

Further Uses of Applied Geochemical Methods of Analysis of the Colorimetric Type

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Synopsis

THIS paper is, in part, an amplification of a topic recently discussed by Davies (*Mining Mag.*, **106**, 137-139, 1962) and aims primarily at confirming, by means of examples, that the rapid and simple colorimetric methods of analysis, designed for geochemical prospecting, can frequently be used to facilitate the solution of problems encountered in the various fields of mining. Evidence is also presented in support of the contention that without resorting to more elaborate analytical techniques the scope of geochemical prospecting can be considerably enlarged. Finally, it is emphasised, largely by discussion of actual examples, that these colorimetric methods can be used to assist in the solution of certain fundamental geological problems as well as others in the fields of biology, archaeology, medicine, etc.

Most who are concerned with the investigation of problems in the various branches of pure and applied science would probably agree that the solution of many of these problems would be greatly facilitated were it possible to obtain semi-quantitative data cheaply, simply and rapidly. That the application of colorimetric methods of analysis currently employed during geochemical exploration can often be used to obtain such data in fields other than that for which they were specifically designed does not seem to be generally appreciated. When working at the Camborne School of Mines O'Keeffe (1960) demonstrated that the rapid and simple colorimetric method for tin, in which gallein figures, and which is used by applied geochemists for determining trace amounts of the element in soils, etc., could be equally well pressed into service by the mineral dresser to estimate, virtually on the spot, the tin content of tailings from flotation plants and dredges. O'Keeffe also suggested that close mill-control might be achieved by making much fuller use of the various geochemical colorimetric methods of analysis.

More recently Davies (1962) has given support to the contention that these rapid analytical techniques can be used to solve a number of problems confronting the mill-man and the mining engineer. He mentions, in particular, an operation involving the leaching of an old copper tailings dump, followed by removal of the copper from solution by precipitation on scrap-iron, which was

controlled by analyses of the type under discussion. He also describes a suspected case of salting which was largely unravelled by resorting to the geochemist's analytical methods.

This paper is written in order to add to the number of problems in various branches of science which have been, or which might be, solved at least, in part by adopting these simple colorimetric methods, and also to demonstrate that the scope of geochemical prospecting itself is capable of being considerably widened without resorting, of necessity, to more complex analytical procedures.

General characteristics of the analytical methods.

In order to establish a fitting background for that which follows it is necessary to make a brief résumé of the major characteristics of the analytical methods in question.

To date, reliable methods have been developed for many elements, including the following: Ag, As, Au, Be, Co, Cr, Cu, Fe, Ge, Hg, Mn, Mo, Ni, Pb, Sb, Sn, U, W, and Zn. In the majority of cases the element can be determined over the range of a few parts per million to several thousand parts with an accuracy which varies from c. 10 to 40 per cent. Zinc, copper and lead are exceptional in that a few parts per hundred million of these can be determined in natural waters without preliminary concentration, whilst the only rapid colorimetric method for small quantities of gold which has been described to date (Martinet and Genin, 1956) is atypical in that it lacks the degree of sensitivity common to the others. All the methods are of the colorimetric type, and whilst the majority depend on the production of a solution whose colour is matched either against standards similarly prepared or against artificial ones, a few depend on the production of a coloured precipitate on filter paper by chromatographic, confined or unconfined spot techniques: in these, also, the 'spot' derived from the sample under test is compared with similarly prepared standards. The apparatus required for all the methods is cheap, and, with few exceptions, readily transportable. A Primus is a perfectly satisfactory source of heat, and the productivity per man-day (8 hours) varies from about 50 to 200 (depending primarily on the analytical method being used). The chemicals vary greatly in cost and not all are easily obtainable outside Britain: furthermore, some are distinctly unstable, and others are dangerous to use unless the analyst is fully aware of their properties. Throughout all the work it is necessary to take rigorous precautions against contamination: many of the solutions which are commonly used have to undergo preliminary treatment to remove interfering elements, and all aqueous solutions should be prepared with metal-free water. In order to ensure that the analytical results are meaningful, blanks and samples of known metal content must always be included in every batch of samples analyzed. As many of the methods used by the geochemical

prospector have been developed by simplifying more precise methods [such as have been described, for example, by Sandell (1950)] - in order to achieve greater productivity and to enable them to be used in the field laboratory - they often lack the degree of specificity of the parents. However, those who have been responsible for the stream-lining have usually so carried it out that the elements commonly associated in rocks, lodes and their natural derivatives with the one for which the analytical method was designed do not seriously interfere. It must, of course, be borne in mind that serious errors **could** accrue were a given method used for purposes other than that for which it was developed (for example, to determine the trace amount of a given element in the presence of a large amount of an element with which it is not normally associated naturally). It is of the utmost importance that before these methods are used for novel purposes the degree to which other elements can be tolerated should be established, either by consulting the literature, or by conducting appropriate preliminary experiments.

To date, no comprehensive text-book of applied geochemical analytical method is available, but many of the analyses which are in common use are to be found either in the publications of the U.S. Geological Survey or in the Transactions of the Institution of Mining and Metallurgy (London).

New, or little known, applications of the analytical methods.

With few exceptions the prospector has used rapid colorimetric analytical methods to establish anomalous concentrations of metal in hard-rock, soil, stream sediments, stream waters and in plants. Usually, if, say, a sub-outcropping copper lode is to be traced geochemically, copper is the element determined in the soil cover, but, on occasion, either because the element of major economic importance is sparsely distributed in the ore-body, or because its estimation offers analytical problems, an associated element is determined in its stead. Thus, in Southern Rhodesia, both arsenic and antimony have served as 'path-finder' elements for gold-bearing lodes, and there, also, the writer has used chromium in order to delineate a mass of corundum which happened to be coated with, and to some extent veined by, fuchsite. (Hosking. Unpublished studies.)

As a result of the work completed recently at the Camborne School of Mines it is now clear that a comparative study of the trace element content of the deposits of neighbouring creeks or estuaries - which can be carried out by means of the analytical methods under review - not only enables (at least, on occasion) differentiation to be made between rivers which drain ore-deposits and those which do not, but it may also yield considerable information about the nature of the major rock types of the hinterland. Thus, in the Helford district of South-West Cornwall the trace-element content of the creek deposits not only establishes which rivers drain the

in copper/tungsten lodes, but also indicates the general location of the granite and serpentine masses. Although the deposits in the upper reaches of the creeks are the most revealing, samples analyzed from near the junctions of the creeks with the estuary proper enable the same conclusions to be reached without difficulty. (As an aside it may be added that the trace element content, as determined by simple colorimetric methods, of the brown alga *fucus ceranoides* (which borders the distributary channels in the creeks) varies from creek to creek in much the same way as that of the associated sediments, even though these plants, having no root systems, derive their metallic elements entirely from the out-flowing stream waters. This example also demonstrates that these simple analytical techniques can play an important rôle in biological studies.) The importance of the examination of creek and estuarine deposits as an aid to prospecting lies in the fact that the sampling sites are readily accessible by boat. Thus, when applicable, such an examination should considerably accelerate the selection of the most favourable river systems for more detailed investigation during the reconnaissance phases of a regional prospecting programme to be carried out over terrain which offers certain difficulties because of its topography, vegetation or soil cover. It is also to be noted that in the very areas where work of this nature is likely to be most rewarding, settlements would be few, and hence the danger of obtaining spurious results because of contamination due to human activity would be reduced to a minimum. Clearly, the method is most likely to yield meaningful results when the rivers are short, as they are in Cornwall: certainly there is good reason for believing that it could be employed to advantage in such places as the Philippines and the Maratime Provinces of Canada.

That the water of creeks and estuaries can be studied profitably in conjunction with the sediments has been indicated by a recent study of that of the estuary of the Fal (Hosking and Burn. Unpublished studies.) During the period of falling tide the surface water emerging from Restronguet Creek, which is fed by rivers intersecting copper, and other, ore-deposits, and by water emerging from the County Adit (which drains the copper-rich St. Day field), contains c.25 $\mu\text{g.}$ of heavy metals per 50 ml., whereas waters from the neighbouring creeks generally contains only a few micrograms. Furthermore, during the period when the tide is falling, distinctly anomalous concentrations of these metals persist in the surface water of the Restronguet current belt for at least a mile below the point where it leaves the creek and enters that part of the estuary proper known as the Carrick Road.

It is still often assumed that a geochemical investigation of the sediments of rivers which have been contaminated by earlier mining operations would assist but little in the search for ore-deposits. That this is not always the case has been established by work in the

Carn Menellis district. (Hosking and Curtis. Unpublished studies.) On this granite moorland considerable alluvial tin-mining occurred in the past, yet lodes intersected by the streams were revealed by geochemical analysis, even when the study area was highly disturbed. This interesting state of affairs has largely arisen firstly because virtually all the superficial deposits of economic importance are underlain by what is left of the parent lodes; secondly, because the alluvial mining operations were such that the richer the ground the greater the losses, and thirdly, because most of the cassiterite that failed to be recovered remained at, or was returned to, its original site. In the vicinity of these alluvial workings the tin content of the stream sediments commonly rises to seven thousand parts per million, but at a point where they overlie a lode a peak value of thirty thousand, or more, parts is often recorded. Elsewhere in Cornwall, and for different reasons, copper-rich lodes have yielded tell-tale anomalies in the sediments of streams transecting them, even when these same streams have received the tailings from old copper mines.

Sub-surface waters circulating in a mineralised zone may dissolve some of the components of ore-bodies and transport the liberated ions considerable distances, causing the zone to be haloed by ground waters whose metal content is distinctly anomalous. It follows, then, that particularly in areas of youthful or mature relief, the establishment of such an anomalous halo might point to blind ore-bodies which other geochemical techniques might fail to reveal. The Russians seem to be more convinced of the potential of this method than others, as they recommend — particularly in terrain of the type noted above — the analysis of spring and well waters, and, in addition, they are of the opinion that “exploratory borings for waters (for geochemical analyses) are feasible in areas considered to be most promising geologically. It is desirable to make the exploratory borings for water contemporaneously with the deeper ones, for mapping and prospecting purposes.” (Ginzburg, 1960-217.) In Mid-Cornwall it has recently been established (by means of an ‘on-the-spot’ analytical technique) that the zone of tin lodes fringing the south and south-eastern parts of Belowda Beacon is aureoled by ground-water which contains $2.5 \mu\text{g.}$, or more, of heavy metals per 50 ml., whereas the regional background is not greater than $0.5 \mu\text{g.}$ This state of affairs is extremely interesting as the lodes in question are distinctly poor in base-metal sulphides. The results suggest that examination of ground waters by the analytical method adopted in the Belowda district might have a considerably greater potential than has hitherto been credited to it. (Hosking, Derici and Lwin. Unpublished studies.)

The composition of every beach must reflect the biological character of the littoral and neritic zones in addition to the geological nature of the cliffs and adjacent offshore consolidated and

unconsolidated deposits. Furthermore, if it is associated with a river its composition will also indicate, to some degree, the geology of the drainage basin. This follows because a beach is a natural concentrating table, so the denser resistates, in particular, will tend to be concentrated there, and even sulphides behave as resistates in the littoral zone. Studies of the stretch of beach between Gwithian and Hayle, by mapping profiles exposed in trenches, by mineralogical studies, and by analysis of samples by rapid colorimetric methods, have confirmed the above conclusions and, in addition, they have established the fact that the employment of the analytical methods under review greatly facilitates determination of the economic potential of a beach: it is also of considerable assistance when an understanding of the mechanism of beach development is attempted. (Hosking, Ong and Curtis. Unpublished studies.)

A cross-cut or a diamond drill may pass near, or approach, an ore-body, and yet optical examination of rock samples may give no indication of this. However, the envelope of anomalous metal concentration, which probably invariably surrounds an ore-body, may have been intersected, and this is capable of being established by geochemical analysis. It follows, then, that samples taken at comparatively short intervals from both walls of an exploratory cross-cut, and either the core or sludge produced during prospecting by diamond drilling, should be subjected, as a matter of routine, to the appropriate, and invariably cheap, geochemical analyses. By analyzing samples from a cross-cut in a certain mine for lead and zinc the writer was able to establish the presence of galena/sphalerite replacement bodies in limestone even when the samples themselves showed no obvious signs of the close proximity of ore. In this case the success of the method hinged upon the fact that lead and zinc, in trace amounts, had leaked away along joints from the centres of deposition during the phase of ore development and this, in turn, stresses the importance of utilising geochemical methods in conjunction with 'normal' underground mapping and not as a substitute for it. (Hosking. Unpublished studies.)

Frequently, analysis of the sludge in lieu of the diamond drill core yields perfectly satisfactory geochemical data, but in any given area the reliability of sludge analysis must be confirmed before it is accepted as a routine procedure. In New Brunswick, for example, sludge was collected in a polythene bath and subsequently analyzed for tin and molybdenum by rapid geochemical methods. The tin content, although somewhat greater than that in the corresponding core (due to clay, etc., being lost from the bath) was a reliable indication of the manner in which the tin varied in the rock penetrated. On the other hand, because some of the liberated molybdenite was smeared around the walls of the hole and some was lost from the collecting bath, because it floated in the unavoidably oily water, the molybdenum content of the sludge did **not** reliably reflect

that of the corresponding core. (Riddell, Hosking and Ruitenberg. Unpublished studies.)

The analysis, by rapid geochemical methods, of sludge obtained by 'long-hole' drilling has been used successfully at South Crofty Mine, near Camborne, in order to delineate the economic limits of a portion of a stockwork containing cassiterite (the component of major importance), wolframite, arsenopyrite and a little chalcopyrite. Tin, tungsten, arsenic and copper were determined and sections showing the distribution characters of each were compiled. The tin results agreed reasonably well with those obtained by vaning assays, but the geochemical approach is superior to the latter in that anyone with a slight chemical background who possesses average intelligence can, after a week's training, analyze about a hundred samples a day for the metal in question, whereas a long period of training is necessary before a person is a really proficient vanner, and then he can only make about thirty determinations per day. In addition, the geochemist can easily deal with any of a large number of elements. (Hosking and Burn. Unpublished studies.)

Simple colorimetric methods may also, on occasion, assist the quarryman. Thus, in a certain limestone quarry in the West of England the magnesia content varied considerably from point to point, and, as one of the products sold was powdered limestone, with a guaranteed content of magnesia of less than one per cent, chemical control had to be employed. Initially the magnesia was determined by a classical method but the output per man-day was very small. Subsequently it was shown that the oxide could be determined with a satisfactory accuracy simply by grinding a measured volume of the powder for a few minutes with solutions of sodium hydroxide and Titan yellow and matching the colour of the slurry with those of standards similarly prepared from precisely assayed samples from the same quarry. This simple method enabled a productivity of about a hundred samples per man-day to be achieved. (Hosking, 1956.)

The reaction noted above forms the basis of a method developed at Camborne for determining the percentage of MgO in ilmenite. This is of some value to the diamond prospector because ilmenite derived from kimberlites contains from 4 to 5 per cent of the oxide. (Hosking. Unpublished studies.) Doubtless the analytical methods under review could be used with advantage much more widely than hitherto in order to determine the trace amounts of elements in discrete minerals in connection with a wide variety of mineralogical, geological and mineral-dressing investigations.

Many geological problems which necessitate a study of the migration of elements for their solution can be successfully tackled by utilising the semi-quantitative colorimetric methods of the geo-

chemist — particularly when it is realised that comparative rather than absolute values are often all that are necessary. The writer has, for example, determined, by such a method, the tin content of samples from the greisenised granite cusp at Cameron Quarry, St. Agnes. The results indicate that the tin-content of the granite is generally directly proportional to the degree of greisenising, but in the vicinity of bands which have been silicified and tourmalinised the greisen is comparatively poor in the element in question. However, within the silicified bands certain feldspar voids are infilled with cassiterite. It seems, therefore, difficult to escape from the conclusion that some of the cassiterite, at least, developed from tin which was originally accommodated by the sericite of the greisen and was subsequently mobilised during the silification and tourmalinisation stages. (Hosking. Unpublished studies.)

Little need be said about the application of geochemical analyses to surface geological mapping as it has long been known that by their employment to determine appropriate trace elements in residual soils over contacts the position of the latter can, on occasion, be determined more precisely than by other methods. It is also known that differentiation between superficially similar rocks can sometimes be rapidly achieved by these analytical methods. The surprising thing is that these powerful aids are completely neglected by the majority who are presently engaged in geological mapping.

Many aspects of the research into sedimentary processes can be accelerated by adopting quick analytical methods. Thus, for example, by taking a number of sediment samples at well-spaced points along the Menalhyl River (Mid-Cornwall), then, splitting each into several 'size' fractions and analyzing each for tungsten and tin by colorimetric means, it has been possible to compare the fate of wolframite with that of cassiterite in the drainage system. The source of both these minerals is near the upper reaches of the river, but whilst the wolframite, because of its perfect cleavages, is easily disintegrated, and so concentrates in progressively finer fractions as the distance from the source is increased, the cassiterite behaves in quite a different way. As this latter species is tough, dense and chemically inert, fragments liberated into the river are not readily decreased in size, and so comparatively coarse grains are found at points considerably removed from the source. In addition, in the river in question, the size fraction in which the bulk of the cassiterite occurs at a given point is not dependent, primarily, at least, on the distance between the point and the source, but rather on those factors which determine the concentrating power of the river at that point. (Hosking, Naik, Burn and Ong. Unpublished studies.)

The biological applications of these colorimetric methods are endless, and already a study of the trace element content of samples

of a species of *Fucus*, which has been made by means of them, has been referred to. In the field of zoology these same techniques have enabled Hosking and Burn (unpublished studies) to confirm that oysters are capable of concentrating, to a surprising degree, copper, zinc and tin. (See Rankama and Sahama 700, 714 and 736, 1950.) In addition, they have established that *Ostrea edulis* from the Fal estuary and associated creeks accumulates these, and certain other elements (including lead, arsenic, tungsten and molybdenum) roughly in proportion to the amounts occurring in the muds and out-flowing waters with which they are associated during their development.

It follows that if these methods are of value to the biologist they will almost certainly be useful to those working in the closely allied fields of agriculture, horticulture and forestry. They can be used, for example, to establish, very rapidly and simply metal deficiencies and excesses in soil and vegetation. In particular, in areas similar to West Cornwall, where much of the land used for farming and horticulture is heavily contaminated as a result of widespread mining activity, employment of these quickly analytical methods is likely to be most rewarding, as it is of the utmost importance to know something of the metal content both of the soil and of the vegetation because an excess of certain elements may inhibit healthy plant growth or have an adverse effect on grazing animals. (In the latter case it is obviously important to know what percentage of the potentially toxic element assimilated by plants on which animals graze is accumulated in the above-surface organs.)

The distribution of people suffering from certain diseases is such that it is difficult to escape from the conclusion that these diseases are, at least in part, geologically controlled. Indeed, there is no doubt that pernicious anaemia is most prevalent where the soils are deficient in available cobalt, and goitre where they are low in available iodine. Within the past year or two Warren (1961) — an applied geochemist — has accumulated a vast amount of data which indicates that in temperate regions cases of multiple sclerosis are most prevalent in 'lead-high' areas. Considerable scope exists in such investigations for the application of rapid colorimetric methods of analysis and the writer has, in fact, already used them, to a limited extent for such purposes.

So far as the writer is aware little use has yet been made, by archaeologists, of these rapid analytical techniques, yet they could surely use them to advantage. A few years ago Mr. A. C. Thomas established in the writer's laboratory that it was possible to differentiate between pieces of pottery, which were superficially similar, but which had, in fact, been manufactured at widely separated points, by determining their abrasion pH. (See Stevens and Carron, 1948.) It seems reasonable to suggest that by subjecting such speci-

mens to appropriate colorimetric analyses further characteristics of diagnostic importance might be revealed and, on occasion, clues to the places of origin of the raw materials might also be obtained.

Conclusion.

It is becoming increasingly apparent that workers in one science can often benefit from developments in another. That they are often slow to take advantage of such developments may be due to lack of knowledge, lack of imagination or prejudice. Applied geochemistry has fostered the development of those rapid colorimetric methods of analysis with which this paper is concerned and its present stature is to no small measure due to them: they have still a major rôle to play in the future developments of the science. For some years many of the methods have been available to workers in other fields, yet the extent to which they have adopted them is still remarkably small.

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CROSSWORD—Answers. Across:—

1. Central Heating. 9. He. 10. Peridot. 12. Eve. 15. Eskimo.
17. Andsome. 19. A.A. 20. Act. 22. Tap. 23. Bridge. 24. Health. 25. Sid.
26. Peg. 28. Zinc. 29. At. 30. One. 31. St. 33. Teenager. 34. Stag.
36. Aid. 38. Err. 39. Mansfield. 44. Skip. 45. Silver Bullet.

Down:—

1. Copper Belt. 2. Nor. 3. Red. 4. Late. 5. Elevated. 6. Theodolite.
7. i.e. 8. Go. 11. Illiad. 13. Toothpaste. 14. Seepage. 16. Magazines.
18. Ma. 21. Chic. 25. Snag. 27. Overall. 29. An. 30. Oral. 32. Tar.
35. Grape. 37. Idol. 40. Fir. 41. Emu. 42. Est. 43. S.S.