considerable quantity of Head had accumulated in the valley and when the land was in the process of rising *ca.* 40 feet above the present O.D. The reason for the above statement concerning the timing of the cementation is given later.

During the early stages, at least, when the valley was becoming infilled with Head, the floor of the valley was marshy. The direct evidence for this is the occurrence of framboidal pyrite embedded in the manganiferous cement of the basal conglomerate. Such pyrite bodies develop in an alkaline reducing environment and are to be found in the buried peat deposits of many of the Cornish valleys. One of us (K.H.) has, for example, found marked concentrations of these spherules in a peat deposit *ca.* 27 ft O.D. in the Red River valley and close to the study area. As the area was, during the accumulation of much, or all, of the Head, subject to permafrost conditions, it would be strange were the partly infected valley not swampy during a portion of each year.

The presence of marshes in the valley means that organic acids, derived from the decomposition of aquatic and other plants, were available, and under the reducing conditions which characterise this environment it seems likely that these were responsible for the mobilisation of those elements which were later deposited as cement. It must also be remembered that in the valley much of the most readily available slate was in a finely communicated state in the Head: that is to say, the Head was in an ideal state for leaching as it possessed a very large free surface area to weight ratio. There is also a further possibility that appreciable quantities of metals in the ionic form might have been liberated as a result of abrasion disrupting the lattices of the slate minerals during the migration of the frost-shattered debris into the valley.

It is not known whether the iron and manganese which were liberated from the slates were transported in the ionic form or as colloids to the site of deposition, nor is it known whether deposition was effected entirely by inorganic means or by the partial assistance of bacteria[1] but the following hypothesis, which is based, in part, on Krauskopf's studies (1957), suggests itself as the most reasonable one to the writers.

It is assumed that under the reducing conditions prevailing in the Godrevy valley during accumulation of the Head organic acids released bivalent iron and manganese and various trace elements largely from the Head but in part also from the highly jointed slate forming the southern flank of the valley. Some further

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[1] Numerous views, based in part on experiments, have been recorded concerning the mode of transport of iron and manganese by water from zones of weathering, and the means by which these elements can be separated so that iron-rich and manganese-rich deposits can develop. (For further details see Rankama and Saharra 1952, pp. 647-52, 672-6; Krauskopf, 1957).

additions, of unknown magnitude, may have been made as a result of ions liberated by abrasion which were reduced when they entered the marshy valley bottom.

To what extent these liberated components were transported as colloids and to what extent as ions is unknown, but in the writers' opinion they were in the latter form.

It is thought that ground waters charged with slate-derived metal ions migrated to the floor of the valley and from thence seeped via the unconsolidated basal pebble horizon of the underlying beach towards the sea. Due to contact with comminuted shells and/or seawater the pH was raised to a point at which ferric hydroxide was precipitated. The pH of the manganese-enriched solution which was left increased due to further additions of seawater during its seaward migration and/or because it came into contract with further shell fragments as it was carried into the higher horizons of the beach as the water table rose at each high tide period. If this postulated separation mechanism operated during the time when the land was rising with respect to the sea, cementation would commence in the upper reaches of the valley and progress seaward with time.

It is further postulated that the iron and manganese were precipitated as colloidal ferric hydroxide and manganese dioxide respectively and that each of these colloids selectively coprecipitated some of the accompanying slate-derived trace elements. Precisely how this selective scavenging was achieved is not clear. Adsorption, doubtless, played a part, and it is likely that arsenic and molybdenum report with iron because they were adsorbed as arsenate and molybdate ions respectively on positively charged ferric hydroxide colloid, but it is difficult to ascribe the entire process of trace element partition between the iron-and marganese-rich precipitates to this cause. Whatever the mechanisms involved, it is clear that removal of appropriate trace elements from solution was approximately proportional to the quantity of scavenging colloid developed. Furthermore, after the colloid was flocculated it must have been subject to rapid physical changes which rendered it incapable of adsorbing further ions from subsequent waters with which it came into contract: had this not been so the sympathetic relationships between the elements of the cements which analyses have revealed would not occur.

The reversal of the iron and manganese bands which occurs immediately beneath the Head is due to seepages of metal-charged water during periods of thaw of the frost-disturbed solifluction product into the shell-charged upper horizons of the beach. The pH of the droplets would progressively increase as they descended into the sand so that first ferric hydroxide and then manganese dioxide would be deposited.

What has been written above concerning the partition of the trace elements between the iron and manganese rich horizons at the base of the beach is equally applicable to these higher deposits. That the latter developed from water seeping from the Head into the sand is indicated by the globular masses locally attached to the under-surface of the manganese band.

To unravel the genesis of the deposition pipes of the St. Agnes deposits, the following questions must be answered:—

(i) What was the source of the material of the cement of the pipes?

(ii) How are they disposed within the Pliocene deposits?

(iii) What determined the structure of these cemented bodies?

(iv) When were these pipe-like bodies developed?

Although, unfortunately, analyses of the St. Agnes killas is not available it can be tentatively concluded that it was essentially the source of the components of the cement of the pipes.

From the scanty evidence it appears that these pipes occur as flat-dipping bodies near the base of the Pliocene deposits and it seems likely, therefore, that they represent the extensions into the sand of preferred groundwater channels.

Water entering the sand would tend to flow down the maximum slope but, at the same time some would diffuse outwards, and diffusion would be greater laterally than in an upward direction. Downward migration may have been limited by the adjacent bedrock.

If the pH of the water diffusing into the sand is progressively increased a point will be reached when first ferric hydroxide and certain trace elements are precipitated and then manganese dioxide and certain other trace elements. This, plus the nature of the diffusion of the water in the sand, will result in the development of cones, with crudely ellipsoidal cross sections, consisting of strongly cemented walls and poorly cemented cores.

As the initial cone develops at a given point, its wall, by progressive cementation, will eventually become impermeable, and then as water can no longer pass through the cone it will tend to flow along its outer wall where further pipes will develop. This process of complex pipe-aggregate building will continue as long as the ground water confines itself to its original channels and as long as it is heavily charged with the components necessary for the development of the cement.

The period when the pipes were formed is unknown, but in the writers' opinion it seems likely that they are not of Pliocene age but were developed from material released from the Head in glacial and post-glacial times and so have much in common with the Godrevy deposits.

Today, marked cementation of sands and pebbles by ferruginous cement only occurs in the Cornish beaches where waters emerge from adits of abandoned mines in which oxidising sulphides, particularly pyrite, occur. Groundwater emerging from barren slate contains such minute concentrations of the cement forming compounds under review that they are incapable of producing deposits of the Godrevy and St. Agnes types. This has been amply demonstrated as a result of intensive Banka drilling of the beach sands, from the surface to the underlying platform, between Godrevy and Hayle.

There is, therefore, the interesting state of affairs that intensive leaching, leading to the deposition of iron and manganese deposits was the order of the day in glaciated and adjacent peripheral regions during inter-glacial and immediate post-glacial times yet it is not so now, in these same areas, despite the fact that climatic conditions—particularly because of the general increase in temperature—are more favourable for the chemical reactions which bring about the decomposition of rocks at the surface. It can only be concluded that in inter-glacial and immediate post-glacial times, in the areas under discussion, material was available which was much more amenable to leaching than that available today. This material was the frost-shattered debris which, apart from being in a particularly good state for attack by ground waters, because, as remarked earlier, of its very high free surface to weight ratio, was also composed of fragments with fresh edges and corners, which, because of disruption of the lattices there, were chemically highly reactive.

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PLATE 1. Photograph of the large complex, ferruginous deposition pipe from the St. Agnes Pliocene beds. The poorly cemented areas are much in evidence. In transverse section the body measures 8 in. x 3 in. Analyses of portions of this pipe appear in FIG. 5.

PLATE 2. Photograph of transverse section of manganese dioxide-cemented globules hanging in uncemented, essentially quartz, sand from the Wheal Coates area, St. Agnes.

The core is dull black, or brown-black, and consists of poorly-cemented sand grains. The rim, which is heavily-cemented by manganese dioxide, is hard, and dull grey and metallic when subject to a minimum amount of polishing. (x 4.)

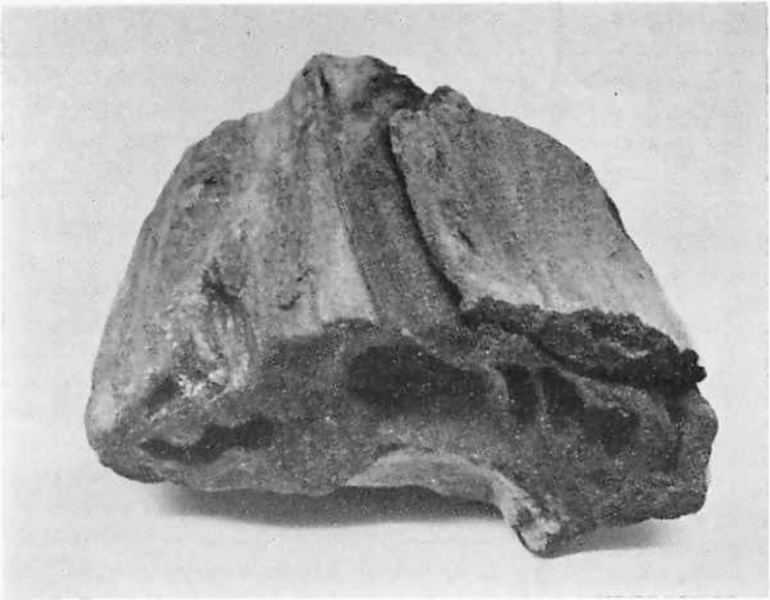

PLATE 1.

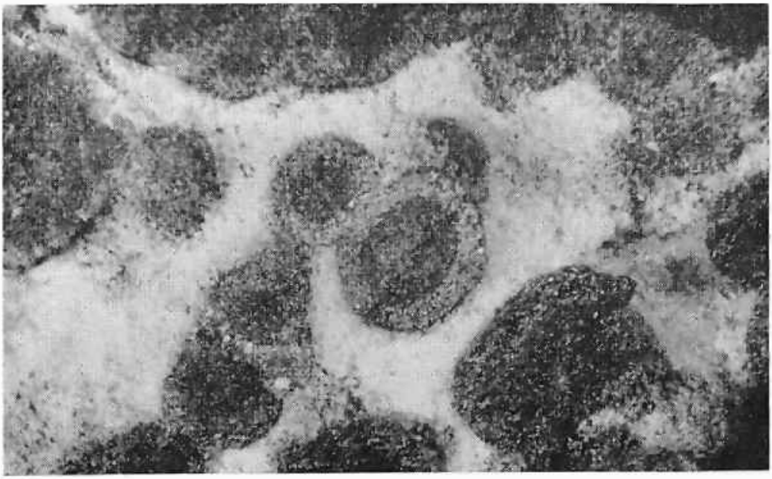

PLATE 2.